Management of Pollutant Emission from Landfills and Sludge

Małgorzata Pawłowska & Lucjan Pawłowski – EDITORS

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Preface

The management of municipal waste and sewage sludge is one of the major problems of modern civilization. The amount of waste generated by the human population is constantly growing, especially in the developed world. According to the Organization for Economic Cooperation and Development (*OECD, 2004*) the greatest amount of municipal waste is generated in the most developed countries. For example, the annual amount of waste generated *per capita* in the United States is 730 kg, in Australia 690 kg, Denmark 660 kg, and Switzerland 660 kg. Significantly less waste is generated in less developed countries like Poland, the Czech Republic and Mexico (280–320 kg *per capita* per year). In addition, the production of sewage sludge is growing across the globe. In the UK, for example, the total amount of sewage sludge produced per year has increased from 896 Gg of dry mass in 1986 to 1368 Gg in 2004 (*e-Digest Statistics*, *2006*). Most of this was used on farmland (64%), about 19% was incinerated and about 11% was used in land reclamation (2004 figures). Production of municipal sewage sludge in Poland increased from 360 Gg to 486 Gg of dry mass between 2000 and 2005, but almost 31% was deposited (in landfills, lagoons, drying beds) and only 14% was used on farmland.

The oldest and most popular method of disposal of municipal waste is in specifically-designed landfill sites. The oldest landfill was opened in Athens about 500 B.C., and since that time the number of landfills (and the area they occupy) has been growing steadily. However, a recent decrease in the number of new landfills, especially in developed countries, has been observed. The number of landfills in the United States decreased from 8000 in 1988 to 1654 in 2005 (*EPA data*). In Poland, landfill surface area increased about 5.6% between 2001 and 2004 (from 3207 to 3385 ha) but fell to 3359.5 ha by 2005 (*CSO*, *2002–2006*). Such trends reflect changes in waste management systems. In many countries, including Mexico, Poland, New Zealand, Greece, Italy, and Hungary, about 90% of waste is deposited. But in other countries, this type of waste management is not popular, mainly due to the long-term negative impact of landfills on the environment. In Japan, Switzerland and Denmark for example, only 11%, 13% and 17% of municipal solid waste, respectively, is disposed of in landfills (*OECD, 2004*).

Despite recent advances in the technology of waste and sewage disposal, there is still a great need for environmentally-friendly management systems. Both landfill sites and sewage sludge processing can affect the environment on a local as well as a global scale. Local problems include deterioration of the landscape, leaching of pollutants into soil–water systems, and odor emissions. On a global level, waste emits greenhouse gases and contributes to global warming. In particular, methane is a major greenhouse gas which molecule absorbs twenty times more ultra-red radiation the carbon dioxide, and is therefore twenty times more lethal to the greenhouse effect than carbon dioxide. According to Hieb (2003), methane accounts for about 7% of the greenhouse effect, caused in part by the 50 to 73 Tg of methane emitted from landfills per year, and the 25 Tg from wastewater treatment processing (*IPCC*, *2001*).

Methane concentrations in the atmosphere have been increasing since 1850 (the beginning of the industrial revolution), mostly owing to emissions from landfill sites. According to the Third Assessment Report (*IPCC*, *2001*), methane concentrations have grown from 0.715 ppm (pre-industrial value) to 1.774 ppm in 2005. Over the same period, carbon dioxide levels have grown from 280 ppm to 370 ppm.

However, the rate of increase in methane concentrations has slowed down since the early 1990s, owing to the stabilization of total anthropogenic emissions (*IPCC*, *2007*). Recovery of methane from landfills has been a major factor in this decrease of anthropogenic emissions of methane to the atmosphere. However, utilization of methane as a source of energy is possible, if the methane content in a biogas is above 30%. The number of recovery facilities in Poland has grown from 20 in 1998 to 38 in 2005 (*CSO data*, *2006).* Biogas is produced for about 10–15 years, during the so-called stable methanogenic phase, after which methane emissions gradually decrease for years. Decomposition of the methane by chemical or biochemical oxidation is of great importance for minimization of the greenhouse effect. Aerobic stabilization of old landfills is another way to mitigate methane's effect on the environment. In the first chapter of this book, biochemical oxidation of methane and aeration of the waste is discussed.

Biochemical processes occurring in landfills and during sewage sludge processing also lead to the formation of nonvolatile substances. Nonvolatile substances leak into the water–soil environment, with the water percolating through the waste layer and producing a leachate that is highly polluted. Hazardous substances such as persistent organic pollutants (POPs), heavy metal ions, nitrates and ammonia may be present in landfill and sewage processing leachates. The issues of migration, transformation, environmental impacts and possible treatment methods of those pollutants are debated in the following chapters.

Prevention of gas emissions to the atmosphere and leachate percolation to the soil–water systems are both essential to minimize the impact of waste and sewage sludge on the environment. Better protection of the bottom and cap of landfills, and disintegration of sludge before its anaerobic digestion, are both possible ways of achieving this goal, and are described in the fourth chapter.

The problem of sewage sludge and organic waste could be partially solved by putting the waste to practical use. Specific methods for the conversion of sewage sludge and waste into useful products, like building materials or compost, are discussed in some of the following papers.

Finally, the results of application of biotests (such as *ToxAlert 100®* and, *Microtox® Model 500*) in the assessment of the quality of solid waste are presented.

An International Workshop on *Management of Pollutant Emission from Landfills and Sludges* was held in Kazimierz Dolny, the old, beautiful town located on the banks of the Vistula river, between September 17 and 20, 2006. During this workshop, 86 papers were presented on different aspects of management of emissions from landfills and sludge processing – 31 papers were selected for publication in this volume, and are arranged in 7 chapters:

- Mitigation of gas emission from landfills
- Pathway of POPs in waste, wastewater and landfill leachate
- Migration of heavy metals from waste disposal sites and sewage sludge
- Minimization of the impact of waste and sewage sludge on the environment
- Chemical composition and treatment of landfill leachate
- Possibility of practical utilization of waste and sewage sludge
- Miscellanea.

Finally, the editors would like to express appreciation to all who have helped to prepare this book. Dr Gordon Filby of InnovEdit performed a Herculean task working with great patience, helping many authors to improve the linguistic side of their papers. We also thank the anonymous reviewers who have not only evaluated papers, but very often made valuable suggestions, helping authors and editors to improve the scientific standard of this book. And finally, last but definitely not least, we thank Mrs Katarzyna Wójcik-Oliveira for her invaluable help in preparing the layout of all papers.

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About the Editors

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Małgorzata Pawłowska, Ph.D., was born in 1969 in Sanok, Poland. She received her M.Sc of the protection of the environment at the Catholic University of Lublin in 1993. Since that time she has been working in the Lublin University of Technology, in the Institute of Environmental Protection Engineering. She received her Ph.D. in agrophysics from Institute of Agrophysics, Polish Academy of Sciences in Lublin in 1999 after defence of the thesis entitled: "A possibility of the reduction of methane emission from landfill by its biochemical oxidation in landfill cover – a model study".

She has published 1 monograph, edited (together with M.R. Dudzińska) a book on "Pathways of pollutants and mitigation strategies of their impact on the ecosystems" and co-authored 21 papers and 2 chapters in books.

LUCJAN PAWŁOWSKI

Lucjan Pawłowski, was born in Poland, 1946. Dean of Faculty of Environmental Engineering and Director of the Institute of Environmental Protection Engineering of the Lublin University of Technology, Member of the European Academy of Science and Arts, honorary professor of China Academy of Science. He got his Ph.D. in 1976, and D.Sc. (habilitation in 1980 both at the Wrocław University of Technology). He started research on the application of ion exchange for water and wastewater treatment. As a result he together with B. Bolto from CSIRO Australia, has published a book "Wastewater Treatment by Ion Exchange" in which they summarized their own results and experience of the ion exchange area. In 1980 L. Pawłowski was elected President of International Committee "Chemistry for Protection of the Environment". He was Chairman of the Environmental Chemistry Division of the Polish Chemical Society from 1980–1984. In 1994 he was elected the Deputy President of the Polish Chemical Society and in the same year, the Deputy President of the Presidium Polish Academy of Science Committee "Men and Biosphere". In 1999 he was elected a President of the Committee "Environmental Engineering" of the Polish Academy of Science. In 1991 he was elected the Deputy Reactor of the Lublin University of Technology, and this post he held for two terms (1991–1996). He has published 19 books, over 128 papers, and authored 68 patents, and is a member of the editorial board of numerous international and national scientific and technical journals.

Mitigation of gas emission from landfills

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Reduction of methane emission from landfills by its microbial oxidation in filter bed

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ABSTRACT: Decomposition of the biodegradable fraction of wastes deposited in a landfill make a significant source of methane emission to the atmosphere. Reduction or elimination of methane emission from this source is possible even at the absence of a degassing installation, by making use of the methanotrophic properties of microorganisms. The paper presents a survey of knowledge concerning factors that determine the oxidation of methane contained in the biogas emitted from a landfill and, at the same time, are important from the viewpoint of practical applications. The methane oxidation capacity of methanotrophic organisms depends primarily on the material in which the process occurs. Gas diffusivity, the content of mineral salts and the pH value mainly depend on chemical composition and physical properties of the porous medium. An adequately selected medium can enhance results of reducing methane emission from landfills and for this reason the paper presents an analysis of methanotrophic capacity of various materials that are commonly used to form landfill covers or biofilter packing.

Keywords: Methane, oxidation, biofilter, landfill cover.

1 INTRODUCTION

The role of methane on the green-house effect has been known since the 1940's, when Migeotte had found strong absorption bands in the infra-red region of the solar spectrum attributed to the presence of methane. It absorbs long wave radiation emitted from the Earth's surface in the 4–100 μm atmospheric window (according to Whalen, 1993). First accounts on atmospheric methane were given by Hutchinson (1954). Systematic worldwide measurements of the tropospheric methane concentration were started in 1978 (Whalen, 1993). In the following years, multiple measurements of the mixing ratio of CH_4 in the atmosphere have been performed and atmospheric methane changes have been analyzed.

The atmosphere is biologically controlled. Living forms control the composition of the atmosphere both qualitatively and quantitatively. Carbon is one of the basic chemical elements of compounds present in the atmosphere. Methanogenic and methanotrophic bacteria are very important elements of the global carbon cycle. ^{14}C analyses of atmospheric methane indicate that no more than 10% of it is released by fossil sources (Ehhalt, 1979) while the remaining part is of biogenic origin.

The annual global methane emission is many times larger than the annual amount of methane accumulating in the atmosphere, which indicates that there are mechanisms of methane uptake in nature. The main mechanism of these processes is a set of chemical reactions of methane with $OH^{\bullet}$ radicals in the troposphere. However, the significance of microbial pathway of the atmospheric methane oxidation cannot be ignored. According to the IPCC data (2001) the contribution of the microbial oxidation to the methane uptake from the atmosphere is about 5 per cent, which makes *ca.* 30 Tg of methane annually.

Microorganisms responsible for this process, so-called methanotrophs, are common bacteria that can use methane as the sole carbon and energy source. Methanotrophic bacteria that can oxidize CH_4 in oxic conditions were isolated for the first time from soil close to a leakage of natural gas by Söngen in 1906 (Mancinelli et al., 1981; Topp & Pattey, 1997). Methanotrophic microorganisms are mainly bacteria, but a methane oxidizing ability has also been observed in the case of yeast (Mancinelli, 1995) and other types of fungi (Adamse et al., 1972). Apart from methane almost all known methanotrophs can also use methanol as a carbon and energy source (Whittenbury et al., 1970; Mancinelli et al., 1981), but not all bacteria that use methanol- can also oxidize methane (Mancinelli et al., 1981).

According to Todd et al. (2007) methanotrophic bacteria have been classified into three types (I, II and X) based on the structures of their internal membranes and their carbon assimilation pathways.

There are two types of the methane monooxygenase: sMMO, of low substrate specificity and limited dependence on copper availability and pMMO, of high substrate specificity and strong dependence on copper availability (Buchholz et al., 1995). Methanotrophs of type I have a membrane-bound (particulate) methane monooxygenase enzyme (pMMO), cluster phylogenetically with the *Gammaproteobacteria*, and are considered to proliferate under high-oxygen, low-methane conditions (Hanson and Hanson, 1996). Type II methanotrophs have pMMO enzyme, but can also produce a more reactive cytoplasmic (soluble) methane monooxygenase enzyme (sMMO) under copper-limiting conditions (Hanson & Hanson, 1996). Type II methanotrophs cluster with the *Alphaproteobacteria* and proliferate under high methane-to-oxygen ratios (Hanson & Hanson, 1996). Type X methanotrophs exhibit characteristics of both Type I and Type II methanotrophs, and cluster phylogenetically with the *Gammaproteobacteria* (Hanson & Hanson, 1996). The sMMO presence in a bacteria cell (methanotrophs of the types II and X) is coupled with low affinity to CH_4, which is the reason why those bacteria cannot oxidize CH_4 when its concentration is low. Most of methanotrophs are gram-negative bacteria (Whittenbury et al., 1970). Methanotrophs can use ammonium salts, nitrite and nitrate salts, and in some cases urea as nitrogen sources (Whittenbury et al., 1970; Adamse et al., 1972).

With respect to the oxygen demand, methanotrophic bacteria are classified into two functional groups: obligatory aerobic bacteria that cannot live in anaerobic conditions and bacteria that can survive an anaerobic period and reactivate in aerobic conditions. Most of methanotrophs belong to obligatory microaerophiles. They prefer oxygen concentrations below atmospheric (Mancinelli, 1995).

As far as methane availability is concerned methanotrophic bacteria can be differentiated into two groups. They are characterized by the determination of Michaelis-Menten kinetics parameters. Bender and Conrad (1992, 1993) have distinguished methanotrophs of the following characteristics:

1) High values of potential methanotrophic activity (V_{max}), low affinity to CH_4 (reciprocal of Michaelis constant K_M) and high threshold value of CH_4 concentration, below which methanotrophic activity disappears. This type of methane oxidizing bacteria has been isolated from soil exposed to high CH_4 concentrations, for example from landfill cover soils and from bog or paddy field soils. Most probably, obligatory methanotrophs that grow only in the presence of CH_4 belong to this group.
2) Low values of potential methanotrophic activity (V_{max}), high affinity to CH_4 and low threshold value of CH_4 concentrations. This type of methanotrophs has been found in the soil exposed to low (atmospheric) CH_4 concentrations. Probably, facultative methanotrophs (bacteria and yeast) belong to the group (Bender & Conrad, 1992; Bender & Conrad, 1993; Kightley et al., 1995).

Nearly all methanotrophs grow at pH values >5, and they prefer mesophilic conditions (optimum temperature above 15°C). However, psychrophilic methanotrophs preferring temperatures $<15°C$ (Zavarzin, 1995) have also been found. A few types of microorganisms that have been found in an aerobic zone of a landfill can grow at temperatures lower than 0°C (Nozhevnikova & Lebedev, 1995). The most numerous types of methanotrophic bacteria are *Methylocystis parvus, Methylobacter chroococcum, Methylobacter bovis, Methylomonas albus.*

The cell number of methanotrophic bacteria can be influenced by many factors, among them the CH_4 concentration. The highest number of methanotrophic bacteria cells, within the range from 10^5 to 10^{11} cells in 1 g of moist material has been found in the upper part of wastes, in landfill cover soils or in biofilters for methane oxidation (Nozhevnikova et al., 1993; Lebedev et al., 1994, Gebert et al., 2003, Kallistova et al., 2005). The amount of methanotrophs determined in the bottom sediments of the Bering Sea and the North Sea has been found to be lower than *ca.* 10^4 cells per cm^3 of sediment, and in the sediments of the Black Sea – of *ca.* 10^6 cells per cm^3 (Galchenko, 1995).

Methanotrophs contribute to the reduction of atmospheric methane concentration not only by capturing it from the atmosphere (acting as an absorbent) but also by preventing methane emission from various environments. The latter type of the methanotrophic activity seems to be the more important. According to estimates by Reeburgh et al. (1993) soils exposed to high methane concentrations (landfill cover soils, surface layer of bog soils) prevent the emission of about 700 Tg of CH_4 annually. When methane migrates from its source to the atmosphere it passes through an aerated layer, where the oxidation process takes place. Biochemical changes in methanotroph cells lead to the production of CO_2, H_2O and an increase in organic matter. Absorption of infra-red radiation by carbon dioxide is more than 20 times lower (on a molecule for molecule basis) than that of methane.

A simplified scheme of the methane oxidation reaction based only on the balance of substrates and products is following:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Stoichiometrically, oxidation of 1 mole of CH_4 by 2 moles of O_2 results in the production of 1 mole of CO_2. Practically, the O_2 uptake and the CO_2 production per unit CH_4 volume are lower than the theoretically obtained values. This is related to the binding of some of the carbon derived from CH_4 into the cell biomass (so-called assimilation pathways). In the initial stage of the methanotrophic culture growth, when a significant biomass increase can be observed, a large amount of carbon is assimilated. The value of assimilated carbon decreases with time and reaches a relatively steady-state level (Hoeks, 1972). Should a dissimilation pathway of the process prevail all the CH_4 is converted into CO_2.

Both types of the chemical changes run in a number of phases: The first phase consists of the change of CH_4 into CH_3OH in the presence of molecular O_2, with the participation of an enzyme – methane monooxygenase (MMO) that contains copper and iron.

The next phase consists of the production of formaldehyde. It can be oxidized to formic acid or be assimilated by the cell. Formic acid can be oxidized to CO_2. Carbon dioxide is removed from the cell or assimilated by it.

The process of CH_4 oxidation is of exoergic character. Energy released during the process can be used for the synthesis of cell matter (assimilation of carbohydrates). The total value of energy produced during the CH_4 oxidation process is a sum of the energy values released at individual stages of the process.

$$\underset{\text{methane}}{CH_4} \xrightarrow{-109,34} \underset{\text{methanol}}{CH_3OH} \xrightarrow{-187,58} \underset{\text{formaldehyde}}{HCOH} \rightarrow$$

$$\xrightarrow{-239,23} \underset{\text{formic acid}}{HCOOH} \xrightarrow{-243,83} \underset{\text{carbon dioxide}}{CO_2}$$

Energy released during the above presented process is expressed in kJ mol^{-1} (Hoeks, 1972). The process of CH_4 oxidation in soil runs according to the kinetic equation of Michaelis-Menten that is between first and zero order reaction kinetics. A curve that illustrates its course is often called a substrate saturation curve and can be described as follows:

$$V = V_{\max} \frac{1}{1 + \frac{K_M}{C}}$$

where:
V – actual rate of the reaction [$m^3 m^3 s^{-1}$]
V_{max} – maximum reaction rate [$m^3 m^3 s^{-1}$]
K_M – Michaelis constant [$m^3 m^{-3}$]
C – CH_4 concentration [$m^3 m^{-3}$]

The described process can be observed in the upper part of an aerated layer of landfilled wastes or in landfill cover soils. When biogas passes through the layer inhabited by methanotrophs, it loses some of its methane. The reduction of methane emission from a landfill varies depends on the methane load emitted from the waste layer as well as on the parameters that characterize its cover (thickness, kind of material) and climate conditions (the season etc).

2 REVIEW OF CONDITIONS FOR THE MICROBIAL METHANE OXIDATION

The first found in the literature research reports concerning biochemical oxidation of hydrocarbons were published in the fifties, sixties and seventies of the 20th century (ZoBell, 1946; Hutton & ZoBell, 1949; Voroshilova & Dianova, 1950; Van der Linden and Thijsse, 1965; Kung and Wagner, 1970; Hoeks, 1972). Initially, the research projects were carried out by microbiologists and dealt mainly with metabolic pathways of changes leading to methane oxidation by various types of bacteria (Patel and Hoare, 1971; Ferenci et al., 1975; Patel, et al., 1976; Patel et al., 1978). The investigations were continued in the following years (Jones and Morita, 1983; Hyman and Wood, 1983; Traore et al., 1983; Leak and Dalton, 1986; Ward 1987; Dalton et al. 1990).

The potential of methane-utilizing bacteria to induce other processes like oxidation of carbon monoxide or ammonia has also been a subject of numerous investigations (De Bont and Mulder, 1974; Hubley et al., 1974; Daniels et al., 1977; O'Neill and Wilkinson, 1977; Dalton, 1977; Suzuki et al., 1976; Patel et al., 1980). O'Neill and Wilkinson (1977) showed that ammonia can inhibit the methane oxidation activity. Weaver and Dugan (1972) noticed an increase of the oxidizing activity when clay minerals were applied. At the end of the seventies and eighties researchers turned to methane oxidation in anoxic conditions in waters or sea and lake sediments (Panganiban et al., 1979; Laurinavichus et al., 1979, Reeburgh, 1980; Zehnder & Brock, 1980; Devol, 1983; Iversen et al., 1987; King, 1990).

As early as the seventies the carbon isotope ^{14}C was used to determine the rate of microbiological methane oxidation (Beliaev et al., 1975). The isotope fractionation of carbon that occurs in the course of methane oxidation was made the basis for the evaluation of methane oxidation efficiency (Barker and Fritz, 1981; Ivanov et al., 1981; Liptay et al., 1998, Mahieu et al., 2006). Another method that can be applied for that purpose is methane concentration measurement by means of chromatography. The method has been recommended by Saralov (1979) and is presently very popular. A survey of methods for measuring methane oxidation in landfills can be found in the paper by Nozhevnikova et al. (2003). Godlewska-Lipowa (1979) have pointed to practical applications of methanotrophic bacteria such as to reduce hazards related to the presence of methane in coal-mines.

In the early nineties a renaissance of studies of methane oxidation in natural continental ecosystems (Whalen & Reeburgh, 1990, Topp, E., Pattey, E., 1997) and in waste landfills, began (Whalen, et al., 1990; Jones & Nedwell, 1993; Bogner and Spokas, 1993).

The presence of methanotrophic bacteria in landfills had already been investigated in the eighties when Mancinelli & McKay (1984) observed the occurrence of bacteria able to oxidize methane in sanitary landfills.

King (1990) has emphasized the significance of the methane oxidation process applied to reduce its emission from wetlands to the atmosphere, while Börjesson & Svensson (1997) as well as Czepiel et al. (1996) have analyzed the reducing effect of methane oxidation on the emission of that gas from landfills.

Starting from the nineties of the 20th century an intensive development of investigations into methane oxidation in various kinds of soil that vary by their graining, use, climate zone *etc* has been observed (Bronson & Mosier, 1991; Miura et al., 1992; Bender & Conrad, 1993; Hütsch et al., 1993; Situala & Bakken, 1993; Hütsch et al., 1994; Murase & Kimura, 1994a; Murase & Kimura, 1994b; Bender & Conrad, 1995; Watanabe et al., 1995; Hütsch, 1996; Hütsch et al., 1996; Whalen & Reeburgh, 1996; Benstead & King, 1997; Powlson et al., 1997; Boeckx et al., 1998; Hütsch, 1998; Bodelier et al., 2000; Suwanware and Robertson, 2005; Teh et al., 2005, Jang et al., 2006; Jacinthe & Lal, 2006; Jugnia et al., 2006).

2.1 *The role of physical properties of the medium on methane oxidation*

The size and shapes of the structural elements of the soil influence the methanotrophic properties of the material by determining its porosity and the surface accessible for microorganisms. Soil porosity determines the gas diffusion rate and consequently the availability of substrates (CH_4 and O_2) for methanotrophs and the removal of gases that have formed resulting from the metabolism (CO_2). According to Born et al. (1990) and Dörr et al. (1993) the methanotrophic capacity of soils of prevalent clay and silt fractions is diffusion-limited. Diffusion also determinates the depth of the oxidation zone in soil. Bender and Conrad (1995) found that, when a grain diameter decreases from above 2 mm to below 0.05 mm, the maximal methanotrophic activity is reduced and the time for soil to reach it lengthened although the number of methanotrophs remains basically unchanged. Tests performed on soils of various textures have proved that the mean methanotrophic activity in soils of considerable sand fraction content ($\geq 65\%$) and with an insignificant amount of clay ($\leq 18\%$) is greater by an order of magnitude than in a fine-grain material containing over 35% clay (Dörr et al., 1993). A higher oxidizing capacity of soils collected from landfill covers composed mostly of coarse sand as compared to a soil of higher silt and clay content and a sandy soil of prevalent fine sand has also been observed. The degree CH_4 oxidation in coarse sand was 61%, while for the two remaining materials the value of 40% was obtained. The difference can be explained mostly by easier gas diffusion in the more porous material. It prevails over the effect of biogene accessibility for microorganisms, which is greater in the case of coarse-grain soils (Kightley et al., 1995).

The diffusion rate also depends on the moisture content and temperature of the soil material. In a dry soil diffusion proceeds easier than in a moist soil but despite optimal conditions for substrate accessibility CH_4 oxidation is limited then because the lack of water cause a physiological stress to methanotrophs. On the other hand, an excess of water obstructs diffusion of CH_4 and O_2 as the diffusion rate of these gases is *ca.* 10^4 times slower in water than in air (Boeckx et al., 1996).

Another factor that influences the efficiency of gas flow in soil is its compaction. The CH_4 oxidation potential is lower in a compact soil (Hansen et al., 1993). Tractor compacting of a sandy soil from the density of 1.21 to 1.3 gcm^3, has a reducing effect on its methanotrophic capacity of 52%.

Moisture is an important physical factor that indirectly influences gas diffusion by changing the porosity of the medium and directly affects the development of microorganisms that need water. A strong dependence of methanotrophic capacity on the water content in soil has been experimentally confirmed. A negative correlation between CH_4 uptake rate and the moisture content in soil within the range of 30–50% v/v has been proved by tests performed on forest soil of the temperate climate zone (Lessard et al., 1994). The above results are concordant with the observations of Whalen & Reeburgh (1996), who have also indicated a decrease of methanotrophic activity within the mentioned range of moisture content in soils that are not exposed to permanent flooding. In waterlogged soils, a decrease of methanotrophic capacity occurs for higher moisture contents. The above mentioned authors have shown that there is an optimal value that can be expressed as a percentage of the total water holding capacity (WHC) of soils. It corresponds to the state of complete filling of soil pores with water. The optimal moisture content for CH_4 oxidation in Alaskan forest soils has been shown to be *ca*. 21 and 27% of the WHC, while in waterlogged soils of that area it reached up to 50% of that capacity. The optimal soil moisture content for CH_4 oxidation in a loamy sand has been shown to be *ca.* 13% by weight (Park et al., 2002). The optimal weight moisture content in a meadow cambisol ranged from 15 to 22% (Bender & Conrad, 1995). Experiments carried out on sandy and sandy-clay soils taken from landfill covers have shown that the rate of methane oxidation is highest at a water content of 11–20% (w/w) (Whalen et al., 1990; Boeckx & Van Cleemput, 1996; Boeckx et al., 1996). It has been shown that the optimal moistness is equal to *ca.* half the value of the soil water holding capacity. The WHC value mainly depends on the granulometric composition of the soil, which determines the porosity and water-holding ability of a medium.

Einola et al. (2007) have confirmed that the response of CH_4 consumption to water content is temperature-dependent. In the temperature range from 1 to 6°C, CH_4 consumption increases along with the water content (33–67% of water holding capacity) while in the range from 12 to 19°C the response was curvilinear, peaking at 50% of WHC.

In the case of highly porous soils CH_4 oxidation is temperature dependent to a considerable degree. The temperature coefficient of the reaction rate calculated from the Van't Hoff equation shows how much the reaction rate changes with a temperature increase of 10°C makes it possible to determine which factor limits the reaction. In the case of a biochemically limited reaction the coefficient varies in the range from 2 to 3. If the value is <2 the process is assumed to be limited by physical factors (King, 1997).

In practice it is moisture, the factor that influences diffusion of gases in a porous medium that is more important than temperature for the modification of methanotrophic capacity of non-flooded soils. The Q_{10} values obtained for these kinds of soils are smaller than 2, which supports the above arguments. The value for forest soils is *ca.* 1.5 within the temperature range of 5–15°C (Born et al., 1990; Lessard et al., 1994), for soils of a landfill cover it is *ca.* 1.9. Whalen et al., (1990) have obtained such a value with the temperature range of 5–26°C, while Boeckx et al. (1996) – for temperatures of 10–20°C. It suggests that the low sensitivity of the CH_4 oxidation process to temperature variations would cause only small daily variations of the oxidation rate.

The temperature effect becomes more significant in the case of waterlogged or highly porous soils, where substrate availability for microrganisms is not diffusion limited. In the case of Alaskan bog soils the Q_{10} value is 2.1 within the temperature range of 4°C–13°C. The CH_4 oxidation process in such soils can be considerably dependent on inhibitors and catalysts specific for the process. Einola et al., 2007 have found very high Q_{10} values (ranging from 6.5 to 8.4) for CH_4 consumption in a landfill cover soil in a boreal climate.

Investigations carried out by Whalen et al. (1990) on a sandy-clay soil of the landfill cover surface layer, within the temperature range of 5–46°C, indicate that there is a temperature optimum of 31°C. Temperatures decrease below that value bring about a smooth decline of methanotrophic activity, while an increase of the temperature up to the values exceeding the optimum causes a rapid drop in the activity to almost zero at 46°C. This is related to the denaturation processes of proteins contained in methanotrophic cells. A similar value of the temperature optimum contained within the range of 25–30°C has been obtained for a soil of a prevalent sand fraction also taken from a landfill cover (Boeckx & Van Cleemput, 1994; Boeckx & Van Cleemput, 1996). A little lower optimum value of 23°C has been obtained for Alaskan waterlogged soils (Whalen & Reeburgh, 1996).

Results of Boeckx et al. investigations (1996) performed on a sandy-clay soil of a landfill cover indicate that the temperature optimum value varies depending on the moisture content of the soil material. Within the moistness range of 10–30% of weight, the temperature optimum decreases along with the increasing moisture content from 27.1°C at the lowest moistness level to 20.1°C at the upper limit of the range. Increasing the moisture content results in a reducing effect on the gas transport to the bacteria cell. This can eventually lead to a situation in which the substrate supply is smaller than the oxidizing capacity of microorganisms at a given temperature. Thus, at higher moisture content the CH_4 transport becomes a limiting factor for the oxidation process. When the moisture content is low, the limiting factor is the activity of microorganisms.

2.2 *The role of chemical and physical-chemical factors*

Results of lab tests show that there is a distinct influence of the CH_4 concentration on the soil oxidizing capacity. Bykova et al. (2007) noted an increase in the CH_4 oxidizing activity by *ca.* 10^5-times and a twofold increase in the total number of methanotrophs in an arable soil pre-incubated at elevated CH_4 concentrations ($100\,\mathrm{ml}\ CH_4\ \mathrm{l}^{-1}$). Methanotrophic capacity measured in soil taken out of a landfill cover increased by more than fourfold with an increase of CH_4 concentration from 1.7 to 84 000 ppm (Bogner et al., 1997).

There are numerous experimental results which indicate that the kinetics of the CH_4 oxidation process can be described by the Michaelis-Menten equation originally introduced to describe enzyme kinetics. The Michaelis curve shape and kinetic parameters of the reaction (V_{max} and K_M) mainly depend on the CH_4, concentration in the natural environment from whence the soil was sampled. Soils exposed to high CH_4, concentration like those taken from a landfill cover, rice fields and waterlogged areas are characterized by high methanotrophic activity and low affinity to CH_4 (high K_M). The situation is different in the case of soils exposed to the atmospheric concentration of CH_4. Their methanotrophic activity is low but they can oxidize CH_4 even if its concentration is insignificant. Such kinetics can be observed in forest, meadow and arable soils. V_{max} values obtained in a sand material exposed to high methane concentration ranged from $0.11 \cdot 10^{-3} - 0.86 \cdot 10^{-3}\,\mathrm{cm}^3\,\mathrm{kg\ d.w.}^{-1}\mathrm{s}^{-1}$(Pawłowska & Stępniewski, 2006) and they are similar to those obtained by Whalen et al. (1990) in a soil from the top of the landfill cover. These values were approximately one order of magnitude lower than the potential methanotrophic activity measured by Kightley et al. (1995) in coarse-grained sand taken from a landfill cover; by Stein and Hettiaratchi (2001) in loam soil from a landfill cover, and by Gebert et al. (2003) in crushed expanded clay material tested as a biofilter for landfill gas, and equal to $6.49–7.29 \cdot 10^{-3}$, $6.2 \cdot 10^{-3}$ and $11.08 \cdot 10^{-3}$ cm^3 kg d.w.$^{-1}s^{-1}$, respectively. For comparison, the V_{max} values measured in forest soils were lower by several orders of magnitude, and varied between $4.9 \cdot 10^{-6}$ and $56.8 \cdot 10^{-6}$ cm^3 kg d.w.$^{-1}s^{-1}$ (Bender and Conrad, 1993; Whalen & Reeburgh, 1996; Benstead & King, 1997).

K_M values for CH_4 measured in field conditions or in conditions of a simulated landfill cover or biofilter given in the literature range between 0.08% and 2.9% (Whalen et al., 1990; Kightley et al., 1995; Bogner et al., 1997, De Visscher et al., 2001; Gebert et al., 2003; Scheutz & Kjeldsen, 2004; Pawłowska & Stępniewski, 2006).

The measured affinity for methane in forest soils is several orders of magnitude greater. The Michaelis constant found by Benstead & King (1997) is *ca.* $0.8\,10^{-3}$ and by Whalen & Reeburgh (1996) -9.9 10^{-3}% of CH_4. Comparison of kinetic parameters measured in waterlogged and forest soils of the boreal zone shows that affinity for CH_4 in the first type of soils, exposed to high CH_4 concentration is about 10-times lower, and the V_{max} about 1000-times higher (Whalen & Reeburgh, 1996).

Results of many research projects have shown that methanotrophic activity of a soil linearly increases together with the CH_4, concentration growth, which indicates kinetics of the 1st order. It can mean that the considered range of CH_4, concentrations was much below the saturation value. First order reaction kinetics was also observed during testing of the methanotrophic capacity of landfill cover soils in the CH_4, concentration range from 100 to 5,000 ppm. Also as the CH_4, concentration range extended up to 77.000 ppm the CH_4 oxidation in a landfill over soil followed 1st order kinetics (Whalen et al., 1990). However, Kightley et al. (1995) found the CH_4 saturating values in landfill cover soils at CH_4, concentrations below 50.000 ppm.

The process of CH_4 oxidation in soil begins when the concentration of that gas exceeds a certain threshold value. Many authors claim that the value is within the range of 0.1–0.3 ppm CH_4 (Bender & Conrad, 1992; Adamsen & King, 1993; Bender & Conrad, 1993; Heipieper & Debont, 1997). Induction of a methanotrophic process in a forest luvisol, meadow and arable cambisol, as well as in a rice field soil requires CH_4 concentrations within the range of 100–1000 ppm (Bender & Conrad, 1995; Kightley et al., 1995). Methanotrophs incubated in the CH_4 concentrations below 0.03 ppm lose their capacity to oxidize methane (Benstead & King, 1997). The threshold value for CH_4 concentration in sediments is higher than in the case of soils and equals 2–3 ppm (Mancinelli, 1995).

Schnell & King (1995) have found that a reduction of O_2 concentration from the atmospheric value to 2 and 0.2% is reflected in a decline of the forest soil methanotrophic activity. The threshold concentration value for O_2 dissolved in soil water of pure cultures of the methanotrophs Methylosinus trichosporium and Methylobacter luteus investigated by Ren et al. (1997) was 5.7 μM. Examination of the O_2 concentration effect on CH_4 oxidation in a soil sampled in the vicinity of natural gas leakage have shown that the reaction kinetics can be described by the Michaelis-Menten equation. The K_M value for O_2 is within the concentration range of 0.2–1.2% depending on the soil incubation temperature which ranged from 13.5 to 20.5°C (Hoeks, 1972). The V_{max} value measured in a sandy material exposed to high CH_4 concentration was equal to 5.88×10^{-4} CH_4 $cm^3kg^{-1}s^{-1}$, which is a value *ca.* one order of magnitude smaller than those obtained by Geber et al. (2003) in the expanded clay material flushed by landfill gas ($V_{max} = 8.52 \times 10^{-3}$ $cm^3kg^{-1}s^{-1}$). The K_M value for O_2 was *ca.* 10.5% (v/v), which is >twofold higher than the K_{MO2} measured by Geber et al. (2003), equal to 4.6% (v/v). The half saturation constants found by other authors in various habitats were many times lower. Watson et al. (1999) found the K_{MO2} in a peat soil is of *ca.* 2.5%. Hoeks (1972) obtained the K_M values for O_2 within the range from 0.2 to 1.2% depending on the temperature of soil incubation, which ranged from 13.5 to 20°C. His examinations were performed on a soil taken in the vicinity of natural gas leakages. According to De Visscher et al. (1999) the K_M value measured at a simulated landfill cover was about 1.24%.

Those high K_M values suggest that the methane-oxidizing bacteria were not microaerofiles. Geber et al. (2003) did not detect any substantial methane oxidizing activity in expanded clay material below the O_2 concentration of 1.7–2.6.% (v/v).

Apart from the direct effect of oxygen concentration on the CH_4 oxidation rate Wilshusen, et al. 2004a found an indirect mechanism that has an influence on the EPS production. At high oxygen concentration the EPS production was about 250% of the amount produced at low oxygen concentration, which is probably the reason for the diminished gas diffusion.

The CH_4 oxidation process occurs within a comparatively wide pH range from pH < 4 in sandy (Hoeks, 1972) and bog soils (Powlson et al., 1997) up to >9 in bog soils (King, 1990). At lower pH values it is possible that the drop in CH_4 concentration could result from the activity of yeast that easily adapts to an acidified medium. The optimal pH for the growth of methanotrophic bacteria isolated from dune sands located in the vicinity of natural gas leakage was *ca.* 7.0, although their growth was also observed in the pH range 5.5–8.0 (Adamse et al., 1972). Arif et al. (1996) have noted a slightly narrower pH range (5.9–7.7) in agriculturally used sandy soils. The optimum pH in an acid forest luvisol was *ca.* 6.3 (Bender and Conrad, 1995), while in bog soils the most intensive oxidation occurred at pH 6–8 (King, 1990).

The pH effect is not direct. According to Powlson et al., (1997) it is related to the changes that accompany acidification e.g., to the release of toxic ions Al^{3+} in acid media. The effect of increasing the pH value by soil liming led to ambiguous results. Liming of acid forest soils (the pH changed from 3.6 to 4.7) at the atmospheric CH_4 content level did not alter their methanotrophic activity, while results of lab tests performed by Yavitt et al. (1993) on bog soils show that the methanotrophic process becomes inhibited and the pH increases from 4.7 to 5.4 after liming. Contrary to the above observations are the results of testing performed in Sweden on forest soils (Klemedtsson & Klemedtsson, 1997), where the effect of liming stimulated the CH_4 oxidation. The effect of liming may also be related to the action of lime additives. For instance, acetylene-residue lime which is the product of an acetylene producing reaction can act as an inhibitor owing to the presence of reaction by-products.

King (1997) found that soil acidification resulting from acid rain and the presence of CO_2 that forms in the methanotrophic process can reduce a soil's capacity to oxidize CH_4.

Many authors confirm inhibition or total inhibition of the CH_4 oxidation process under the influence of nitrogenous fertilization in the ammonium form (Bender & Conrad, 1994; Willison et al., 1995; Klemedtsson & Klemedtsson, 1997; Roslev et al., 1997, Bykova et al., 2007). Long-term (130 years) application of nitrogenous fertilizers in the form of $(NH_4)_2SO_4$ at an annual dose of 96–144 kg N ha^{-1} totally inhibited the CH_4 oxidation process in cultivated lands (Hütsch et al., 1994). Even when the fertilization was discontinued for three years, the methanotrophic capacity of the soil was not restored. Incubation experiments have been performed on arable soils with and without ammonium (100 mg N kg^{-1}) addition. After the pre-incubation with ammonium, CH_4 oxidation was completely inhibited; although no change in the methanotrophic community structure was detected Bykova et al. (2007).

A strong inhibition effect was also brought about by a one-time application of NH_4^+ and NO_3^- ions to the soil (Kightley et al., 1995). Addition of NH_4NO_3 to a sandy soil sampled from a landfill cover in an amount equivalent to 2 g N kg of $soil^{-1}$ caused a 65% drop in methanotrophic capacity as compared to a non-fertilized soil, while an addition to arable soils of a 10-times lower nitrogen dose (0.21 g N kg^{-1}) in the form of $(NH_4)_2SO_4$ resulted in complete inhibition of the CH_4 oxidation (Hütsch et al., 1996). An even smaller amount of N, (0.025 g kg^{-1}), in the form NH_4Cl reduced the methanotrophic capacity of clay sand by 78–89% (Bronson & Mosier, 1994). Boeckx & Van Cleemput (1996) observed that the CH_4 concentration drop rate in the headspace of a landfill cover soil that was decreasing with an increasing dose of N-NH_4^+ from 0.025 to 0.1 g N kg^{-1} is negatively correlated with the N_2O concentration growth. The negative correlation between methanotrophic activity and the nitrification rate manifested by the N_2O production has also been noted by Situala & Bakken (1993). Competition of NH_4^+ and CH_4 ions for a non-specific enzyme (methane monooxygenase) is often deemed to be the reason for the occurrence of the phenomenon. Both methanotrophs and nitrifying bacteria can oxidize CH_4 and NH_4^+. Similarity of the molecule shapes and sizes, low MMO specificity and probably higher aggressiveness of NH_4^+ as a substrate are the reasons why, in the presence of ammonium ions, CH_4 is not bound to active centers of the enzyme. MMO masking by the first product of NH_4^+ oxidation-oxammonium (NH_2OH) – as well as by NO_2^- ions can provide another explanation for that phenomenon (Boeckx et al., 1996; King & Schnell 1994; Boeckx & Van Cleemput, 1996). It has been noticed that the intensity of the NH_4^+ action does not directly depend on their concentration but rather should be related to the nitrogen change rate. (Hütsch et al., 1994; Situala & Bakken, 1993). There are soils where, despite a high concentration of NH_4^+, the CH_4 oxidation process proceeds intensively. It has been shown that inhibition of that process occurs when intensive change of the matter from organic-to-mineral takes place, which is manifested by a low C/N ratio. Inhibition of the process did not occur in the case of the weak mineralization manifested by a high C/N ratio (Boeckx & Van Cleemput, 1996). Bender & Conrad (1995) have noticed that the application of low NH_4^+ concentrations is advantageous, while reduction of the CH_4 oxidation rate occurs only when a certain dose of the ions is exceeded. In the case of a meadow and arable cambisol 10 mM was the limiting dose. The positive action of low NH_4^+ concentrations can be related to the demand for nitrogen that is indispensable for the growth of microorganisms and enzyme production. It is also possible that the observation time (6h) was too short to reveal the inhibiting effect (Bender and Conrad, 1995). The fact that not all methanotrophs react the same way to the presence of NH_4^+ ions in the substrate can also be of some explicative value. Test results have proved that e.g., *Methylobacter albus* is more sensitive to their presence than *Methylosinus trichosporium*. It has also been noted that the inhibition power decreases in parallel with the concentration increase of CH_4 that is accessible for microorganisms as well as with the increasing moisture of the soil. The higher the water content the less distinct is the inhibiting effect of ammonium fertilization, which follows from the limited accessibility of oxygen that is indispensable for the oxidation process (King and Schnell, 1994).

In many cases the CH_4 oxidation inhibition by NO_3^- ions introduced in the form of KNO_3 or $NaNO_3$ was much weaker than in the case of NH_4^+ ions or did not occur at all (Hütsch et al., 1993; Powlson et al., 1997, Park et al., 2002). KNO_3 added to a forest soil, in the amount equivalent to $0.025\,g\ N\ kg^{-1}$ of the soil brought about a decline in its methanotrophic capacity by 27–46% (Situala & Bakken, 1993). On the other hand, according to Nesbit and Breitenbeck (1992) the inhibiting action of that compound was only shown at higher concentration values ($0.49\,g\,N\,kg^{-1}$). A complete diminution of methanotrophic activity in sandy arable soils has been observed when $NaNO_3$ equivalent to $0.21\,g\,N\,kg^{-1}$, was added. The same amount of nitrogen in soils formed on a loess base significantly limited the process but without its complete inhibition. It indicates a relationship between the fertilization effect and the granulometric composition of a soil (Hütsch et al., 1996). The results of the presented investigation do not give an unambiguous answer to the question of which kind of added ions brings about the change in methanotrophic capacity. It is possible that it is not NO_3^- ions but rather that Na^+ ions play a greater role in the CH_4 oxidation process. Similar doubts concern the above discussed effect of KNO_3 and ammonium fertilization in the form of $(NH_4)_2SO_4$ and NH_4Cl.

Fertilization of a clay soil with urea equivalent to $218\,kg\,ha^{-1}$ either did not cause any change in methanotrophic capacity (Bronson & Mosier, 1991) or else its effect was insignificant (Crill et al., 1994).

K_2HPO_4 added to soil in the amount equivalent to $0.1\,g\,P\,kg^{-1}$ did not bring about any conspicuous changes in the methanotrophic activity of a landfill cover soil with coarse-sand granulometric composition (Kightley et al., 1995). However, testing performed on arable soils fertilized with various kinds of organic and mineral fertilizers for many years showed the highest methanotrophic activity of soil fertilized with phosphorus and potassium (24 kg P, $75\,kg\,K\,ha^{-1}$) (Hütsch, 1996).

Hoeks (1972) found that mineral fertilization applied in the form of a mixture of various salts ($NaNO_3$, $MgSO_4$, Na_2HPO_4, NaH_2PO_4, KCl, $CaCl_2$, $FeSO_4$, $CuSO_4$, H_3BO_3, $MnSO_4$, $ZnSO_4$) brought about quicker adaptation of microorganisms and better growth of the methanotrophic cultures.

Organic fertilization in the form of manure did not show any significant influence on the methanotrophic capacity of arable soils (Powlson et al., 1997). On the other hand, Kightley et al. (1995) found that sewage sludge ($2.5\,g\,kg^{-1}$) added to a sandy soil from a landfill cover caused a methanotrophic activity increase by 26% as compared to a non-fertilized soil.

Addition of Cu^{2+} ions to a rice-field soil up to the concentration of 4.2 mM had a stimulating effect of the CH_4 oxidation process, which can be explained by the participation of Cu^{2+} ions in the structure of a methane monooxygenase molecule. However, at the concentration of 5.5 mM copper toxicity was revealed in the soil water causing a 50% inhibition of the CH_4 oxidation (Bender & Conrad, 1995). According to Schnell and King the oxidizing capacity remained unchanged when Cu^{2+} ions were introduced to forest soils (1995).

Strong inhibition of the oxidation process was observed when nitropyrine (2-chloro-6-trichloromethylo-pyridine), a nitrification inhibitor, was added to soil. A dose of $5\,mg\,kg^{-1}$ added to sandy and clay soils produced a 52–89% reduction of their methanotrophic capacity (Bronson &i Mosier, 1994). Arif et al., (1996) have also observed the strongly inhibiting effect of nitropyrine. Acetylene is another strong inhibitor. A dose of $5\,\mu l\,C_2H_2$ per a liter of air over the soil reduced the process rate by 76–100% (Bronson & Mosier, 1994). Nearly complete inhibition by acetylene added ($30–60\,\mu l\,l^{-1}$) to air over the soil has also been observed in rice-field soils (Watanabe et al., 1995). Acetylene causes an irreversible inactivation of methane monooxygenase (Bronson & Mosier, 1994).

An inhibiting effect of acetic acid has also been found. The acid added ($4\,\mu mol\,g^{-1}$ ($90\,\mu l\,g^{-1}$) to a soil produced an 88% decline of the soil oxidizing capacity (Benstead & King, 1997). The action of that acid can be of importance for the CH_4 oxidation process in a landfill as it forms in the aerobic phase of waste decomposition.

Methanol that forms in the decomposition of lignins and pectins and makes an alternative substrate to methane monooxygenase caused a temporary decline of the methanotrophic activity (Benstead & King, 1997). A similar phenomenon has been observed by Watanabe et al. (1995) for an addition of propylene. Inhibiting action with respect to the CH_4 oxidation process has been also exhibited by carbon monoxide (Bender & Conrad, 1994) and acetone (Watanabe et al., 1995).

An inhibiting effect on the CH_4 oxidation is exhibited by most of the tested pesticides. The intensity of the inhibiting action depends not only on the pesticide dose but also on the kind of soil and the way it is used. Testing of six selected herbicides and one fungicide performed by Boeckx et al. (1998) has shown considerable differentiation in the inhibition strength depending on the soil graining. In the case of a sandy soil, inhibition was stronger than for clay. On the other hand, no inhibiting effect of any pesticide on the CH_4 oxidation in a landfill cover soil was observed even at a 10-times higher dose than the one applied to arable soils. Arif et al. (1996) have noted a complete inhibition of the CH_4 oxidation in arable soils when 25 ppm of a herbicide – dichlorophenoxyacetic acid (2,4-D) was applied.

3 TECHNOLOGICAL SOLUTIONS FOR METHANE OXIDATION IN MUNICIPAL WASTE DUMPS

The nineties also mark the beginning of research into the possibilities of methane oxidation in cover soils of waste landfills (Kightley et al., 1995; Kjeldsen et al., 1997, Humer & Lechner,1999; De Visscher et al.,1999; Bogner et al., 1999).

Selection of the most efficient material from the viewpoint of methane emission reduction has often been an objective of such investigations. Mostly, soils have been tested because they are easily available and landfill covers are material-consuming structures. Testing of landfill cover soils or other mineral or organic materials apart from its cognitive character is also of a pragmatic value as its objective is to optimize methane oxidation conditions in various materials that can potentially be used to make landfill covers or biofilter fillings. The effect of physical factors (like temperature, moisture) and chemical ones (such as methane and oxygen concentrations, pH value, presence of nitrogen compounds, pesticides) on the activity of methanotrophic bacteria has been analyzed (Boeckx and Van Cleemput 1996; Visvanathan et al., 1999; Börjesson et al., 1998; Boeckx et al., 1998; Christophersen & Kjeldsen, 2001; Scheutz and Kjeldsen, 2004, Pawlowska and Stepniewski 2004; Yuan et al., 2005, Kallistova et al., 2005, Einola et al., 2007). At the end of the nineties the formation of polysaccharide compounds that obstruct gas diffusion in materials used as methanotrophic biological deposits was observed. They are referred to as Exopolysaccharides or in short – EPS (Hilger et al., 1999). The problem makes another subject of considerations for researchers (Wilshusen, et al., 2004a).

Tests of the oxidizing capacity for methane are usually performed on a laboratory scale in a dynamic system composed of columns that are filled with the tested materials (Kightley et al., 1995, Damman et al., 1999; Park et al., 2002; Streese et al., 2003; Wilshusen et al., 2004b; Pawlowska & Stepniewski, 2006, Kettunen et al., 2006; Haubrichs & Widmann, 2006) or less frequently – in field conditions (Gebert et al., 2003; Streese et al., 2003; Gebert & Gröengröeft, 2006). Initially, the testing was performed on materials drawn from landfill covers and on potential materials for the formation of those covers. Then the focus was shifted to the search for the best-applicable materials from the methane oxidation viewpoint to be used as biofilter fillings.

New legal regulations concerning waste management make it necessary to change forms of biological deposits that are meant for methane oxidation.

As it is required that the bottom and the top cap of a landfill are insulated the cover cannot serve a filter for the emitted gas any more. According to the legal regulations there should be an intake and a collector for the biogas. When its calorific value is high enough it can be used as a fuel but when the methane content is insufficient (<30% v/v) or its productivity is low (<30 m^3/h) (Dammann et al., 1999) it seems purposeful to apply biological deposits to oxidize the methane. As the top cap should be insulated it is biofilters and not landfill covers that seem to be more useful. Hence the interest in methane-oxidizing biofilters (Park et al., 2002; Streese and Stegmann, 2003; Park et al., 2004; Wilshusen, et al., 2004b; Haubrichs and Widmann, 2006). Various kinds of compost comprise the most often tested biofilter filling (Wilshusen, et al., 2004b, Powelson et al., 2006; Zeiss, 2006, Haubrichs and Widmann, 2006). However, investigations concerning landfill covers are still continued. These are both case-studies and projects, whose objective is to increase the oxidizing activity (Börjesson et al., 2004; Scheutz et al., 2004; Kallistova 2005; Yuan et al., 2005; Zeiss, C.A., 2006; Abichou et al., 2006; Scheutz & Kjeldsen, 2005).

Porous material, both of the mineral and organic kind, can make a habitat for the growth of methanotrophic microorganisms. The shape of the deposit and its volume can be selected depending on kind of landfill (organized with the insulated bottom and top cap, organized with the top layer unpacked, unorganized), predicted volume of the biogas production (of various methane content). Table 1 presents possible technological solutions.

The term "cover" means a layer of porous material that covers a layer of wastes, where diffusion of gases and migration of precipitation water are possible (Fig. 1a). Presently, the cover application potential is limited because of regulations that in many countries impose a requirement that the bottom and the top layer of a landfill are insulated [Directive 1999/31/EC]. The top cap insulation protects against an uncontrolled release of landfill gases as well as against excessive production of the precipitation water reflux. Such packing should consist of four layers, one should be impermeable. The soil cover, which is the outermost layer of the packing does not contribute to the reduction of methane and odor emissions but is meant to provide a biological phase of the landfill reclamation possible.

Table 1. Forms of a filterbed for methane oxidation and their possible applications.

Kind of a filterbed	Characteristics	Possible applications
Traditional landfill cover	Soil material layer put directly on the waste layer.	Old, inadequately protected landfills of low biogas content or landfills in poor countries. The solution is partial, inexpensive but easy to apply.
Modified landfill cover	Soil material layer put on an insulated layer of wastes. Biogas escapes from a well to a draining layer from where it migrates to an oxidizing layer.	Organized landfills with insulation and a degassing system Possible application when there is no biogas collection or with the on-ground part of the degassing system uninstalled (at the biogas quality decrease).
Biofilter	Container that is an independent unit for biogas filtration. It can be also be installed into the cover as a so-called "degassing window" or "bio-window".	Organized landfills: small ones –expected short-time production of a high-quality biogas, big ones – with the biogas collection when their operation for energy-winning purposes is over, when the decreased quality of biogas makes it useless as a fuel, big ones – where the amount of organic substances is low – low biogas quality.

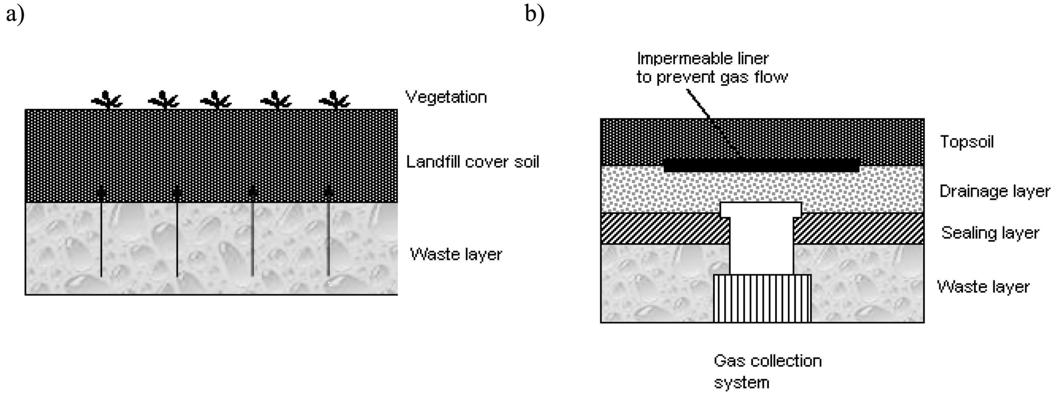

Figure 1. Two types of a landfill cover: (a) traditional and (b) modified landfill cover soil proposed by Ettala & Väisänen (2000).

Nevertheless, a cover as a form of a filtrating deposit can be applied to reclaim old landfills that produce small amounts of biogas. It is a partial but inexpensive solution to the problem of CH_4 and odor emissions in poor countries.

Finnish researchers (Ettala & Väisänen, 2000) have proposed an interesting methanotrophy-based technology that can be applied in the case of landfills equipped with a passive degassing system but where biogas collection is not economically justified. Biogas is released from a degassing well and migrates to a draining layer before it reaches a topsoil layer. It does not move directly upwards but passes over a strongly porous material along a tight partition located perpendicularly over the well at the junction of a draining layer and a soil cover. Due to the fact that the biogas flux that escapes from the well is directed sideways it passes through the soil cover and is oxidized therein (Fig. 1b).

Presently, investigations into the application of methanotrophs to reduce methane emission from landfills focus on the methane oxidation in biofilters. A biofilter is the chamber of a volume that is determined on the basis of the supplied biogas load size. The chamber is filled with a material that makes a biological deposit and is located at the biogas outlets (Fig. 2). A biofilter can also be in-built into the cover where the packing has been previously removed. (Fig. 3). A biofilter can work with both a passive and an active degassing system. The advantage of biofilters that operate with active degassing is that it is possible to control the process e.g., by supplying air to the biofilter bottom and controlling the gas moisture. The amount of material for the biofilter filling is smaller than the

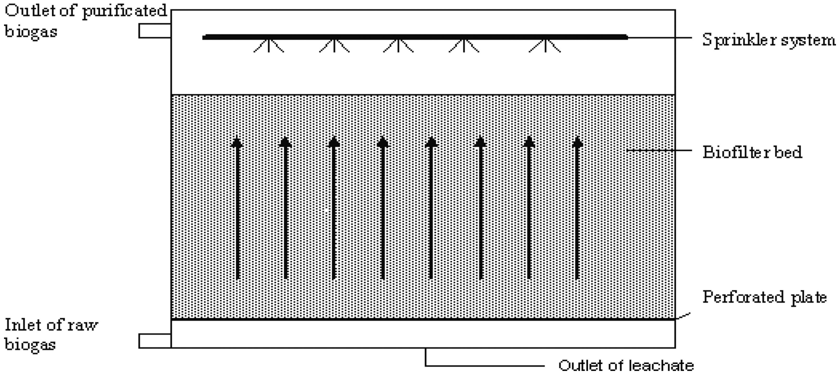

Figure 2. Diagram of a biofilter for biogas purification (Bilitewski et al., 2003, modified).

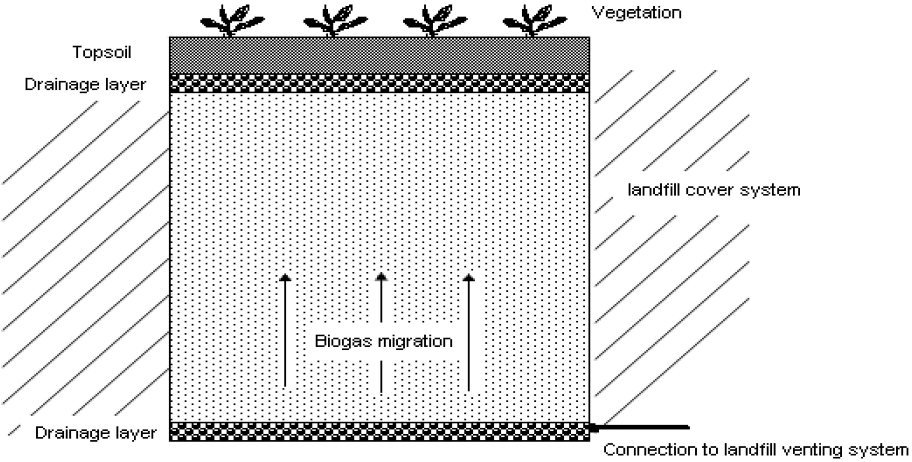

Figure 3. Diagram of a biogas biofilter of the "degassing window" type (after Gebert et al., 2003).

amount of material needed for the cover formation, hence the variety of materials that can make the deposit is greater. The application of that method is possible in the case of new landfills, whose bottom and top are insulated and where the collection of biogas to be used as a fuel is not economically justified. The mentioned conditions occur when biogas emission decreases with landfill age or in landfills that are so small that their time of producing biogas of high methane content would be too short for making the installation of a degassing system profitable. Biological deposit can also be applied as a supplementary method for a biogas recovery system e.g., in a situation when the biogas quality decreases to a value that makes it useless as a fuel or when a breakdown of energy generators or a flare occurs.

The application of a deposit for the CH_4 oxidation is particularly useful in cases when the biogas emission is low ($<30\,m^3/h$) or when the CH_4 concentration in it is low ($<30\%$). Such biogas is useless as a fuel (Dammann et al., 1999). As the EU regulations require gradual reduction of the biodegradable fraction deposited in landfills, installation of degassing systems in municipal dumps will not be profitable in the future.

In such a situation methanotrophy-based solutions seem to be better for municipal dumps because of their low cost and easy application.

4 METHANOTROPHIC CAPACITY OF POROUS MATERIALS USED IN THE BIOFILTERS

The efficiency of the CH_4 oxidation measured by the ratio of the amount of CH_4 emitted from the surface to the amount of that gas supplied to the deposit layer depends on the conditions for the growth of methanotrophic bacteria. The conditions are mainly determined by the surface that is accessible for the methanotrophs, which depends on the material specific surface, by the biogene accessibility, and diffusibility of substrates and gas products. They vary depending on materials used for the testing of methanotrophic capacity. It is quite a difficult task to perform a reliable comparative analysis of the oxidizing capacity for methane in various materials based on data obtained by various authors. The methane oxidation rate essentially changes in the course of an experiment. In its first phase the rate usually grows to its maximum value and then decreases to a relatively constant value. A decline of methanotrophic capacity is explained by the formation of exopolymers (polysaccharides) that are produced by methanotrophic microorganisms. These substances reduce the porosity of the deposit and consequently the gas exchange potential. The time to reach the stabilization phase varies depends on the material and hence it is impossible to formulate reliable conclusions even when, for comparative reasons, a specific day starting from the experiment beginning is set.

4.1 *Methane oxidation in mineral soils and materials*

Tests performed on sandy and gravel materials (fractions of 0.25–0.5 mm; 0.5–1.0 mm; 1.0–2.0 mm; 2.0–4.0 mm) inoculated with soil taken from an old municipal landfill cover in the weight ratio of 2% indicate that it is possible to grow methanotrophic microorganisms in those materials (Pawlowska et al., 2003). A model investigation was carried out. The testing was performed in columns made of PCV (0.15 m diameter). CH_4 was supplied through them from their base. The volumetric charge of methane supplied to each of the columns was *ca.* 400 $dm^3m^{-2}d^{-1}$. Sand of the 0.5–1.0 mm fraction exhibited the highest oxidation rate ranging from 217 to 238 $dm^3m^{-2}d^{-1}$. The methanotrophic capacity of the three remaining materials did not essentially differ and, with the confidence intervals, taken into account the values ranged from 187 to 215 $dm^3m^{-2}d^{-1}$. The degree of methane oxidation (in percent) in the most efficiently CH_4oxidizing material was 57.1 ± 2.6, while in the remaining ones it fluctuated around the value of 50%.

Testing performed by Kightley et al. (1995), on samples of three soils of various graining drawn from a landfill cover surface layer has shown was in sandy soil where the methane oxidation rate was the highest. The sample contained *ca.* 70% of coarse sand and was sampled from an area where CH_4 emission from the surface had indeed been observed. The CH_4 oxidation rate there was 233 $dm^3m^{-2}d^{-1}$. Methanotrophic capacity in materials of prevalent fine sand fraction or in clay taken from a landfill cover was smaller and fluctuated around the value of 153 $dm^3m^{-2}d^{-1}$.

As far as the order of magnitude is concerned the oxidation rate values given above are in agreement with most of the results of testing landfill cover soils. Whalen et al. (1990) have obtained slightly lower values (67 $dm^3m^{-2}d^{-1}$), while higher ones of *ca.* 336 $dm^3m^{-2}d^{-1}$ and 270 $dm^3m^{-2}d^{-1}$ have been observed by De Visscher et al. (1999) and Stein & Hettairatchi (2001) respectively.

The fact that landfill cover soils are exposed to high CH_4 concentrations for a long time seems to justify the assumption that their oxidizing capacity for CH_4 is higher than that of soils exposed to the atmospheric methane concentration. However, tests performed on arable soils have also shown significant methanotrophic activity. The mean value obtained for CH_4 oxidation in a clay arable soil was 240 $dm^3m^{-2}d^{-1}$ (De Visscher et al., 1999). Arable soils, including clays, that were tested by Stein & Hettairatchi (2001) showed a lower CH_4 oxidation rate of *ca.* 160 $dm^3m^{-2}d^{-1}$ at the stabilization stage of the process.

The CH_4 oxidation rate measured at field testing in a landfill-located biofilter filled with two sand fractions (coarse sand covered with a fine sand layer) with a methane charge supplied to the biofilter ranging from 250 to 500 $g\,m^{-2}d^{-1}$ was 303.9 $dm^3\,m^{-2}d^{-1}$ (Powelson et al., 2006). The obtained value did not differ much from the one obtained in a compost biofilter.

4.2 *Methane oxidation in organic materials*

Compost is the most often used filling for biofilters. Wilshusen et al. (2004b) tested four kinds of compost: municipal leaf compost with an admixture of manure taken from a zoo, Home Depot garden store compost, of un-screened wood chips (WC) and of municipal solid wastes (MSW). The compost samples were placed in columns through which CH_4 was passed. The air diffused upwards. Over the first hundred days of the experiment the leaf-based compost exhibited the highest methanotrophic activity (*ca.* 590 $dm^3m^{-2}d^{-1}$). With time the value gradually decreased to the value of *ca.* 100 $dm^3m^{-2}d^{-1}$ and finally became equal to the activity level of the MSW and WC compost. The lowest values were observed in Home Depot compost.

Field tests performed by Powelson et al. (2006) on a biofilter filled with compost made of garden wastes (mainly leaves and tree branches) with expanded polystyrene pellets added, and a methane charge supplied to the biofilter of 375–750 $dm^3m^{-2}d^{-1}$ showed that the CH_4 oxidation rate of 362.3 $dm^3m^{-2}d^{-1}$ was comparable to the value obtained in the bi-layer biofilter filled with coarse sand covered with a fine sand layer (303.9 $dm^3m^{-2}d^{-1}$).

Peat is another kind of organic material used for biofiltering of gases. A maximal CH_4 oxidation rate was observed in a peat moss tested by Stein & Hettiaratchi (2001). Its value was *ca.* 200 $dm^3\,m^{-2}d^{-1}$. After 200 days it decreased to *ca.* 140 $dm^3m^{-2}d^{-1}$.

The capacity for CH_4 oxidation in peat was close to the oxidizing activity exhibited by the arable soil tested by the authors. It follows from their investigation that the CH_4 oxidation rate was not subject to any significant changes depending on the varied charge of methane supplied to the system.

4.3 *Methane oxidation in biofilters with mixed filling*

In order to improve conditions for the growth of methanotrophs by providing them with an adequate surface for the culture formation and proper gas exchange, multi-material filters have been designed. The various materials that they include are either mixed in various ratios or applied as layers. In order to develop the specific surface and, at the same time, maintain favorable conditions for gas diffusion mineral materials are mixed with compost, peat, ground wood fibers, bark and sometimes even synthetics. This results in an improved efficiency of CH_4 oxidation.

Streese and Stegmann (2003) have performed model testing on the efficiency of biofilters with non-uniform fillings. They tested three kinds of biofilter filling: mature yard waste compost made of yard and garden wastes, mixed filling composed of equal volumes of compost, peat and compressed spruce wood fibers, and a layered filling made of compost with 2 cm-thick wood fibre layers introduced every 15 cm of the compost volume. The volumetric charge of methane supplied to the biofilter ranged from 238 to 2534 $dm^3m^{-2}d^{-1}$. The CH_4 oxidation rate varied with time. For the first *ca.* 100 days in all the materials it increased and gradually decreased afterwards. Over the first 100 days the highest oxidation rate was observed for the compost biofilter (1314 $dm^3m^{-2}d^{-1}$), but with the passage of time oxidizing of the two remaining biofilters (of the mixed and layered fillings) exceeded values obtained with the compost-filled biofilter. After the lapse of *ca.* 7 months the highest oxidation rate was recorded at the biofilter with mixed filling (420 $dm^3m^{-2}d^{-1}$ at the average).

Gebert et al., 2003 performed field testing on the CH_4 oxidation at a multi-layer biofilter located in a landfill equipped with a passive degassing system. The latter was built into the landfill cover.

A filling of crushed expanded clay (clumpy mineral material of high porosity and low volumetric density of 0.35 g/cm^3 produced in high temperature out of clay) comprised the main part of the biofilter. The material was placed between two draining layers (a lower one made of gravel and an upper double one of gravel and sand) with a 10 cm-thick layer of cover soil at the top. The CH_4 oxidation rate calculated on the basis of a potential methanotrophic activity obtained by lab tests ranged from 52 to 163 g $CH_4m^{-3}h^{-1}$. The obtained values recalculated per surface unit (at the assumed biofilter height of 80 cm) yield 1006–3133 $dm^3m^{-2}d^{-1}$, which is the highest CH_4 oxidation rate value ever found in the literature. However, as it is not an experimentally measured value but calculated on the basis of a potential activity it might be considerably overestimated.

Table 2 presents a summary of CH_4, oxidation rates obtained for the tested materials in laboratory or field conditions.

5 CONCLUSIONS

Based on the performed literature survey concerning CH_4 oxidation in various types of materials it can be concluded that:

- the highest CH_4 oxidation rate values contained within the range of 1006–3133 $dm^3m^{-2}d^{-1}$, and calculated on the basis of a potential methanotrophic activity have been recorded for a biofilter filling of crushed expanded clay:
- the highest measured value of CH_4 oxidation rate obtained based on long-term (11 months) investigations has been found for biofilters of a mixed filling composed of equal compost, peat and wood fiber volumes. The CH_4 oxidation rate therein was *ca.* 420 $dm^3m^{-2}d^{-1}$.
- the highest CH_4 oxidation rate values obtained by short-term investigations have been recorded for compost-fillings. They range from 590 to 1314 $dm^3m^{-2}d^{-1}$.
- sandy soils and materials present lower oxidizing capacity than in compost and the obtained values are within the range of 67.4–336 $dm^3m^{-2}d^{-1}$ (with maximal values neglected),
- peat material (moss peat) did not exhibit any significant methanotrophic activity. At the stabilization stage of the process it was ca. 140 $dm^3m^{-2}d^{-1}$.
- it follows from the comparison of the quoted methanotrophic capacity values to the rate of CH_4 formation in landfills that in the case of low methane emission (<200 $dm^3m^{-2}d^{-1}$) it is possible to apply mineral materials to the biofiltering,
- at the expected higher methane emissions application of multi-material biofilters composed of both mineral and organic materials, is recommended. They create better conditions for the growth of methanotrophs (accessibility of biogenes and microelements) and enhance the porosity of the material, thus facilitating gas diffusion.

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Table 2. Methane oxidation rates measured in various materials.

	Tested material	Oxidation rate (dm^3CH_4 $m^{-2}d^{-1}$)	Comments
Whalen et al., 1990	Landfill cover topsoil	67,4	Lab testing in a closed system
Kightley et al., 1995	Top soils of the landfill cover –coarse sand –fine sand –clay	232.96 ± 2.24 154.56 ± 6.72 152.32 ± 6.72	Model testing in columns Values obtained at the stabilization stage of the process
De Visscher et al., 1999	Arable soil Landfill cover soil	240 336	Model testing in columns Mean values
Stein & Hettairatchi, 2001	Arable soil – clay Landfill cover soil Moss peat	224/160 450/270 240/144	Model testing in columns Maximum values/values at the stabilization stage
Pawłowska & Stepniewski, 2003	Coarse sand Fine gravel	227.4 ± 10.6 202.4 ± 12.2	Model testing in columns Mean values
Wilshusen et al., 2004b	Leaf-based compost	590/150	Maximum value/value at the stabilization stage
Powelson et al., 2006	Coarse sand layer covered with fine sand. Green waste compost	303.9 362.3	Mean values obtained in a biofilter at field conditions
Streese & Stegmann, 2003	Green waste compost. Mixed filling Layered filling	1314/320 950/420 950/350	Model testing in biofilters Maximal values/mean values after the 7-month lapse Description of fillings – in the text
Gebert et al., 2003	Filling of crushed expanded clay covered with a soil layer	1006 –3133	Field testing in a biofilter Value calculated based on a potential activity

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Impact of different biocover designs on methane mitigation

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ABSTRACT: Field trials with differently designed biocovers were performed on two municipal solid waste landfills in Austria. Methane mitigation efficiency were determined using gas composition and temperature profiles measurements, surface methane concentration mapping, and gas flux measurements. While a 30 cm coarse gravel layer functioned as a gas distribution to balance gas fluxes, a 30 cm layer made of sand failed. Consequently, the methane mitigation efficiency of the cover designs varied strongly; the relative comparison with an uncovered reference area shows up to nearly 100% emission reduction in optimized biocovers over the entire year, while reduction efficiency in simplified biocovers or in conventionally styled covers including a compacted loamy material was smaller than 70%. The structure of the composts not only affected gas permeability and thereby the location of the active oxidation layer, but also the temperature insulation performance during winter.

Keywords: Methane oxidation, biocover, landfill gas emissions, landfill top cover.

1 INTRODUCTION

Over the past decades, municipal solid waste management has relied largely on landfilling in most parts of the world. Some 57% of municipal waste in Western Europe (Eurostat, 2002) and about 84% in Central and Eastern Europe were landfilled in 1999 (DHV CR, 2001). While only 10% of the released carbon broken down in a bioreactor landfill remain in the organic load of the leachate, 90% are found in landfill gas in terms of methane (60%) and carbon dioxide (40%). The biochemical reactions that produce gas typically continue long after a landfill is capped, so that even after closure, gas emissions can continue. Because of the high methane content and its high global warming potential, landfill gas emissions are of paramount importance at a global scale for contributing to the manmade greenhouse effect. Landfills are among the largest anthropogenic sources of methane in many developed countries. In Europe, an estimated 30% of anthropogenic methane emissions are from landfills (EEA, 2001).

Between 1990 and 2001, EU-wide methane emissions from landfills declined by 28% (Gugele et al., 2003). Emission reductions are partly due to the (early) implementation of the landfill waste directive and similar legislation in the Member States. The EU landfill waste directive was adopted in 1999 and requires Member States to reduce the amount of untreated biodegradable waste disposed at landfills and to install landfill gas recovery at new landfill sites containing biodegradable waste. The largest reductions occurred in Germany and the United Kingdom (about 40%), whereas Greece, Portugal and Spain had large increases of more than 40% (Gugele et al., 2003). While most European countries focus on the quantitative and qualitative limitation on biodegradable landfilled wastes to minimize methane generation potential, other nations encourage the installation of gas collection and recovery systems on MSW-landfills (e.g., the landfill Methane Outreach Program in the US; US EPA, 1999) to minimize methane emissions. However, despite these counteracting waste management strategies, in some parts of the globe, landfill practices are likely to increase rather than decrease methane emissions in future. This will be particularly true for developing countries, where most of the non-engineered waste dumps with current aerobic degradation conditions may be replaced with sanitary bioreactor landfills that will produce methane, but presumably will not operate gas collection systems due to missing technical and financial facilities. Meadows et al. (1997) estimate that total global methane emissions will increase significantly by about 150 percent till 2025, mainly due to increased waste generation and changing landfill practices in developing countries.

Enhancing the natural process of microbial methane oxidation through improved landfill cover design provides one simple and cost-efficient way to mitigate landfill methane emissions. Top covers, which optimize environmental conditions for methane oxidizing bacteria are often called "biocovers", functioning as vast bio-filters. A biocover usually consists of a suitable cover material and a subjacent gas distribution layer to homogenize landfill gas fluxes. Since biocovers are typically spread over an entire landfill area or sector, availability and cost become critical factors in material selection, consequently, often waste materials, such as diverse composts, mechanically-biologically treated waste, dewatered sewage sludge or yard waste, are used. Previous laboratory investigations of methane oxidation in compost materials (Figueroa, 1993; Humer & Lechner, 1999; Felske, 2003; Wilshusen et al., 2004a) show high oxidation capacity. Moreover, first field trials (Humer & Lechner, 2001a; Barlaz et al., 2004; Bogner et al., 2005) indicate the suitability of compost biocovers for practical application.

2 MATERIALS AND METHODS

2.1 *Experimental sites*

Two field trials to investigate compost biocovers were carried out on two different Austrian landfills between spring 1999 and winter 2002. The goal was to develop a suitable cover layer design to enhance methane uptake, as well as to test the methane oxidation potential in different compost covers under changing seasonal conditions. Additionally, at "Landfill II" the water balance in methane-oxidizing compost covers as well as the interaction of methane oxidation and different vegetation layers (data not shown) were primarily investigated.

2.1.1 *"Landfill I" and test cell design*

This municipal solid waste landfill is about 14 ha in size and has been operating since 1974 with about 60,000 tons of waste received each year, mainly household and bio-waste, sewage sludge, demolition waste and some industrial waste. A gas extraction system is in operation on the landfill and the collected gas is used in a gas engine as a source of energy. However, the remaining gas emissions were still high, as initial surface Flame-Ionization-Detection measurements (FID) showed (peak emissions higher than 5,000 ppmv). Furthermore, waste samples were taken at the location prior to test cells installation and the gas production potential was measured in incubation tests in the laboratory (according to Binner et al., 1999). The gas production measured in the incubations over 90 days resulted in 120 to 165 l gas/kg dry matter (DM) waste. By extrapolating these gas amounts to the landfill test site, a maximum gas generation rate of 1.3 to 2.2 m^3 gas/m^2d was estimated.

Table 1. Designs of the test cells on "Landfill I" (MSW = municipal solid waste, SS = sewage sludge).

Test cell 1	Test cell 2
– 0.9 m SS-compost – 0.3 m coarse gravel (gas distribution) – about 15 m MSW	– 0.9 m MSW- compost – 0.3 m coarse gravel (gas distribution) – about 15 m MSW
Test cell 3	**Test cell 4**
– 0.4 m SS- compost – about 15 m MSW	– 0.3 m SS-compost – 0.3 m compacted loam – about 15 m MSW
Test cell 5 (reference cell) uncovered landfill (about 15 m MSW)	

Five test cells were constructed in spring 1999; each cell was approximately 25 × 25 meters in size. The test cell covers were placed over waste that was actively producing methane. All cells contained about 10–12 m of waste that was deposited during 1975 to 1995, overlain by about 3 m of fresh, organic waste that was deposited between autumn of 1998 and spring of 1999, shortly before the test cells were put into place. The test cells were placed in the potential sphere of influence of two adjacent gas extraction wells, which were in operation over the whole test phase. The various test covers were designed as shown in Table 1. Geosynthetic clay liners were placed around each cell so that lateral methane migration was prevented and the test areas were isolated from one another.

On test cells 1, 3, and 4 mature, about two year old sewage sludge compost was used as cover material. The raw material of the compost was 50% w/w stabilized sewage sludge from a municipal water treatment plant mixed with wood chips (50: 50% w/w) and composted in open windrows. The compost was not sieved before applying on the test cells, therefore the compost structure was quite coarse containing wood chips up to a size of 200 mm. On test cell 2 a mature municipal solid waste compost (after mechanical-biological treatment, about 16 months old) was applied. This compost was sieved to a particle size <25 mm to get rid off trash pieces like plastics and glass cullet. Thus, the MSW-compost had a comparative finer structure than the sewage sludge compost. A coarse silicate gravel (grain size >63 mm) deficient in lime (<30% w/w $CaCO_3$) was used for the gas distribution layer below the compost covers on test cells 1 and 2. A clayey, loamy material conventionally used for landfill cover, was applied as sub-layer on test cell 4.

The compost covers were placed without any artificial compaction, and we took care not to compress the deposited compost with heavy machinery in order to achieve sufficient porosity and satisfactory gas permeability. Table 3 shows some data on cover materials as analyzed at the beginning of the field trials. Before applying the composts in the field trials, they were tested for their methane oxidation capacity in the laboratory in column tests over 70 days (test method see Humer & Lechner, 1999). Both substrates reached constant rates of 100% methane oxidation (at methane supply of 300 l/m^{2}d) after 7 days (SS-compost) and 5 days (MSW-compost) of adaptation, respectively. The test cells were not planted with special vegetation. Spontaneously growing, indigenous herbaceous vegetation (mostly weeds and grass) was established naturally and was mowed twice per year.

A closely-spaced grid of fixed gas probes and temperature probes was installed. By this equipment the gas concentration and temperature profiles within the covers as well as in the landfill were constantly measured. On each test cell (except cell 5) nine gas probe nests were installed, each nest consisting of several probes finished at depths ranging between 10 and 150 cm. The gas probes consisted of stainless steel tubes (20 mm i.d.), which were closed at the bottom and perforated with four sets of holes (4 holes per set, diagonally arranged, contorted by a 90° angel) over the lower 4 cm. Additionally, three temperature probe nests with several probes (stainless "Kompoststecksonde", pT100, TestoTherm, Austria) reaching into different depths (10–130 cm) were installed on each of test cells 1 to 4. On test cell 5 three gas probe nests and one temperature probe nest were placed.

2.1.2 *"Landfill II" and test cell design*

"Landfill II" is a smaller, closed site about 3.1 hectares in size. The test cells were situated on a younger section of the landfill, where primarily household waste (about 141,000 tons) was dumped between 1990 and 1998. No gas extraction system was operated in this landfill section. The calculated gas production potential (according to Tabasaran & Rettenberger, 1987) for the test period was quite low (0.13 to 0.19 m^3 gas/m^2 d).

Six different test cells were set up over an area of 5,400 m^2, with each cell about 900 m^2. A compensation and gas distribution layer made up of 30 cm of sand was placed over the landfill beneath the compost layers. Beneath this compensation layer, three gas supply trenches (reaching one meter deep into the waste) filled with coarse gravel (grain size 16/32) were placed to improve the landfill gas supply to the test cells. Two different cover layers were constructed (see Table 2). Municipal solid waste compost (MSWC) and sewage sludge compost (SSC) or a mixture (70 : 30% v/v) of these composts with sand, respectively, were applied.

Table 2. Design of the test cells on "Landfill II"; (MSW = municipal solid waste; SS = Sewage sludge).

Test cell	Construction	Vegetation
Test cell B1 Test cell B2 Test cell B3	– 1.2 m mixture of MSW/ SS-compost + sand – 0.3 m layer of sand – about 8–9 m MSW	Miscanthus Poplar Uncultivated (control)
Test cell A1 Test cell A2 Test cell A3	– 0.4 m mixture of MSW/ SS-compost + sand – 0.8 m MSW/SS-compost – 0.3 m layer of sand – about 8–9 m MSW	Miscanthus Poplar Uncultivated (control)

The substrates were placed at the test area using a front-end loader, taking care not to compact the compost covers. Due to a lack of proper MSWC, on test cell A3 mainly sewage sludge compost was used. Data for the composts as well as the compost/sand mixtures are shown in Table 4. The test cells were separated by geosynthetic clay liners and the surrounding area of the test cells was covered by geosynthetic clay liners and a clay cap, respectively, to prohibit lateral methane escape. The test cells were cultivated with poplar and Miscanthus, a reed-like C4-plant with high biomass production and high transpiration capacity. Its biomass can be used as an alternative fuel for the production of energy as well as an alternative raw material for diverse purposes.

Per test cell, two temperature probe nests (depths 10, 30, 60, 80, 110 cm in the compost covers, and 160 cm in the waste) and four gas-probe nests (depths of 10, 40, 70, and 100 cm in the compost cover and 150 cm at the interface of the sand layer and the waste), similar to those used on "Landfill I", were installed. Additionally, in the middle of each test cell a control probe reaching into the waste was placed (250 cm depth).

2.2 *Investigation methods*

2.2.1 *Cover material characterization*

At the beginning, and consecutively every quarter on "Landfill I" and yearly on "Landfill II", respectively, compost samples were taken from different depths of the covers using a soil-sampler ("Holländer-Bohrer"). The water content, some chemical parameters (nitrate, nitrite, ammonium, organic content, Ntotal, TOC, pH, conductivity, phosphorus), and respiration activity were then analyzed. The analyses of the standard chemical parameters were carried out in complete agreement with the Austrian Norm "Analytic Methods and Quality Control of Composts" (ÖNORM S 2023, 1993) by using a DX–120 Ion-chromatograph (Dionex, Sunnyvale, CA), and a spectrophotometer (HITACHI Ltd., Tokyo, Japan). Respiratory activity in the sapromat (Sapromat E, Voith Sulzer, Ravensburg, Germany) was measured according to Binner et al. (1999). Additionally, on "Landfill I" the composition of the microbial community (using Polymerase Chain Reaction (PCR) and Denaturing Gradient Gel Electrophoresis (DGGE); data not shown) was determined. Furthermore on "Landfill I", in March and in August 2001 the air-filled pore volume was analyzed in different depths of the compost covers of test cell 1 and 2. In different depths at nine sampling points on each cell, triplicate compost samples were taken using soil cutters. The samples were then immediately sealed at the top and the bottom in the cylindrical cutters to achieve a widely undisturbed sample. The air filled pore volume in the compost samples was then determined gravimetrically (before and after water infiltration via flooding) in the laboratory.

2.2.2 *Evaluation of methane oxidation performance and methane mitigation efficiency*

Measurements of gas concentration and temperature profiles were carried out once per week at the beginning of the investigations (first year of investigations), and in the later test phase two to three times per month. The temperature profiles were constantly recorded using a digital temperature measuring device (Testo 110, TestoTherm, Germany, with an accuracy of ±0.2°C in a range of -25 to $+75$°C) during gas measurement campaigns. At the gas probes, which were normally closed at the top by a rubber plug, a mobile gas analyzer (Gas Data LMS, MLU, Austria) was connected gas-tightly and, via an internal pump, the landfill gas was extracted and methane, carbon dioxide, and oxygen were detected. The extracted gas was cleaned via two particle and moisture filters connected in series (tube filled with silica gel, and a "Midisart 2000 $-0.20\,\mu$m PTFE"-membrane filter). The gas-analyzer contained an infra-red methane and carbon dioxide detector (precision of measurement: ±0.1% in the range of 0 to 10%, and ±1% in the range of 10 to 80%), coupled with an oxygen detector by means of a galvanic sensor (precision of measurement: ±0.5% in the range of 0–25%). The pumped flow was adjustable between 200 and 300 ml/min and the required pumping time was calculated considering the different lengths of the gas probes. Before applying the gas analyzer in the field, it was verified by comparison with GC/FID-measurements in the laboratory. When no methane was detected with the LFG analyzer, a portable FID (lower detection limit of 0.1 ppmv; see below) was used for verifying the measurements at various gas probes.

On "Landfill I" methane concentrations at the surface were screened on a 1.5 × 1.5 m grid using a portable Flame Ionisation Detector (FID), which is capable of detecting very small concentrations of hydrocarbons. The FID (microFID, PE Photovac, US) worked at two calibration ranges (0.5 ppmv–5,000 ppmv CH with an accuracy of ±0.3 ppmv, resolution 0.1 ppmv; and 10–50,000 ppmv CH with an accuracy of ±3 ppm; resolution 1 ppmv); it was calibrated before the measurements started and it was also checked after the measurements using a test gas (Scotty-Gas mixture; 500 ppmv CH_4 in N_2). A funnel-shaped probe was directly put on the surface and via an integrated pump the emitted gas was drawn through the FID. The recorded surface concentrations were later plotted on a schematic map. These investigations were carried out every second week over a two year investigation period. On "Landfill II", methane concentrations were surveyed by the staff of the landfill operator (NUA) according to a similar procedure once per month using a portable FID (Telegan, GAS TEC MK II).

Additionally, surface emissions have also been quantitatively calculated using a specially adapted open flux-tunnel on "Landfill I" (Röder et al., 2004; Humer & Lechner, 2001a). The flow inside the tunnel (induced by natural wind velocity) as well as the temperature, methane (using FID, see above) and carbon dioxide (using WMA-2 CO2-controller; 0–2,000 and 1,000–10,000 ppmv) concentrations at the front and the rear of the tunnel were continuously measured. Before the field trials, the flux-tunnel was tested in the laboratory to improve the measurement system and to quantify the accuracy of the system (Röder et al., 2004). The placement of the flux-tunnel was guided by the FID-mapping. Two to three measuring campaigns per month were carried out between February and September 2001.

On "Landfill II" flux measurements using a dynamic chamber method (according to VDI-guideline 3790/2, 2000) were performed monthly in the year 2001. Via a funnel-shaped chamber (covered area 1 × 1 m) a gas flux between 85 and 125 l/min (evaluated in retrieval experiments on a test bed; flux depending on the meteorological conditions) was sucked through the chamber and methane (FID, Testa 123-GE 0602) and carbon dioxide (gas analyzer ULTRAMAT 23, Siemens) were continuously recorded.

For the comparison of the methane reduction efficiency of the different cover designs, two approaches were conducted. On "landfill I" the flux emission data of the four differently covered test cells were compared to the emissions from the adjacent uncovered reference cell at the same testing conditions. On "Landfill II", where no uncovered landfill area was available as a reference, a mean annual cell specific emission rate was calculated from at least four chamber measurements (placements) per cell and measuring day, and then compared relatively to each other as well as to a modeled gas generation rate for the test area using the calculation method of Tabasaran & Rettenberger (1987).

3 RESULTS AND DISCUSSION

In the following, some exemplary results and main findings derived from the two field trials are summarized. First results from the field trial on "Landfill I", particularly regarding gas and temperature profiles and methane surface concentrations (FID-measurements), have been already published in Humer & Lechner (2001a).

3.1 *Characterization of cover materials*

In Tables 3 and 4 some data characterizing the cover materials used in both field trials are shown. The standard chemical parameters of the SS-compost and the MSW-compost on "Landfill I" do not differ very much. Both compost were mature substrates (low respiration activity) and high in organic content and nutrients. A high maturity of compost materials is crucial for efficient methane consumption, as was shown in previous laboratory tests (Humer & Lechner, 1999 and 2001b). The high content of phosphorus in the SS-compost is caused by phosphate precipitation due to an admixture of iron sulfate in the sewage treatment plant, whereby iron phosphate was formed and accumulated in the sludge.

The covers of test cells 1 and 2 on "Landfill I" differed mainly in the structure of the applied composts. The SS-compost (composted with big wood chips as bulky material) exhibited very good gas permeability due to its coarse texture (particle size distribution: 20% w/w 0.63–2.0 mm, and about 80% w/w 2.0–60 mm; some bulky pieces up to 200 mm) and its high air-filled pore volume (about 41% at 10–15 cm depth; 37% at 30–35 cm; 32% at 50–55 cm), even at higher moisture contents (up to 45% w/w) and after natural consolidation (subsidence processes due to mineralization of compost, rainfall, etc.) in the third investigation year. In contrast, the MSW-compost used on test cell 2 was sieved to a particle size smaller than 25 mm and showed finer structure (particle size distribution: 55% w/w 0.63–2.0 mm, and 45% w/w 2.0–25 mm), smaller air-filled pore volumes (about 31% at 10–15 cm depth; 24% at 30–35 cm; 12% at 50–55 cm measured at the same moisture conditions in the third investigation year as described above), and consequently lower gas permeability.

In the coarse SS-compost, oxygen penetrated deeper into the cover layer than in the finely-sieved municipal solid waste compost, allowing the methane oxidation process to take place in deeper parts of the covers, where the moisture and temperature conditions were more favorable and consistent than in upper layers. Furthermore, the varying porosity of the compost substrates influenced the temperature conditions within the cover layers due to a different temperature insulation effect. In test cell 1 the temperature was nearly constant in a depth between 80 and 130 cm throughout the year, while in test cell 2 seasonal temperature fluctuations were monitored deeper in the cover. During winter, the temperatures within the cover on test cell 2 were about 10 to 15°C lower than compared to test cell 1. Because of the density and porosity, microbially produced heat during methane oxidation as well as heat from the waste decomposition were better maintained in the coarse SS-compost than in the fine MSW-compost throughout the year. This is

Table 3. Some data on the substrates used as landfill cover materials in the field trial on "Landfill I" (DM = dry matter; SS = sewage sludge; MSW = municipal solid waste).

	SS-compost	MSW-compost	Loamy material
Conductivity [mS/cm]	1.0	2.3	0.2
pH value	7.2	7.4	6.9
NH_4^+-N [ppm DM]	10	10	1
NO_2-N [ppm DM]	Not detectable		
NO_3-N [ppm DM]	230	610	4
N_{total} [% DM]	1.20	0.96	0.06
Organic content [% DM]	30	28	3
TOC [%DM]	15.0	14.0	0.5
Phosphorus [%DM]	2.9	0.9	0.1
Respiration activity in 7 days [mg O_2/g DM]	1.7	3.1	0.2
Moisture content [%wet matter]	43	30	11
Water holding capacity [%DM]	120	90	34
Bulk density [kg/l]	0.82	0.9	1.3

Table 4. Some data on the substrates used as landfill cover materials in the field trial at "Landfill II" (n.d. = not detectable, DM = dry matter, MSW = municipal solid waste, SS = sewage sludge).

	MSW/SS-compost	Mixture MSW/SS-compost + sand
Conductivity [mS/cm]	2.9	1.8
pH value	8.0	7.9
NH_4^+-N [ppm DM]	100	50
NO_2-N [ppm DM]	n.d.	n.d.
NO_3-N [ppm DM]	260	140
N_{total} [%DM]	0.9	0.5
Organic content [%DM]	29	15
TOC [%DM]	13	9
Phosphorus [%DM]	0.9	0.6
Respiration activity in 7 days [mg O_2/g DM]	4.7	3.0
Moisture content [%wet matter]	29	25
Water holding capacity [%DM]	75	60
Bulk density [kg/l]	0.86	1.05

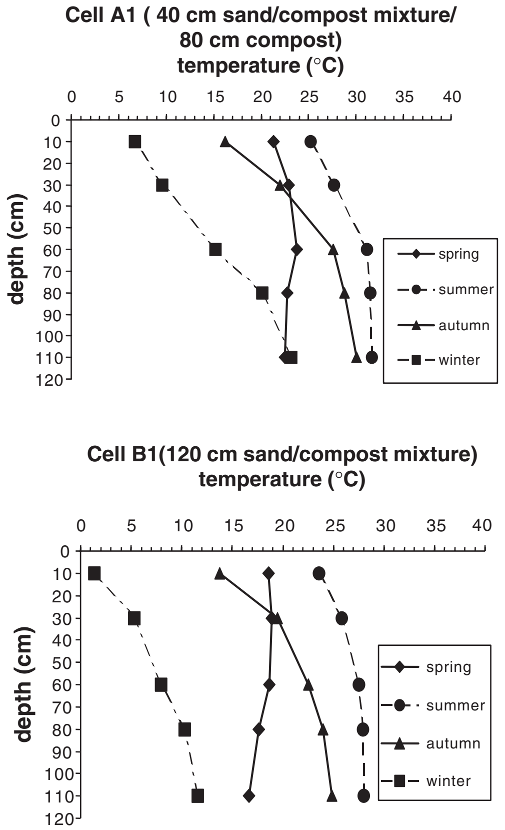

Figure 1. Seasonal temperature profiles measured in test cells A1 and B1 on "Landfill II" in the year 2000 (each data point = mean value of 6 measurements).

due to the lower thermal conductivity of coarse substrates with a high amount of air-filled space and lower compaction (Scheffer & Schachtschabel, 1989).

Exemplary seasonal temperature profiles measured on "Landfill II" are shown in Figure 1. The data reflect once more, that the physical properties of the substrates impact the temperature performance, since the more compact sand mixture in the entire profile on test cell B1 exhibited a lower temperature insulation effect than test cell A1, particularly during winter. Thus, by choosing the right substrate quality, even the temperature conditions for methane-oxidizing microorganisms can be strongly manipulated.

During the entire investigation period of more than two years in all compost substrates the nutrient supply was always adequate for methane oxidation – particularly in the main methane oxidation layer in greater depths. Furthermore, even after more than two years, large wood chips were still visible in test cell 1 on landfill I when the covers were excavated at the end of the field trials, giving it good porosity and gas permeability on long-term. This indicates, that the nutrient pool in mature composts as well as the structure in bulky substrates is sufficient for methanotrophic activity over a long time.

3.2 *Evaluation of methane oxidation performance and methane mitigation efficiency*

3.2.1 *Gas composition within the cover layers*

Gas concentration profiles in landfill covers are quite difficult to interpret because gas composition in the covers is controlled by many different influencing factors, like numerous microbial processes (uptake of gases and release), bio-chemical processes (e.g., carbon dioxide fixation) and physical conditions. Gas movements in soil are controlled by convective and diffusive processes. Convective processes can dominate during periods of atmospheric pressure changes (Kjeldsen, 1996; Striegl, 1993), or at locations where gas sources are substantially large. Thus, on landfills the exchange between the cover layers and the atmosphere may be widely dominated by convective transports. Gas concentration profiles are always a snapshot representing a single sampling episode, but gas profiles can indicate phenomena typical of methane oxidation and provide a comprehensive insight into the zoning of processes taking place in the cover layers, particularly in combination with temperature profiles and other data.

3.2.1.1 Landfill I

During the first months of investigation (summer and autumn 1999) the main methane consumption took place between a depth of 0.3 to 0.9 m depending on the density and porosity of the two compost substrates on test cells 1 and 2. The methane oxidation horizon was situated deeper in test cell 1 (0.6–0.9 m) than in test cell 2 (0.3–0.5 m). During the first winter the methane oxidation layers shifted downwards in both test cells. The coarse texture of the SS-compost used on test cell 1 allowed oxygen to penetrate deeper into the cover than in cell 2. Furthermore, the respiration activity of the MSW-compost (3.1 mg O_2/g DM) used on test cell 2 was higher than in the SS-compost (1.7 mg O_2/g DM). Consequently, the oxygen removal by non-methanotrophs was higher in the MSW-compost cover leading to a methane oxidation layer situated closer to the top. Most probably due to increased maturity of the MSW compost and to a decline in competitive oxygen removal during winter (decomposition processes slow down at lower temperatures), the methanotrophic bacteria established in deeper regions, providing better temperature conditions during cold winter conditions. The methane concentration profiles showed a sharp decline, while the decrease in carbon dioxide profiles was more gradual in both test cells. Methane was just detectable at atmospheric concentrations in the cover of test cell 1 from a depth of 50 cm upwards and at a depth of 0–10 cm in test cell 2 during the first months of investigations.

The methane to carbon dioxide ratios changed clearly within the profiles, which is regarded as a strong indication for methane consumption (Jones & Nedwell, 1993; Bergmann et al., 1993; Maurice, 2001; Christophersen et al., 2001). However, the CO_2-concentration in the cover is influenced by many processes, e.g., microbial CO_2-production by methanotrophs and non-methanotrophs, root respiration and assimilation, temperature-dependent solubility relationships (Kjeldsen, 1996), sorption on soil particles, and concentration changes in landfill gas. Above all, the large difference in the solubility of methane and carbon dioxide in water may have an impact on the ratios; however, at high landfill gas production this effect will be slight. Above the methane oxidation horizon the CO_2-concentrations showed a relatively constant decrease due to dilution with air. The peak in the temperature curves as well as in the N_2-concentration profiles also indicated methane uptake as well as the locations of the methane oxidation layers in field. The phenomenon of local enrichment of nitrogen in the pore gas exceeding atmospheric content has been described in previous studies (e.g., Bergman et al., 1993; Kjeldsen, 1996; Christophersen et al., 2001; Maurice, 2001; DeVisscher, 2001). N_2-concentrations up to 83% v/v were detectable in the obvious oxidation layers on test cells 1 and 2, due to an accumulation of N_2 induced by the gas volume reduction during methane oxidation.

During the second test year (2000/2001) the profiles changed slightly compared to the first year. Oxygen was detectable to a depth of 120 cm in test cell 1 (gas distribution layer), and methane was just detectable at atmospheric concentrations from a depth of 90 cm upwards. The gas concentration profiles as well as the data of microbiological investigation (semi-quantitative multiplex PCR, data not shown) indicate that methane consumption occurred at a depth of 90–120 cm, the interface between as well as in the gas distribution layer made of coarse gravel. Excavated covers at the end of the field trials showed that the gravel was covered by a biofilm produced by methanotrophic bacteria and confirmed the assumptions derived from the gas profiles. During spring and in summer 2000 the methane oxidation layer shifted slightly upwards in test cell 2, most probably due to a higher microbial activity and oxygen removal at increasing temperatures. The main methane oxidation layer was then situated at a depth between 50 and 70 cm, but shifted downwards again in winter 2000/2001 and established there during the third year of investigation (spring and summer 2001). Oxygen penetrated deep into the covers in both test cells, and finally, methane oxidation was established at a depth between 90 and 120 cm, while the upper parts of the covers were strongly aerated.

In test cell 3 (40 cm SS-compost, simulating a simple interim cover) oxygen penetrated down to the waste over the whole year. During winter, no clear change in the methane to carbon dioxide ratio was visible in the profiles. Obviously, efficient microbial methane uptake did not occur during winter because of low temperatures (about 5 to 8°C on an average in the upper 40 cm) in the cover. The decline in the LFG profiles is probably due only to dilution. A layer of only 40 cm compost does not sufficient temperature insulation during winter. The gas and temperature profiles in test cell 3 showed seasonal variations but similar curves over the whole investigation period.

The cover on test cell 4 was made of 30 cm SS-compost underlain by a 30 cm layer of compacted loamy material (simulating a conventional landfill cover, often applied shortly after waste disposal). The compost layer was characterized by high soil gas oxygen, while in the compacted loamy material oxygen was hardly detectable. The main methane uptake took place at the interface between the compost cover and the loamy layer, which was also less pronounced during winter. Furthermore, the profiles show that landfill gas can permeate through a dense cover layer made of loam or clay, but oxygen input is hindered compared to a coarse cover. Therefore, methane oxidation might take place only in the upper parts of such layers, impacted strongly by temperature and moisture changes, if there is no cover overlaying the loam to provide temperature protection. However, a layer made of 30 cm coarse compost was not sufficient insulation during winter as the profiles reveal (no clear change in the CH_4/CO_2 ratio and temperatures between 0–5°C in the upper part).

Test cell 5, the uncovered reference cell, showed nearly constant methane and carbon dioxide profiles and ratios over the whole investigation period, with about 30–40% carbon dioxide and 60–70% methane. Oxygen was not detectable in the waste. During the investigation period the methane concentrations in the upper 30 cm declined slightly, whereas the carbon dioxide concentrations increased, indicating low methane oxidation activity or increased aerobic respiration in the uncovered waste. The temperatures in the waste fill ranged between 25 to 30°C in a depth of 60 cm during summer and between 5 and 10°C in winter.

On landfill I, in test cells 1 and 2 the methane oxidation layers established deep in the cover quite unaffected from outer temperature and moisture changes, while in cells 3 and 4 the methane turnover took place in depths between 10 to 40 cm, very sensitive to external influences. Compared to other field studies with conventional landfill soils (e.g., Jones &

Nedwell, 1993; Christophersen & Kjeldsen, 2000; Scharff et al., 2001; Maurice, 2001) which reported optimum methane consumption at depths between 10 and 40 cm, the methane oxidation layers were situated much deeper in our compost covers. This was most probably due to the coarse texture of the compost, allowing oxygen to penetrate deep into the cover, and due to the homogeneous and balanced methane supply by means of the gas distribution layer. This is quite coincident with findings from Bergmann et al. (1993), who reported methane oxidation situated in a depth of about 80 cm in an organic rich compost/soil landfill cover with sufficient porosity. The maximum oxidation zone in field investigations of Scheutz et al. (2003) occurred between 60 and 80 cm depth in a final cover layer made of 80 cm silty to sandy loam on top of 40 cm coarse sand. Initial results derived by Hupe et al. (2004) indicate that in a top cover made of 120 cm sandy silt overlain by 30 cm compost/soil mixture the main methane consumption took also place at a depth between 90–120 cm.

3.2.1.2 Landfill II

In Figures 2 and 3 gas composition within the cover layers of test cells A1 and B1 are shown exemplary for the year 2000. There is no big difference in gas composition over depth between the two cover layers. However, in test cell B1 the main methane oxidation activity was obviously situated slightly deeper in the cover (at about 0.9–1.0 m depth) than in A1 (between 0.7 and 0.9 m), reflecting the impact of different physical properties of the substrates. Moreover, the higher respiration activity of the pure compost (4.7 mg O_2/g DM) may have led to a higher oxygen removal by heterotrophic microbes in the upper parts of the cover. The general higher respiration activity of the composts used on "Landfill II" caused that oxygen did not penetrate as deep into the covers as on "Landfill I", in particular at the beginning of the investigation; moreover, the texture was not as coarse as the SS-compost used on test cell 1 on "Landfill I", but similar to the texture of the MSW-compost used on test cell 2. Furthermore, due to an insufficient gas distribution layer (30 cm sand) the gas emissions as well as the gas profiles showed an inhomogeneous pattern. During the investigations it turned out that the 30 cm sand layer was not really acting as a gas distribution layer. The sand texture was too fine and – as moisture content measurements confirmed – became water logged during most time of the year and thereby lost its function. Thus, strong spatial variations in gas composition within the covers as well as in methane emissions occurred. Figures 2 and 3 compare the gas composition of probe nests located directly above the gas supply trenches and unaffected nests on test cells A1 and B1. A clear deviation between the data is evident; all of the methane was consumed at a depth >50 cm at sites unaffected by the gas supply trenches, while methane was still detectable at a depth of 10 cm directly above the trenches. During further investigations in 2001 these deviations leveled off slightly, most probably due to decreasing landfill gas production and more homogeneous gas distribution, because the moisture content of the sand layer decreased due to higher water uptake by the expanding vegetation. In general, oxygen penetrated deeper into the covers over time and the methane oxidation layers shifted downwards, which is coincident with findings from "Landfill I".

3.2.2 *Surface methane concentration mapping*

FID-measurements are qualitative reconnaissance investigations to survey emission patterns and to check the functional efficiency of top covers. Such measurements are just snap-shots of the emission situation at specific environmental and weather conditions. However, repetitive FID measurements at various seasonal conditions gathered over a long investigation period (months to years), can provide reliable comparisons among different cover layers measured under the same basic conditions.

3.2.2.1 Landfill I

Over more than two investigation years, no elevated methane concentrations were detected throughout the entire year on the flat top surfaces of test cell 1 and test cell 2, turned out as the "optimal designs" with a gas distribution layer and a sufficient thickness for the compost layers. In contrast, spatially inhomogeneous but temporally high methane concentrations were detected on test cell 3 and test cell 4. Certainly, the methane concentrations were highest over test cell 5, the reference cell without a cover, although the gas extraction system was operating throughout the whole test period, and two gas extraction wells were located close to the test cells. In the case of test cells 3 and 4, methane escaped through fissures and cracks, most probably because of an unbalanced and inhomogeneous gas supply due to missing gas distribution layer. At spots with methane higher than 5,000 ppmv, gas flow velocity was apparently too high for efficient microbial methane uptake due to short residence time. Such "hot spots" were visible with the naked eye, indicated by a lack of vegetation during the summer and their snow-free status during winter. Temperatures up to 35°C were detected in a depth of 10 cm at such "hot spots" during winter (at outer temperatures of 0°C). Furthermore, the surface was always very dry and hard with a high accumulation of exopolymeric substances (EPS) when excavated.

Spatially and temporally high methane concentrations (up to 5,000 ppmv) occurred over the wind exposed slopes of the surrounding area. Landfill gas often preferably migrates horizontally rather than vertically, due to the waste deposition and compaction in layers (Kjeldsen, 1996). The horizontal gas permeability is expected to be 7 to 10 times higher than

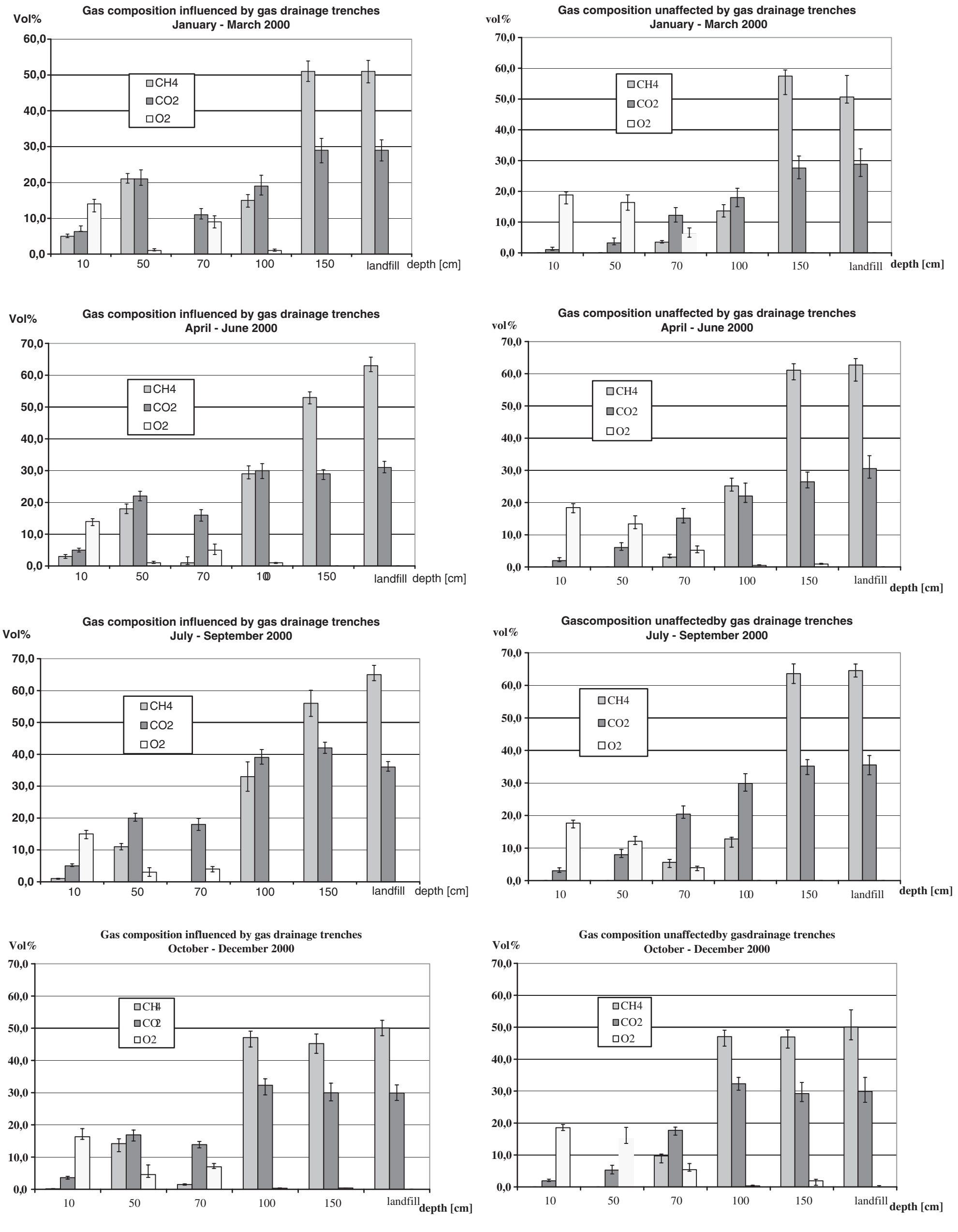

Figure 2. Quarterly mean concentrations of CH_4, CO_2 and O_2 in test cell A1(80 cm MSW/SS-compost and 40 cm mixture MSW/SS-compost + sand) in the year 2000 on "Landfill II" divided in gas probe nests widely affected by the gas supply trenches (left side) and widely unaffected (right side); error bars indicate minimum and maximum values; n = 10 per gas, depth and quarter.

the vertical one in compacted landfills (Scharff et al., 2001). However, methane concentration peaks at the slops mostly depended on wind direction and velocity. For example, higher methane concentrations could be detected with a higher wind velocity (>65 km/h) on the leeward side of the slopes, as opposed to the windward side. Prevailing winds were in 56% of the cases E-NE wind; on the remaining measurement days

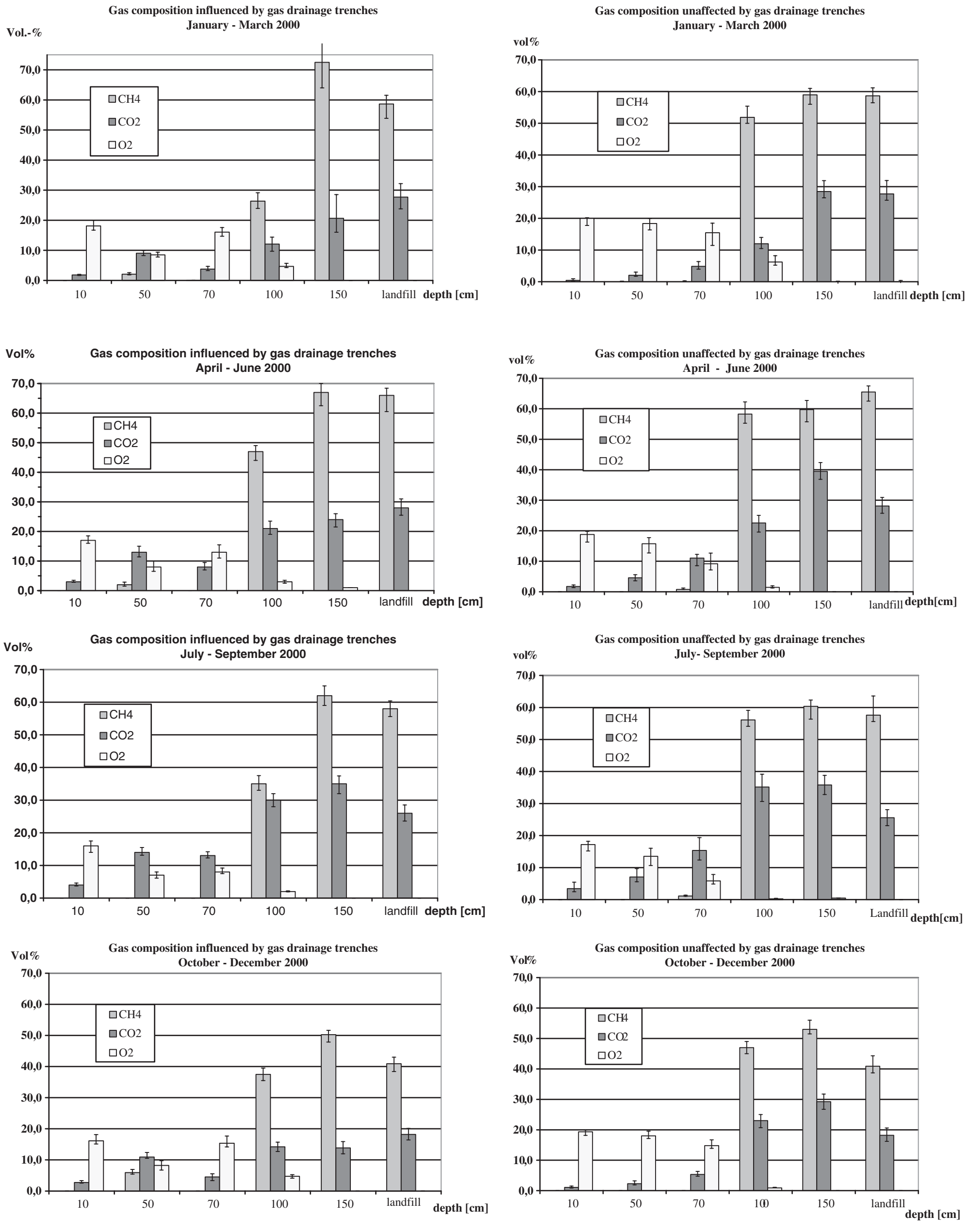

Figure 3. Quarterly mean concentrations of CH_4, CO_2 and O_2 in test cell B1 (120 cm MSW/SS-compost + sand) in the year 2000 on "Landfill II" divided in gas probe nests widely influenced by the gas supply trenches (left side) and widely unaffected (right side); error bars indicate minimum and maximum values; n = 10 per gas, depth and quarter.

W-SW winds occurred. Obviously, wind had induced a near-surface turbulence leading to small gas pressure gradients in the shallow subsurface impacting emission behavior. Such small induced pressure gradients can be potentially important driving forces for emissions. This has been already addressed in literature (Bogner & Scott, 1994). After installing an additional sealing (slurry wall) on the west slope in summer of 2000 the wind influence was reduced. The patterns on test cells 1 to 4 changed only marginally over the two investigation years. That is, if elevated methane concentrations were detected, they occurred at nearly the same locations, even though at slightly varying concentrations, depending on changing environmental conditions (moisture content, wind, temperature, or atmospheric pressure). During winter, a general decline in surface methane concentrations was observed, especially on uncovered cell 5. A decline in methane emissions during winter was detected in field studies carried out by Jones & Nedwell (1993). Furthermore, there was a clear observable difference depending on whether the surface of the test cells were frozen or not. Maurice (2001) also found decreasing methane emissions during winter on Swedish landfills, mostly due to a frozen surface hindering vertical gas release. On the sloping part of another Swedish landfill (Borjesson et al., 2001), the same effect was implicated for the lack of methane emissions during winter. Test cell 5, the uncovered landfill, showed extremely variable surface concentration patterns in space and time over the whole investigation period. Furthermore, the pattern was very sensitive to varying environmental conditions, often changing rapidly within a short time. Even human interferences, like heavy steps on the surface during measuring campaigns, enhanced methane escape. During spring and autumn, and after heavy rainfall in other seasons, puddles formed on the surface of test cell 5, where gas bubbles were visible.

3.2.2.2 Landfill II

The pattern of the FID-mappings were quite similar throughout the whole investigation period, which is coincident with the results derived from the FID-measurements on "Landfill I". Surface methane concentrations decreased generally during winter and over the years as was also observed on "Landfill I". Due to the insufficient gas distribution of the 30 cm sand layer, the location and pattern of the underlying gas supply trenches was visible at the surface of the test cells by vegetation failures, as well as by the FID-measurements (see Figure 4 as an example). The methane peaks above the gas trenches leveled off with time, but the pattern of the trenches were still visible in the vegetation performance and also slightly detectable by the FID in the year 2005. This proves once more the necessity of installing a proper gas distribution layer.

3.2.3 *Gas flux and emission evaluation*

Different techniques for determining methane oxidation in landfill cover soils and other ecosystems are given in Nozhevnikova et al. (2003). A promising approach to quantify the methane oxidation rate directly in the field is the use of the stable isotope method (Liptay et al., 1998; Chanton & Liptay, 2000; Börjesson et al., 2001; De Visscher et al., 2004).

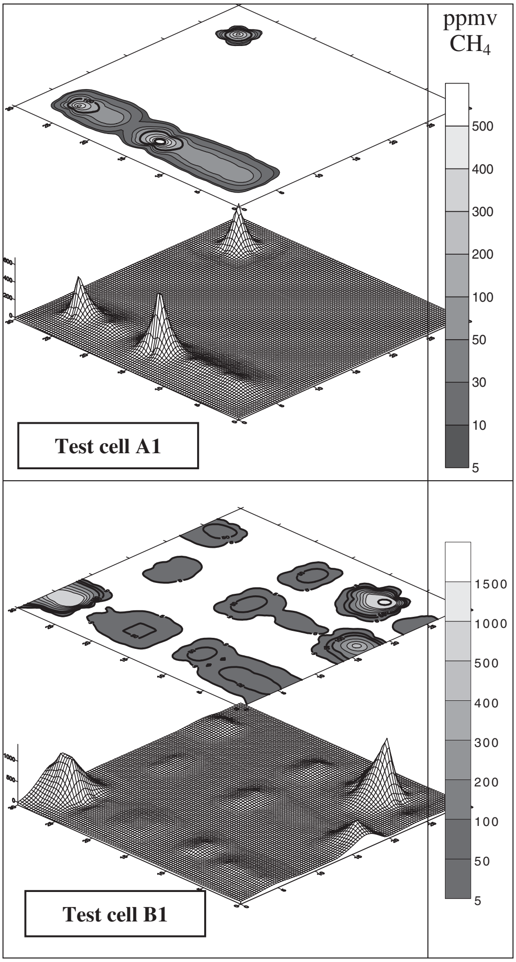

Figure 4. Exemplary FID-mapping at test cells A1 and B1 on "Landfill II" in spring 2000.

In our field trials, evaluation of the methane mitigation efficiency of the different methane oxidising biocovers were approached by quantifying the remaining methane emissions, and the relative comparison between the various cover designs as well as to an uncovered reference area, respectively.

3.2.3.1 Landfill I

The flux data confirmed the results from the FID-measurements. On the flat surface of test cells 1 and 2, no detectable methane fluxes (<0.1 g/m^{2}d) to very low fluxes (1.9 g/m^{2}d) were determined, while high fluxes of CO$_2$ were measured at the same locations. Even negative methane fluxes were detected at some measuring sites, indicating that methane oxidising covers can act as a sink of atmospheric methane rather than as a source of landfill methane. This phenomenon is

Table 5. Mean annual methane emission rates (±standard deviation) measured on the test cells on "Landfill II" in the year 2001; n = 48 per test cell (four chamber placements per cell, one measurement every month).

	Test cells					
	A1	A2	A3	B1	B2	B3
Mean annual methane emission rate (g/m^2d)	4.3 (±8.5)	42.9 (±51.1)	0.0 (±0.0)	6.0 (±9.5)	6.8 (11.8)	1.7 (±1.9)
Mean annual methane emission rate (l/m^2d)	6.0 (±11.9)	60.0 (±71.6)	0.0 (±0.0)	8.4 (±12.3)	9.5 (±16.6)	2.4 (±2.7)

already well documented by Bogner et al. (1995; 1999; and 2003) and Borjesson et al. (1998 and 2001).

On the surrounding slope, higher methane fluxes occurred, as was also observed by Borjesson et al. (2001). They found changing emission rates depending on seasonal conditions; in summer the slopes had higher methane emission rates than the top areas and vice versa during winter. These seasonal differences were not observable in our field trials. Bogner et al. (2003) also found hotspots with high methane emission fluxes at an edge part of a French landfill; and Scharff et al. (2001) reported high methane escape from the slope of a Dutch landfill. This is most probably due to the above mentioned phenomenon that landfill gas preferentially migrates via horizontal paths. Test cells 3 and 4 show high spatial variations (<0.1–249 g CH_4/m^2d), although the high fluxes were spatial infrequent (mostly located over fissures and cracks). On the uncovered reference cell 5, methane emission peaks up to 1,181 g/m^2d were detected. These emissions are of the same order of magnitude reported by Bogner et al. (1995), and Borjesson et al. (1998 and 2001). Methane emission fluxes from landfills, in particular from poorly covered areas, range over several orders of magnitude depending on controlling environmental conditions as well as the measuring method. Bogner et al. (1997) report natural variability of landfill methane emissions spanning more than seven orders of magnitude, from less than 0.0004 to more than 4,000 g/m^2d. Compared to emissions from natural swamps and wetlands as well as emissions from paddy fields, the data show that the emissions from test cells 1 and 2 are of the same order of magnitude as emissions from natural ecosystems (e.g., swamps 0.27 g CH_4/m^2d, Göttlich, 1990; boreal wetlands 0.07–0.41 g CH_4/m^2d, Sadredin et al., 1996; paddy fields 0.07–7.4, Chen et al., 1997). The emissions released from test cells 3 and 4 are substantially higher, and certainly, the emissions from the uncovered cell 5 are the highest of all.

The relative comparison of the emission rates from the covered test cells with the uncovered reference cell indicates that methane fluxes were reduced by nearly 100% by the cover layer on test cell 1; remaining emissions of less than 0.1 g CH_4/m^2d . Comparatively higher mean emission (up to 11.1 g/m^2d) occurred on slopes due to improper sealing using geosynthetic clay liners. The mitigation effect was about 72% on the slope. On test cell 2 the mean emissions were about 0.6 g/m^2d, showing a reduction rate of 98% compared to the emissions from the uncovered landfill. The annual mean mitigation effect on test cells 3 and 4 was lower, 68% and 74%, respectively.

3.2.3.2 Landfill II

The mean annual methane emissions (see Table 5) derived from the flux measurements using a dynamic chamber method showed high spatial variations (indicated by the high standard deviation). The total gas flux ($CH_4 + CO_2$) measured at the surface of the test cells can be regarded as a surrogate indicator for the landfill gas supply per square meter, although it is influenced by many processes in the covers, above all by the decrease in gas volume due to methane oxidation as well as CO_2 generation by decomposition processes. However, the influence on the gas loads by the gas supply trenches and the failure of the insufficient gas distribution layer made of sand can be seen from the data summarized in Table 6. Highest methane emissions were found on cell A2 (0.4 m mixture of MSW/SS-compost + sand, 0.8 m MSW/SS-compost beneath, planted with poplar), mainly due to the comparative high volumetric fluxes appearing above the gas supply trenches on that test cell (see Table 6).

Because of the initial data from the first two investigation years as well as the results from "Landfill I", the remaining area of "Landfill II" (about 16,600 m^2) was covered in autumn 2000 by an optimised layer of 0.5 m of coarse gravel (for gas distribution) overlain by 1.2 m of compost (mixture of sewage sludge compost and MSW-compost). Balanced volumetric gas fluxes occurred (29.3 (±19.2) l gas/m^2d) and methane emissions (0.3 (±0.16)g /m^2d) were barely detected on the remaining area (indicated by FID and chamber measurements), and a calculated mass-balance showed that on an average 96–100% of the produced landfill gas (about 155 l gas/m^2 d) was oxidized in the optimised biocover per year.

Table 6. Mean annual gas volume fluxes ($CH_4 + CO_2$ = total surface gas load) (±standard deviation) in l gas/m^{2}d on the different test cells on "Landfill II" divided in chamber placements affected by the gas supply trenches (GST) and widely unaffected (NGST); n = 24 for each data set.

	Test cells					
	A1	A2	A3	B1	B2	B3
GST	84.5 (±133.1)	267.1 (±224.9)	36.2 (±26.5)	81.8 (±77.2)	113.0 (±82.8)	13.7 (±7.8)
NGST	25.7 (±18.0)	18.2 (±8.7)	12.7 (±9.4)	20.9 (±13.2)	20.2 (±15.0)	12.7 (±8.8)

4 CONCLUSIONS

Simple but well-engineered biocovers can mitigate methane emissions from landfills. The use of recycling and waste materials for biocover construction – both for the oxidation and the gas distribution layer – may represent an ecologically- and economically-suitable solution and provides the added benefit of dispensing with the disposal of former waste.

Mature composts show higher microbial methane consumption relative to conventional landfill soil, which can most probably be related to nutritional factors provided by the compost or to changes in the microbial ecology. Moreover, physical factors such as the increased porosity, water-holding capacity, or thermal insulation properties of compost seem to be responsible for much of the observed positive effects. The good insulation properties of well-dimensioned compost covers used in our field trials (like test cell 1 on "landfill I") was most probably the reason why there appeared no decrease in methane emission mitigation during winter, while other field studies show a strong decline in methane oxidation during winter in conventional or small-dimensioned cover soils (Borjesson et al., 2001; Liptay et al., 1998; Chanton & Liptay, 2000). The high water holding capacity of organic-rich composts is beneficial in arid climates to preserve moisture for the microbes, although, under wet conditions, a high moisture content can reduce gas transport and hinder methane uptake, and in extreme cases, even can produce methane (Barlaz et al., 2004). Thus, good porosity provided by a balanced particle size distribution is crucial to maintain sufficient gas permeability at high moisture contents.

Modifications of biocover designs may be feasible to adapt to local, landfill site specific conditions as well as to various intended purposes. Thus, the dimension and thickness of a biocover vary depending on the materials used to construct it, their local availability and cost, the oxygen-penetration depth, the settlement behaviour (particularly when the covers are placed without any artificial compaction), the climate (precipitation, temperature, frost penetration depth), the expected landfill gas fluxes, the desired function of the cover (final or temporary), as well as the after-use purpose (vegetation, land use). For example, the minimum thickness of a final compost cover to mitigate methane emissions on bioreactor landfills is recommended with at least 1.2 m in the construction phase for climatic conditions in Middle Europe. The natural consolidation and settlement of the non-compacted compost layers in our field trials was about 20% in the first two years of the investigations. Low-engineered and more simplified biocovers, like designs used on test cells 3 and 4 on "Landfill I" can assist reducing gas emissions from landfills with low gas generation and moderate landfill gas fluxes as well as under environmental conditions where barely winter influences are expected. Currently, Bogner et al. (2005) try to determine a minimum biocover design made of recycled materials capable of mitigating methane emissions in subtropical environments.

Homogeneity of landfill gas fluxes and cover material properties are important requirements for efficient methane oxidation. The imperative of installing a sufficient gas distribution layer as already postulated in Humer & Lechner (2001a) was supported by the experiences derived from the investigations on "Landfill II". For landfills with high gas generation and strongly differing spatial gas fluxes, the construction of a 0.5 m thick layer made of a coarse inert material (e.g., gravel >63 mm grain size deficient in lime) is recommended. This layer should not be separated by geo-synthetic mats (non-woven geo-textiles) from the compost cover, since the methane oxidation layer can shift downwards to the interface or even into the gas distribution layer as observed in our investigations. Then such mats will get clogged due to microbially produced biomass, EPS formation and infiltrating fine particles, sweeping off the gas balancing function of the basal gravel layer. Thus, a gas distribution layer shall be at least 0.5 m in size to guarantee a sufficient thickness for unhindered gas distribution even if fine particles from the overlying substrate infiltrate the upper parts of the distribution layer. Alternative materials for constructing gas distribution layers, such as crushed glass are currently investigated in a field trial (Bogner et al., 2005) or others (like tire chips) have already been proven (Barlaz et al., 2004). At the moment, in Austria four closed MSW-landfills, respectively some sections of these sites, are covered with a biocover made of about 0.5 m gas distribution layer of gravel overlain by about 1.2 m of mature, well-structured compost substrates, serving either as the sole means to mitigate methane emissions or in combination with an operating gas extraction system Currently, this design represents quasi state-of-the-art for biocover construction in Austria, and is officially approved for this landfills as an interim cover for a period of about 20 years.

The zone where the top gas distribution layer reaches the slope side must be constructed thoroughly to prevent channelled gas migration and emissions, particularly at "above-ground" landfills and on wind exposed side slopes. Generally, in coarse landfill covers, like biocovers made of compost, wind may have a strong impact on varying gas composition, migration and emissions, as was observed in our field trials. Otherwise, coarse top covers offer the advantage that gas pressures above barometric pressure in the landfill may not occur, as often observed in landfills covered with dense materials, such as clay, forcing lateral gas migration. Furthermore, compost covers are flexible enough to compensate for active subsidence of the decomposing waste. In conventional low permeability covers, settlement depressions followed by the formation of fissures and cracks occur on areas undergoing active subsidence.

Subsequent investigations of biocovers will need to address the long-term durability and bio-active lifetime of the cover material. This will depend, in part, on the nature of the composted material and the depth at which maximum methane uptake occurs. Factors such as temperature, moisture, gas fluxes and gas ratios may influence the optimum depth, which may shift over time as the porosity and other characteristics change, as the compost degrades. The results from both field trials reveal that with increasing decomposition and maturity, and consequently depleting oxygen demand of the compost material, the methane oxidation layer shifts downward with time, making the oxidation process more independent from varying outer conditions. Currently, we have results for methane oxidation in biocovers from an intensive investigation period of about three years and an extensive observation period of about 7 years. The long-term behaviour regarding decades cannot be inferred reliably from results thus far. It can only be extrapolated that under aerobic conditions, the compost layers will mineralize slowly and become more and more soil-like and the texture will become finer. Otherwise, the gas production of the landfill will also decrease with time; only low gas production is expected about 20–30 years after landfill closure (Krümpelbeck, 1999). Within this time the biocovers must operate as a methane oxidizing filter, albeit with decreasing efficiency, since landfill gas generation and consequently methane supply will decline, too. Our previous results indicate that the nutrient status of mature, organic-rich composts will be sufficient for methane oxidation over this time horizon.

Optimised and well-adapted biocovers for landfill gas control offer many advantages compared to conventional gas collection systems and compacted clay or geo-membrane composite covers, including low operation and installation expenses, and low maintenance requirements. As a "low-technology" system, they can be maintained by relatively untrained personnel, which makes them particularly suitable for low-income countries. Where national regulations allow alternative caps and landfill gas management measures, biocovers can be a cost-efficient, complementary strategy to mitigate greenhouse active gas emissions during the operation, closure as well as aftercare phase of MSW- landfills.

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The effect of disinfected sewage sludge amendment on methane oxidation in a model landfill cover

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ABSTRACT: The development of methane oxidation potential was investigated in laboratory-scale PVC columns filled with sand, of which the top layer (20 cm) was mixed with sewage sludge and flushed through with CH_4 for 4 months. The following four experimental treatments were applied: 1 – a control containing unmodified sand, 2 – sand amended with stabilized sewage sludge (37°C), 3 – with sewage sludge additionally disinfected by 24 h incubation at 55°C, and 4 – with sludge treated with 0.3 kg CaO kg^{-1} d.m. of sludge. Oxygen deficiency restricted the activity of microorganisms in deeper layers of the columns containing digested sewage sludge. The limed sludge did not change the physical parameters of the sand significantly. Sewage sludge amendment enhanced the methane oxidation rate of the model landfill cover soil significantly; in contrast the additional disinfection of the sludge by alkalization reduced the CH_4 oxidation potential of the cover soil.

Keywords: Methane oxidation, landfill cover soil, sewage sludge, methanotrophs.

1 INTRODUCTION

The increase in the concentration of methane emitted to the atmosphere over the last few decades is a result of the lack of balance between sources and sinks of this gas. The mitigation of methane accumulation is possible via a reduction in emissions from some ecosystems and the leakage from geological sources, as well as through intensification of microbial oxidation of methane in soils. Therefore methods for reducing CH_4 emission from landfills, an important anthropogenic source of methane, have come into prominence.

The current trends in European policy on waste management aim to reduce land-filling of organic wastes (by virtue of Council Directive 1999/31/EC), including sewage sludge. The problem of sewage sludge disposal is important, particularly in Poland, where the amounts of sludge are increasing as a result of the increasing number of wastewater treatment plants implementing sewage sludge management, especially after accession of Poland to the EU. On the other hand, application of sewage sludge to the soil is problematical, too. The sludge can contain various pollutants, both organic and inorganic, which should not be introduced into the food chain. However, sewage sludge can be used in land reclamation as a component of landfill cover soil instead of humus, compost, peat or other soil types of higher economic and ecological value.

The emission of landfill biogas is frequently reduced by collection systems, the biogas being used in energy production or flared. The carbon dioxide produced during methane burning is many times less active as a greenhouse gas than is methane itself. However, the flaring of biogas is only possible when the CH_4 concentration is higher than 30% (Scharff & Jacobs, 2003). Below this concentration methane can be oxidized by biotechnological methods in biofilters. Production of biogas in many old landfills as well as in landfills containing little organic matter is so low that the biogas collection is unprofitable. In such cases the active soil cover idea is still frequently used.

The landfill cover soil is the top soil layer of a landfill capping. Depending on the landfill's location, the availability of materials and transport costs, the landfill cover layer is constructed using various materials.

The methane oxidation potential of landfill cover soil was observed some years ago (Whalen et al., 1990). The elevated CH_4 concentration which often appears in the cover soil influences the development of methanotrophic bacteria with a high potential for methane oxidation. The highest values of methane oxidation rate 256.2–446.6 $dm^3\ m^{-2}\ d^{-1}$ were observed in a clay soil (Stein & Hettiaratchi, 2001), though values not much lower were obtained for the sandy soil of a landfill cover (Kightley et al., 1995) and for coarse sand (0.5–1.0 mm in diameter) inoculated with landfill cover soil (Pawlowska, 1999).

In landfill cover soil, depending on the construction and materials used, the degree of methane oxidation ranges from 0 to 34% (Chanton et al., 1999; Bogner et al., 2003). Intensification of CH_4 oxidation in the landfill soil is possible, for example by application of sewage sludge (Börjesson et al., 1998; Humer & Lehner, 1999 a, b; Kightley et al., 1995).

Anaerobic mesophilic sludge digestion is the most popular way of sludge stabilisation particularly in large waste-water treatment plants. The sewage sludge obtained in this process can still contain pathogens and should be disinfected by more effective methods prior to utilisation.

Significant areas of landfills e.g. in Poland are covered by large amounts of soil material, which is often sand as the most inexpensive and most easily available material. The incorporation of sewage sludge into the landfill cover soil changes its physical, chemical and biological parameters. It modifies microbial processes and also introduces new populations of microorganisms. The process of sludge stabilization and disinfection reduces the numbers of both the pathogens and of other bacteria including methanotrophs present in the sewage sludge.

The aim of this study was to investigate the influence of stabilized sewage sludge and of sludge additionally disinfected on the intensity of methane oxidation in sand.

2 MATERIALS AND METHODS

2.1 *Soil column experiment*

Four columns were constructed from polyvinyl chloride (PVC) tubes (1 m long, 15.2 cm inner diameter). Gas sampling ports were drilled at 10 cm intervals down the column and plugged with rubber stoppers. The bases of the columns were filled with small stones and gravel. Sand used in this experiment contained the following fractions: 20% of 4.0–1.0 mm fraction; 30% of 1.0–0.5 mm fraction; 40% of 0.5–0.2 mm fraction and 10% of the fraction <0.2 mm. The air-dried sand was packed above the gravel to a height of 90 cm in column No. 1 and to 70 cm in columns Nos. 2–4. The top 20 cm layer of the latter columns was filled with a mixture of sand and sewage sludge (200 Mg d.m. ha^{-1} or 20 kg m^{-2} equivalent of 6.6% dry mass). This is the maximum dose accepted in the Regulation of the Polish Ministry of the Environment on municipal sewage sludge disposal (Dz. U.02.134.1140 from 27th August 2002). The sewage sludge (0.7 kg H_2O kg^{-1} sludge, 50% organic matter) used in this experiment was taken from a municipal waste water treatment plant in Lublin (Poland) after stabilization under mesophilic anaerobic conditions (37°C). This material was used to pack column No. 2 and was additionally disinfected before mixing with sand by 24 h incubation at 55°C (column No. 3) or else by alkalization with 0.3 kg CaO kg^{-1} d.m. of sludge leading to an increase of the temperature up to 70°C for several hours and pH > 12 (column No. 4). The soil material was irrigated weekly with 200 cm^3 of water which corresponds to a mean annual precipitation of 600 mm.

Table 1. The physical parameters of top soil layer (0–20 cm) in columns during the experiment.

Feature	Unit	No. 1	No. 2	No. 3	No. 4
Bulk density	g cm^{-3}	1.53	1.00	1.04	1.12
Specific density	g cm^{-3}	2.63	2.49	2.49	2.49
Total porosity	Vol. %	42	60	58	55
Moisture	Vol. %	9	52	48	31
Gas porosity	Vol. %	33	8	10	24

Some physical parameters of 20 cm top layer of soil cores during the experiment are shown in Table 1.

Pure methane, not the typical biogas was introduced to the base of each column in order to assess the amount of the carbon dioxide production in relation to methane consumption rate. The gas flow was controlled by flow meters and was set to 5 cm^3 min^{-1}. This volume corresponds to the typical methane production rate in a 20 m thick layer of municipal wastes (Kightley et al., 1995). The headspace of the columns was kept open in order to allow free entry of oxygen. The experiment was repeated three times in the following periods: I – February–May 2003, II – June–September 2003, III – November 2003–February 2004. The experiment was conducted at 20°C until stabilization of the methane oxidation rate had been reached – ca. 4 months. All parameters were measured at the beginning of the experiment and after 2 and 4 months. Tables and figures show the mean values from results of three repetitions of this experiment.

2.2 *Gas analysis*

Gas concentrations were measured using samples collected into gas syringes through the gas sampling ports. The samples were analyzed for CH_4, O_2, and CO_2 on a Shimadzu GC-14B type gas chromatograph (thermal conductivity detector; glass columns packed with Porapak Q for CH_4 analysis and Molecular Sieve 5A for oxygen; carrier gas helium 40 $cm^3 min^{-1}$, temperature of injector and column 40°C; detector 60°C, current intensity 150 mA). The concentrations of oxygen were calculated, accounting for the presence of argon.

2.3 *Water content and pH of soil cores*

Samples of soil were taken from columns through the sampling ports and were dried at 105°C for 24 h.

The water content of the soil was calculated as the loss of weight due to drying.

The pH of soil samples from the columns was measured according to Polish norm PN-ISO 10390:1997 in a suspension of air-dried soil in water (ratio 1:5)

2.4 *Methanotrophic activity profile and methane oxidation rate*

Soil samples (2 g wet mass) taken from the columns were placed into 25 cm^3 vials and closed with a rubber stopper. Methane was injected to obtain its final concentration of 15% (vol/vol). Preliminary tests performed at methane concentrations 2, 4, 8, 12, 15 and 20% showed that 15% corresponded to saturation of methanotrophs with methane as a substrate. Also Pawlowska & Stepniewski (2006) found that this CH_4 concentration corresponded to full saturation range. The vials were incubated at 20°C for 96 h. Gas samples were taken from the vials and analyzed each day at 24 h intervals. The activity was expressed in cm^3 kg^{-1} d.m. s^{-1} at 20°C and normal pressure.

For measurement of CH_4 oxidation rates the headspace of a column was closed for 1 hour maximum with a PVC lid containing the gas sampling port so as not to disturb the access of oxygen. Gas samples were taken from the headspace and analyzed every 10 minutes for 1 hour. The activity was expressed in cm^3 kg^{-1} d.m. s^{-1} at 20°C and normal pressure.

The methane oxidation rate was calculated as the difference between the amount of CH_4 at the inlet and outlet from the soil cores.

2.5 *Number of methane oxidizing bacteria*

Fresh soil samples (2 g) taken from the columns were suspended in 20 cm^3 of distilled sterile water with the drop of surfactant solution and shaken to separate bacterial cells from soil particles. The soil suspensions of different dilutions were spread on triplicated Petri dishes with NMS (nitrate mineral salt) medium for methanotrophs (Whittenbury et al. 1970). The plates were incubated at 26°C in an atmosphere of methane:air (20:80). The colonies were counted after their number ceased to increase.

2.6 *Statistical analysis*

All parameters are presented as average values of three replicates. Statistical analyses were performed with the Microsoft Excel 2003. The significance of column experiment results were determined by the F Snedecor function and t-Student test at $\alpha = 0.05$. The results presented in tables and figures are mean values and standard deviation bars.

3 RESULTS

3.1 *Physical conditions*

Physical conditions in the experimental treatments presented in Table 1 indicate an important differentiation between control and the sludge amended columns. The total porosity of the control column was 42% by vol. while the sludge amended treatments showed total porosities of 55–60%. It should be noted that the physical conditions of the control column refer also to the material beneath the sludge amended layer.

The water content of the top layer increased, due to incorporation of the sludge, from 9% in the control treatment to 31% in the limed sludge column, to 48% in the sludge sterilized at 55°C and to 52% in the column 2 with the sludge stabilized under mesophillic conditions. Thus, liming of the sludge reduced the water holding capacity of the sand mixed with such material. The highest differentiation was visible in the air-filled porosity, this being the decisive factor for gas exchange with the atmosphere. It was the highest (33%) in the control, smaller (24%) in the limed sludge treatment and the lowest (8–10%) in the columns 2 and 3. Thus it can be stated that column 2 was characterized by the highest total porosity as well as water content and by the lowest (8%) air-filled porosity. Column No. 4, in turn, had the best gas exchange conditions of the three sludge amended top layers.

3.2 *Gas profiles*

Methane concentrations (Fig. 1) increased distinctly with time in all the treatments and were very high. In columns No. 1 and No. 4 they reached about 70% at the bottom while in the columns Nos. 2 and 3 – even 90%. Special emphasis should be put on the shape of the distribution curves for methane, especially in the two latter treatments characterized by a low air-filled porosity. The concentrations were not very variable in the depth interval 20–80 cm and decreased sharply within the surface layer. It should be underlined that methane under experimental conditions, as the only gas component, was supplied from the bottom with a constant rate. Thus its concentration profile is the resultant effect of the distribution of the gas diffusion coefficient within the column (affecting its migration rate to the atmosphere and the "dilution" process caused by oxygen and nitrogen diffusing downwards from the atmosphere and by carbon dioxide formed) as well as of the distribution of methanotrophic activity consuming methane and producing carbon dioxide.

The oxygen concentration in all the treatments decreased with time and with depth. In column No. 1 (filled only with sand) and in column No. 4 the oxygen concentration stabilized after 8 weeks at the bottom at a level of about 5%. In columns Nos. 2. and 3, characterized by the lowest air-filled porosity, in the top layer the

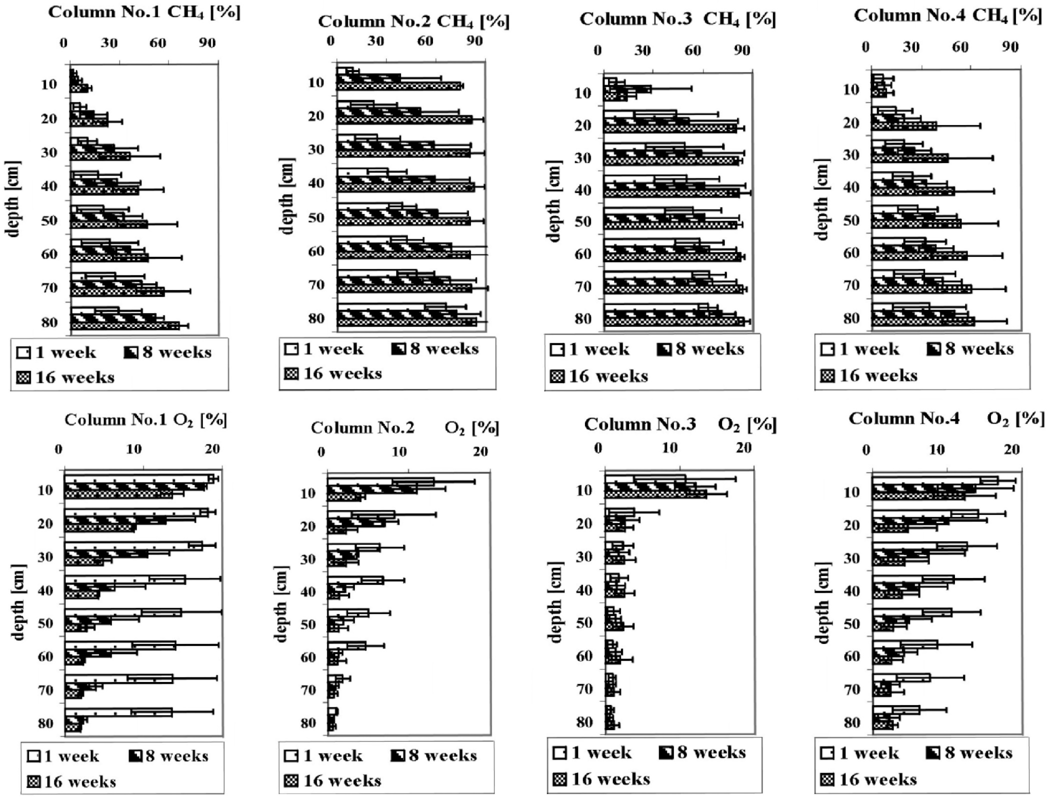

Figure 1. Changes of gas concentration during 16 weeks of purging soil cores with methane (mean value and standard deviation bars) in columns: No. 1 – air dried sand, No. 2 – sewage sludge stabilized under mesophilic conditions (37°C), No. 3 – sewage sludge additionally disinfected by 24 h incubation at 55°C, No. 4 – sewage sludge alkalized using 0.3 kg CaO kg^{-1} d.m. of sludge.

concentration of oxygen sharply decreased with depth under the sludge amended layer and at the bottom of the columns did not exceed 2% after one week and later of incubation. We emphasize that the oxygen distribution was governed by diffusion from the atmosphere against the methane induced upward mass flow from the bottom and by its consumption for microbial oxidation of methane and of organic matter from the sludge.

3.3 *Soil water content*

The profiles of water content in the columns result from the equilibrium or quasi-equilibrium formed between the processes of water generation and migration in combination with the properties of the porous medium itself (conductivity and retention properties). Under the experimental conditions, the only source of water is the methanotrophic process, while water migration (in the liquid and gas phase) depends on the pressurized ventilation induced by methane introduction, evaporation and infiltration downwards (dependent on water conductivity).

Sand, as an easily permeable material of low water retention, contained a small amount of water ranging from 0.03 to 0.04 kg H_2O kg^{-1} soil. The water content increased to 0.08 kg H_2O kg^{-1} soil at the bottom of column No. 1 (Fig. 2). This pattern of water distribution within the sand layer was characteristic of all the columns. The reason for this was probably the capillary barrier, which reduced penetration of water from small pores within sand to the larger pores within the gravel.

The water content within the top layer enriched with sewage sludge is much higher compared to the sand (0.23–0.33 kg H_2O kg^{-1} soil at 10 cm depth) decreasing to the surface (0.16–0.18 kg H_2O kg^{-1} soil) due to drying. It is obvious that this increase is connected with the enrichment with organic matter causing an increase in the water retention.

3.4 *pH profiles*

The sand used in this experiment contained 7.6% of carbonates resulting in alkaline pH (ca. 8.5). After 16 weeks of incubation the pH of the sand in column 1

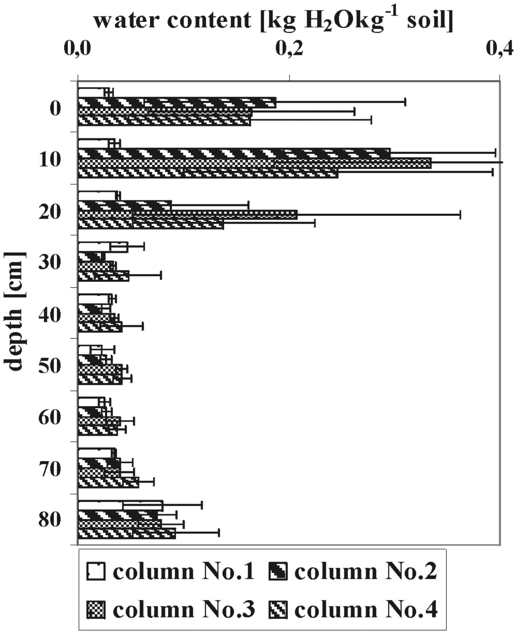

Figure 2. Profiles of water content after 16 weeks of purging soil cores with methane.

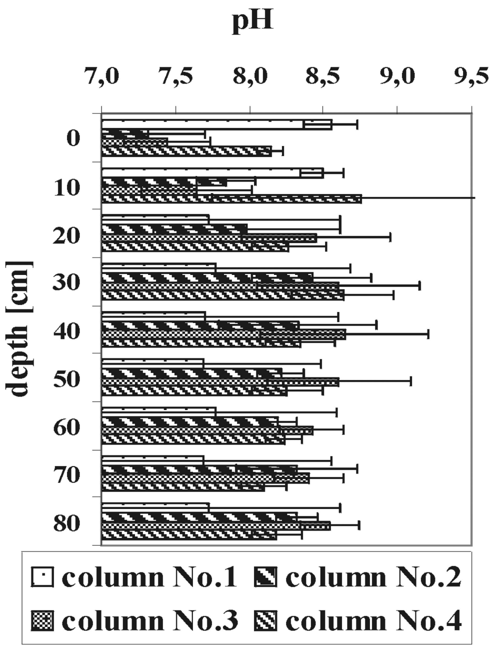

Figure 3. Profiles of pH after 16 weeks of purging soil cores with methane.

below 20 cm depth decreased slightly probably due to elevated CO_2 concentrations. The pH in columns Nos. 2–3 decreased in the top 0–10 cm due to incorporation of sewage sludge of pH = 7.2. At greater depths the pH in these columns remained unchanged. The pH at the surface of the column No. 4, enriched with the limed sludge of pH 13, decreased from the initial value of 11.27 to 8.15 after 16 weeks of the experiment. At greater depths the pH in this column was similar to that of columns 2–3 (Fig. 3).

3.5 *Methanotrophic activity*

Methanotrophic activity was measured in the soil samples taken from various depths of the columns at the end of the experiment.

In the control column No. 1, the methane oxidation rates were similar within the entire soil profile. Only at 0–10 cm from the surface the methanotrophic activity tended to be higher (Fig. 4).

Incorporation of sewage sludge elevated the methanotrophic activity several fold; the increase being the most distinct in the 20 cm top layer but also noticeable in the entire profiles for all the treatments. The highest value of methanotrophic activity, (11.8×10^{-3} cm^3 kg^{-1}d.m.s^{-1}) was observed in the column No. 3 containing sewage sludge additionally disinfected by heat treatment. The maximum values in the columns 2 and 4 were at a level of about 2/3 of that value (8.86×10^{-3} cm^3 kg^{-1}d.m.s^{-1} and 7.1×10^{-3} cm^3 kg^{-1}d.m.s^{-1}, respectively).

3.6 *Number of methane-oxidizing bacteria*

Populations of methanotrophic bacteria increased during the study, especially at the top of the soil cores. At the beginning of the experiment, the numbers of methane-oxidizing bacteria at the bottom and at the top of the columns Nos. 2 and 3 were similar, while columns Nos. 1 and 4 had more methanotrophs at the bottom.

A large number of various bacteria, among them also methanotrophs, failed to survive after the sludge had been mixed with CaO, causing the observed number of methane-oxidizing bacteria at the top of column No. 4 to be much lower than in other cores (Nos. 2 and 3) containing the sewage sludge.

The number of methanotrophs increased in subsequent weeks, particularly in the top layers of the columns. In fact, even a 1000-fold increase in the populations of methane-oxidizing bacteria at 10 cm depth in column No. 4 was observed after 16 weeks (Fig. 5). The results of the experiment show clearly that modified sewage sludge causes an increase in the population of methane-oxidizing bacteria in the sand.

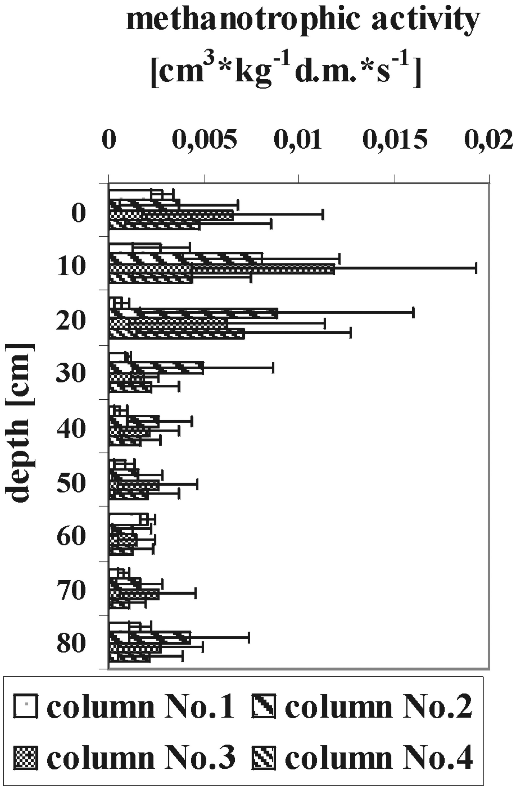

Figure 4. Profiles of methane oxidation activity after 16 weeks.

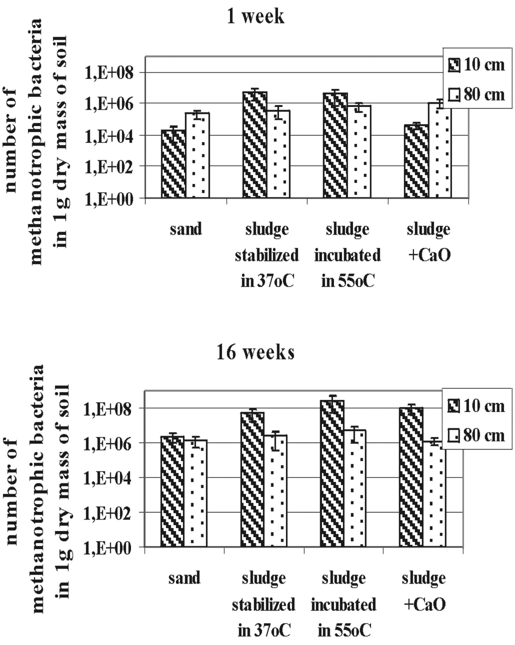

Figure 5. Number of methanotrophic bacteria at 10 and 80 cm depth after 1 and 16 weeks.

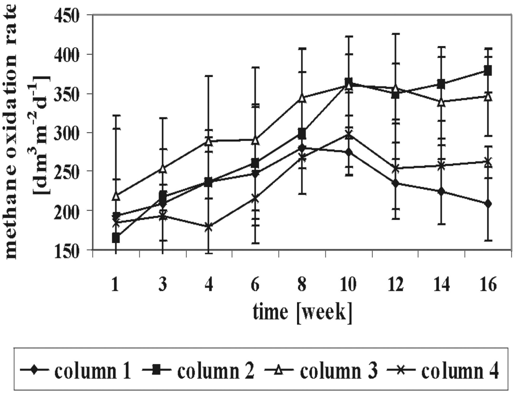

Figure 6. Changes in methane oxidation rate by soil cores during 16 weeks of the experiment.

3.7 *Methane oxidation rate*

The dynamics of methane oxidation rate during the entire experimental period is presented in Fig. 6. The maximum of CH_4 oxidation in the control column was reached after 8 weeks, and in the treatment No. 4 – after 10 weeks. The course of methane oxidation in both cases was similar. After the maximum in both the treatments a decreasing tendency was observed. In treatments 2 and 3 the methanotrophic activity increased during first 10 weeks of incubation up to 379 dm^3 m^{-2} d^{-1} and then apparently stabilized.

Evolution of carbon dioxide (Fig. 7) from columns No. 1 and 4 increased with time while that of the columns 2 and 3 decreased with time. Absolute values of the carbon dioxide evolved were much lower than the methane absorption rate which indicates that part of methane carbon absorbed was used for microbial biomass production either by methanotrophs or by autotrophic microflora fixing carbon dioxide. A decrease of carbon dioxide evolution in columns 2 and 3 despite an increase of methane absorption indicates that in this case the proportion of carbon fixed in microbial biomass increased with time. The final methane oxidation rates expressed in absolute values as well as in terms of percentage total CH_4 introduced into the columns are shown in Table 2. The highest degree of methane oxidation was 93.5% in the treatment No. 2 and the lowest – 51.6% in the control.

Statistically significant differences between average values for CH_4 oxidation rates after 16 weeks of the experiment were noted for columns 1 and 2, for columns 1 and 3, for columns 2 and 4 and also for columns 3 and 4. No significant differences were

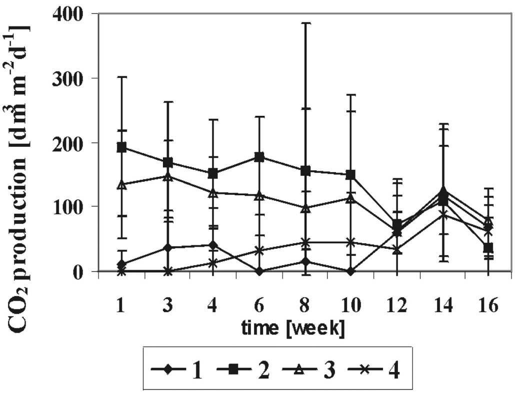

Figure 7. Carbon dioxide emission from soil cores during 16 weeks of the experiment.

Table 2. The mean values of CH_4 oxidation rates in soil cores after 16 weeks of the experiment.

Column	Mean CH_4 oxidation rate ($dm^3m^{-2}d^{-1}$)	Standard deviation ($dm^3m^{-2}d^{-1}$)	Percentage of CH_4 removed (%)
1	208.92	46.63	51.61
2	378.52	27.95	93.5
3	346.33	50.47	85.55
4	262.2	20.10	64.76

found for methane oxidation rates between columns 1 and 4, and between columns 2 and 3. This confirmed that the limed sludge had the lower methane-oxidation potential and only slightly modified the properties of the sand.

4 DISCUSSION

In this experiment, sandy material was used as the main component of a model soil cover of a landfill. Its mechanical composition did not cause any restriction of air flow in the sand layer. Pawlowska (1999) observed that methanotrophic capacity in the 1.0–0.5 mm sand fraction under laboratory column study was higher than that of the smaller (< 0.5 mm), and the coarser fractions (1–2 mm and 2–4 mm). It should be emphasized that the most active sand fraction represents a popular and cheap material used frequently in the reclamation of landfills under the Polish conditions.

The vertical profiles of the concentration of gases changed with time. The CH_4 concentration increased, replacing the components of atmospheric air. The O_2 concentration decreased with depth, even to just 0.5% at the bottom of columns Nos. 2 and 3.

Profiles for the gases in column No. 4 containing the limed sludge were similar to those in the control column (No. 1).

The differences in the gas profiles of the four experimental treatments confirmed that sewage sludge treated by different methods of stabilization are characterized by different physical properties. The quick lime treated sludge mixed with sand was characterized by a crumbly structure and was therefore easily permeable to gases. The sludge stabilized under mesophilic conditions (37°C), and especially that disinfected at 55°C, retained a substantial amount of water and was characterized by a clammy consistence. This led to a reduction in the air-filled porosity of the top layer and, due to this, the air and vertical methane flows in both directions.

The reduction in oxygen flow within the sewage-sludge layer was substantial. Nozhevnikova & Lebedev (1995), cited after Pawlowska (1999), observed oxygen penetration by diffusion even to a depth of one meter. However, the high methane oxidation activity, the high water content and fine-grained structure of the soil material can restrict the presence of oxygen to the top 60 cm (Lebedev et al., 1994) or even 30 cm (Kightley et al., 1995).

The sand is characterized by low water holding capacity. Water drains off rapidly due to gravity and the top soil layer is exposed to drying. It is known that the application of sewage sludge to mineral substrates used for reclamation improves their cation-exchange and water-holding capacity and makes them more fertile (Siuta et al., 1996). In this study, the sewage sludge incorporated into the sand improved the water-holding conditions of the model soil cover markedly. It is important for methanotrophic bacteria and for plants used in reclamation to find available water and fertilizers. The water content in the control sand material did not exceed 0.05 kg H_2O kg^{-1}, but in the layer amended with sewage sludge the maximum water content observed at 10 cm depth was 0.33 kg H_2O kg^{-1}, which leads, in practice, to a doubling of the total water retention in the column. Some authors have found 0.06 kg H_2O kg^{-1} as the critical value of water content for methanotrophic activity in their soils (Stein & Hettiaratchi, 2001; Visvanathan et al., 1999). At water contents below that value a dramatic decrease in microbial activity was observed due to insufficient water availability determined by soil water potential. Lebedev et al., (1994) observed a very low methane oxidation rate in the top 25 cm layer of a landfill cover soil. The latter authors as well as Stein & Hettiaratchi (2001) who used the results of Lebedev et al., (1994) for modeling, explained this observation by the low concentration of CH_4 at this depth.

Methanotrophic bacteria are treated as neutrophiles lacking in any clear adaptations to extreme conditions. The highest CH_4 oxidation rate is usually observed at pH values of 6–7 (Hütsch, 1994; Dunfield et al., 1993). Recently, some authors have observed methanotrophic activity in highly alkaline environments (at pH 10–11) (Khmelenina et al., 1997; Sorokin et al., 2000; Kaluzhnaya et al., 2001), but acidophilic methanotrophs have been also found (Dedysh et al., 2004; Trotsenko & Khmelenina, 2005) confirming the significant adaptive capacity of some methanotrophs.

As the sand used in this study contained calcium carbonate, its pH was alkaline throughout the experiment. The pH profiles, however were different in each column. In the control column filled with sand only, the pH was above 8.0 and slightly increased with time, while in the mixture of sand and sewage sludge it remained almost constant. A strong decrease in pH was observed in the columns with limed sludge, although it never fell below 8. Probably the decrease of pH was a result of CO_2 fixation by presence of $Ca(OH)_2$.

The high pH value in the limed sludge used in this study reduced, in fact, methanotrophic activity for some weeks, but once the pH declined below 8.0 the activity of the methane-oxidizing bacteria increased significantly. Pawlowska (1999) did not observe any significant changes in the methane oxidation rate in the pH range 7.61–8.89, though Hilger et al. (2000b) found that liming the soil increased the intensity of oxidation of CH_4.

The positive effect of sewage-sludge amendment on methane oxidation potential of soils was demonstrated by Kightley et al. (1995), who added 2.5 g of anaerobically-digested sewage sludge to each kg of coarse sand. This enhanced methane oxidation by 26% compared to the unmodified control soil. The usefulness of sewage sludge as a soil fertilizer or biofilter capable of stimulating methanotrophic activity was confirmed by the results of laboratory studies of Humer & Lehner (1999 a, b), as well as by field studies of Börjesson et al. (1998).

However, Kightley et al. (1995) used a very low dose of sewage sludge, which does not solve the problem of its disposal. On the other hand, the reclamation of landfills according to Börjesson et al. (1998) by covering the site with 0.5 m layer of dewatered sludge, is not allowed in Poland on account of the Regulation of the Polish Ministry of the Environment (Dz. U.02.134.1140 from 27th August 2002) on municipal sewage sludge disposal. Polish regulations permit a maximum dose of 200 Mg dry mass of dewatered sewage sludge per ha (20 kg m^{-2}) provided that the sewage sludge is immediately mixed with soil.

Application of sewage sludge for natural (agriculture and reclamation) purposes is allowed if the sanitary standards are fulfilled. According to the above mentioned Regulation, the contents of viable eggs of parasites e.g. Ascaris sp. should not exceed 300 per kg d.m. of sludge and the sewage sludge should contain no Salmonella.

Disinfection of sewage sludge both by heating at 55°C as well as by CaO amendment, reduces not only the number of pathogens, as shown previously by Rozej (2003), but also the population of methanotrophic bacteria (Fig. 6) and finally the CH_4 oxidation potential (Fig. 7) of the soil. Our studies confirmed that even after four months of incubation the methanotrophic capacity of the soil amended with CaO treated sludge was lower than in the soil with the untreated sludge.

Amendment of sewage-sludge to the top soil layer affected the distribution of some important factors influencing CH_4 oxidation. The oxygen flow into the soil cores was restricted to such an extent that the highest methanotrophic activity was observed at 10 cm depth in the sand with the sludge stabilized at 37°C and at 20 cm in the treatment with the additionally disinfected sludge. In the control column the maximum CH_4 oxidation activity was noted at a depth of 60 cm. Other authors have observed highest methane oxidation rates at similar depths: e.g. 60 cm (Pawlowska, 1999), 40–60 cm (Lebedev et al., 1994), 46 cm (Stein & Hettiaratchi, 2001) and 15–40 cm (Visvanathan et al., 1999) dependent on the kind of soil.

It is incontestable that the sewage sludge enhanced the methane oxidation potential of the model soil cover. The highest methanotrophic activity in the column with the sludge stabilized at 37°C was 8.86×10^{-3} $cm^3kg^{-1}d.m.s^{-1}$. This was four times higher than the maximum value observed in the control column. A slightly lower activity of 7.1×10^{-3} $cm^3kg^{-1}d.m.s^{-1}$ was noted in the limed sludge treatment. However, the highest value noted in this study, 11.8×10^{-3} $cm^3kg^{-1}d.m.s^{-1}$, was observed in the 55°C treatment.

Maximum methanotrophic activity values observed in this study for the three treatments containing sewage sludge were similar to the data cited in the literature. They were higher than the methanotrophic activity recorded for sandy loams (Boeckx & Van Cleemput, 1996; de Visscher et al., 2001; Whalen et al., 1990) for loamy sand (Gebert et al., 2003b) and for sand (Kightley et al., 1995; Pawlowska, 1999). Only Börjesson et al., (1998) observed a CH_4 oxidation rate in a sewage sludge landfill cover that was five times greater than the highest value obtained in this study.

The sewage sludge not only changed the physical parameters such as bulk density, water content, total and air – filled porosity of soils but also introduced nutrients and new populations of methane-oxidizing bacteria into the soil. Several days after the beginning of the experiment the number of methanotrophs in the top soil layer of the treatments 2 and 3 was 100-fold higher than that of the control. Fewer bacteria were observed in the limed sludge treatment presumably as a result of the high temperature and alkaline pH following CaO addition. The decrease in the number of methanotrophs at the beginning of the experiment reduced the methane oxidation rate of the entire soil core.

After 16 weeks of experiment the number of methanotrophs was 2.35×10^6 (control), 5.10×10^7 (treatment 2), 2.88×10^8 (treatment 3), and 1.0×10^8 (treatment 4) per g of dry mass of soil at 10 cm depth. This is similar to the literature data obtained in landfill cover soil by Jones & Nedwell (1993) and Lebedev et al. (1994), whereas Gebert et al. (2003 a, b) reported even 1000 times more methanotrophic bacteria in the biofilter filled with mineral soil.

However, the most important parameter characterizing the CH_4 oxidation potential was methane oxidation rate in terms of the amount of CH_4 consumed per unit area of the cover soil layer during unit of time. The sewage-sludge amendment enhanced the methane oxidation rate significantly, hence disinfection of the sludge caused a decrease of the CH_4 oxidation potential. The limed sewage sludge had a lower methane oxidation potential similar to that the control.

The highest methane oxidation rate of 378 dm^3 $m^{-2}d^{-1}$ was observed in the column with the sludge stabilized at 37°C. This was significantly higher than the capacity of sand (225 and 227 dm^3 m^{-2} d^{-1}) reported by Kightley et al. (1995) and Pawlowska (1999), respectively, but similar to the values in the range 256–447 $dm^3 m^{-2}$ d^{-1} obtained for landfill cover soil by de Visscher et al. (1999) and by Stein & Hettiarachi (2001).

The maximum of methane oxidation potential appeared after 10 weeks of purging with methane of the soil cores containing sewage sludge. This was not much later than in the control sand (8 weeks). In preliminary studies, Fornes et al. (2003) estimated the period of development of the methanotrophic potential in a compost containing soil as 6–8 weeks. In turn, Pawlowska (1999) obtained steady-state conditions of CH_4 oxidation in a sand inoculated by a landfill cover soil after 6 weeks, and in a gravel – after 4 weeks. Stein & Hettiaratchi (2001) also reported the beginning of the steady–state phase after 4 weeks in a clay landfill cover soil. They also observed an increase in methanotrophic activity for 5 months, and achievement of the steady-state phase, but after 160 days for a soil not exposed previously to a high CH_4 concentration. In the study of Stein & Hettiaratchi (2001) the presence of methane caused that methanotrophic bacteria started to proliferate. So the period of time over which the steady-state phase developed was in this case longer. In their landfill cover soils there were apparently large populations of methanotrophs, which adapted to the new laboratory conditions within a short period of time.

In all the columns, a decrease in the CH_4 oxidation rate was observed after the soil cores had reached the maximum. Such an effect was also reported by Hilger et al. (1999, 2000b), Visvanathan et al. (1999) and Stein & Hettiaratchi (2001). The accumulation of exo-polysaccharides (EPS) in the biofilm surrounding the soil aggregates often restricts the gas-uptake by methanotrophic bacteria. In this study the presence of EPS was not measured but some soil samples were pink-coloured, which might result from the development of methanotroph populations and the production of exopolimers. Similar observations were mentioned by Humer & Lechner (1999a, b) and Cossu et al. (2003). A lack of stoichiometric balance between methane consumption and carbon dioxide production indicates that a substantial part of the methane carbon was fixed in the microbial biomass. This observation suggests that microbial methane oxidation in landfill cover soil not only reduces global warming potential by conversion of methane to carbon dioxide (characterized by lower radiative activity) but also reduces the total amount of carbon emitted to the atmosphere due to microbial biomass formation.

5 CONCLUSIONS

The results of the studies lead to the following conclusions:

1. The final methane oxidation rates were 378 dm^3 m^{-2} d^{-1} for the column with un-sterilized sludge, 346 dm^3 m^{-2} d^{-1} for that sterilized at 55°C, 262 dm^3 m^{-2} d^{-1} for the limed sludge treatment and 209 dm^3 m^{-2} d^{-1} for the control.
2. Both 55°C and CaO treated sludge can be used as amendments of landfill soil cover as they increase the methane oxidation rate and are environmentally safe. However, the thermally disinfected sludge is characterized by the nuisances of bad odors and clammy consistence unlike the CaO treatment which produces a crumby structure, better gas permeability and lack of odors.
3. Oxygen penetrated to the bottom of the columns but its highest concentrations were observed in the treatment with CaO amended sludge.
4. Amendment of the 20 cm surface layer with the sewage sludge doubled the water holding capacity of the soil cores.
5. Methane oxidation bacteria survived high pH values caused by 30% CaO amendment.
6. Methanotrophic activity increased up to 4 times due to sewage sludge amendment, showing a maximum in the middle of the amended layer, and was the highest in the case of disinfected sludge amendment.
7. Stabilization of the methane oxidation rate took place after 8–10 weeks.

8. The volume of carbon dioxide evolved was lower than the amount of methane absorbed indicating fixation of a substantial part of carbon in the form of microbial biomass.
9. The results of the study should be helpful for decision makers in selecting materials for landfill reclamation.

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Management of Pollutant Emission from Landfills and Sludge – Pawłowska & Pawłowski (eds)

The environmental requirements of methanotrophic bacteria inhabiting coal mine rocks

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ABSTRACT: The aim of this work was to identify the most favourable environmental conditions for growth of methanotrophic bacteria inhabiting coal mine dump rock of differing storage time (0–10 years). The source of the dump rock was the Bogdanka Coal Mine (Lublin Coal Basin). The methanotrophic activity in ground rock material was evaluated from the rate of methane oxidation measured using gas chromatography.

The highest methanotrophic activity (51×10^{-3} m^3 CH_4 m^{-3} rock day^{-1}) was observed for a three-year-dumped rock enriched with 10% CH_4 at 20°C and 50% of total water capacity. It was confirmed that rock material is a favourable environment for methanotrophic bacteria growth up to five years of weathering. Longer periods of dumping caused the oxidation of pyrites resulting in sulphuric acid which is responsible for acidifying the rock to $pH < 3$.

Keywords: Methane oxidation, methanotrophs, coal mine dump rock.

1 INTRODUCTION

During production of coal from plant materials deposited in a swamp environment, pressure and temperature resulted in the generation of a large number of gases, especially methane. The coalbed gas consists of, besides methane (1.28% to 95.3% of coalbed gas) [Thielemann 2004], other hydrocarbons (C_2–C_5), CO_2, O_2, N_2, H_2S, SO_2 [Flores 1998] and noble gases (He) [Clayton 1998].

The high methane reservoir potential of coal and accompanying rocks is due to the efficiency of its structure, i.e. porosity. The bulk of the pores in coal are <0.50 nm in diameter [Harris et al. 1996], but such a small pore size precludes their occupation by water due to the hydrophobicity of coal. Hence only other small molecules, such as methane, (molecular diameter 0.32 nm), or some other hydrocarbons can occupy the pores. Methane is stored in two different ways in coal. Methane can be bound in gaseous form in the interstitial space (10% of the total gas contained in the coal) but the major part is physically adsorbed onto the surface of pores [Harpalani & Schraufnagel 1990 according to Li et al. 2003].

The coal mine dump rocks accompanying the deposits of hard coal are in constant contact with the methane ubiquitous in coal mines, which is emitted from the cracks and pores of coal deposits. This rock material originated in the Carbonaceous period and remained in the anaerobic environment until extracted. After the removal of coal mine dump rock to the earth's surface adaptation of microorganisms able to oxidize the methane in aerobic conditions, occurs. Aerobic methanotrophic bacteria using methane as the sole carbon and energy source are the main component of ecosystems where methane is produced and consumed. Besides the availability of substrates (CH_4 and O_2), the methanotrophs require specific conditions to live. Among these, environmental factors (primarily temperature and moisture) seem to be the most important.

It was confirmed that methanotrophic bacteria occur both in very cold, Arctic environments [Pacheco-Oliver et al. 2002] and in tundra soils where the temperature can decrease below 0°C [Trotsenko & Khmelenina 2005] as well as in temperate and tropical soils [Dubey & Singh 2000, Ishizuka et al. 2000]. Methanotrophs were isolated also from basalt aquifer [Newby et al. 2004] and marine environments [Kotelnikova 2002], but not from coal or coal mine dump rock. In the Záhorie coal mine (southwestern Slovakia) [Pokorný et al. 2005] the occurrence of different microorganisms as well as bacteria and fungi was described, but methanotrophic bacteria was not found. The only report concerning the occurrence of methanotrophs in the water of coal mines is from the Donbas Coal Basin (Ukraine) [Ivanov et al. 1978].

The capacity to oxidise methane is determined also by properties of the rock material, the pH and the grain distribution, which change over storage time.

The aim of our study was to determine the capacity of microorganisms inhabiting the coal mine dump rocks, to oxidise methane under different environmental conditions: temperature, moisture and the substrate CH_4 and O_2 concentrations.

2 MATERIALS AND METHODS

The studied rock material was sampled from the Bogdanka coal mine (Lublin Coal Basin) located in middle east part of Poland (51°18′N, 23°01′E). The coal mine is located near regions with protected environments: Poleski National Park, Leczna Lakeland Landscape Park and Nadwieprzański Landscape Park.

Coal mine dump rock samples of different times of weathering (including fresh) were air-dried and ground in a roller mill to 1 mm diameter (Testchem, Poland). The physicochemical properties of studied rock materials were determined in the pilot experiment. The balanced pH value was defined according to EPA SW-846 Method 9045. The grain distribution was determined by the Bouyoucosa-Casagrande areometric method with Prószyński modification. The total water capacity was measured in small columns ($h = 5$ cm, $d = 2.5$ cm) by estimation the amount of water retained after saturation.

The main characteristics of studied rock materials are presented in Table 1.

Table 1. Physico-chemical characteristics of the rock materials studied.

Sample (time of weathering on dumping area)	Grain-distribution (after grinding) 1–0.1	0.1–0.02	<0.02	pH	Total water capacity	Total carbon
	[mm]			(H_2O)	[g· kg of dry mass $^{-1}$]	[%]
P1 (0 year)	68	14	18	6.29	307	10.0
P2 (1 year)	69	12	19	6.43	320	10.7
P3 (2–3 years)	64	9	27	6.87	313	11.4
P4 (5 years)	45	15	40	4.31	330	11.0
P5 (10 years)	45	16	39	2.73	344	10.9

2.1 *Methanotrophic activity (M.A.)*

The methanotrophic activity was determined by the rate of methane oxidation. The laboratory experiments included the incubation of rock samples with an atmosphere enriched with various amounts of CH_4 (0.5–30%) and at three combinations of moisture up to 50, 100 and 200% of the total water capacity. Gas composition for CH_4, O_2 and CO_2 concentrations during incubation were determined by gas chromatograph, CP-3800 (VARIAN, USA) until to equilibrium conditions. The total number of experiment sets was 280.

2.2 *Scanning Electron Microscopic analyses*

The rock samples were fixed with 3% glutardialdehyde (EM Grade) at 20°C for 48 hours in cacodylate buffer (pH 7.2) and washed four times with demineralized water. Samples were then dehydrated with a series of ethanol solutions (10%, 20%, 30% to 100%, every step for 15 minutes), after the last portion of 100% ethanol, two more 100% ethanol drying steps for 30 minutes and 45 minutes, respectively were carried out. The dehydrated rock material was treated with a series of mixtures (2:1, 1:1, 1:2 ratios) of ethanol and HMDS (hexamethyldisilazane) for 15 minutes and twice with 100% HMDS. After this, the sample was sputter-coated with a 30 nm layer of Au/Pd and analysed in high vacuum mode at an accelerating voltage of 15 kV (Scanning Electron Microscope, Leo 1430 VP equipped with an SE detector).

3 RESULTS AND DISCUSSION

3.1 *Methanotrophic activity (M.A.)*

The methanotrophic capacity of the studied rock material was established on the base of methane concentration dynamics during incubation under laboratory conditions. The highest methanotrophic activity (51×10^{-3} m^3 $CH_4 \cdot m^{-3}$ rock material per day) was observed in a sample 2–3 years old at 20°C, 10% v/v CH_4 and moisture equivalent to 50% of the total water capacity (Fig. 1b).

3.1.1 *Effect of temperature and moisture*

The methane oxidation rate was greatly affected by temperature (Fig. 1). It was found that the optimal temperature of methanotrophic activity varied with soil moisture (Figs 1 & 2). The optimal temperature (20°C) of the most active rock material was observed at moisture 50%, while at moisture levels equivalent to the total water capacity higher values of the methanotrophic activity were obtained at 30°C.

In experiments with sandy-clay soil the decrease of optimal temperature from 27.1°C at moisture 10% to 20.1°C at 30% was confirmed [Boeckx et al. 1996].

Methanotrophic bacteria seem to be more sensitive to varying moisture below the optimal temperature than above it. Studies of paddy soil (plough layer) from rice fields allowed to define the optimum of methane oxidation at the level 280 g/kg [Cai & Yan 1999], which corresponds to the total water capacity of our rock material (Table 1). At moisture 150 g/kg Cai and Yan observed only slow oxidation of headspace CH_4 and very slow increase of activity with time. In our experiment, however, the methanotrophic activity at 50% of total water capacity, was as high or even higher, for some rock material and temperature combinations, than at 100% of total water capacity. This is probably due to better availability of methane.

Material moisture influences methane oxidation in two ways: diffusion i.e. supply of substrates and methanotrophic activity [Xu et al. 2003]. Temperature has a significant effect on the methanotroph population, which can consist of psychrophilic, mesophilic or thermophilic groups. Taxonomic diversity of thermophilic methanotrophic bacteria is limited to genera: *Methylococcus* and *Methylocaldum* [Eshinimaev et al. 2004], i.e. methanotrophs type X. The psychrophilic methanotrophic bacteria included type I and II methanotroph [Trotsenko & Khmelenina 2005].

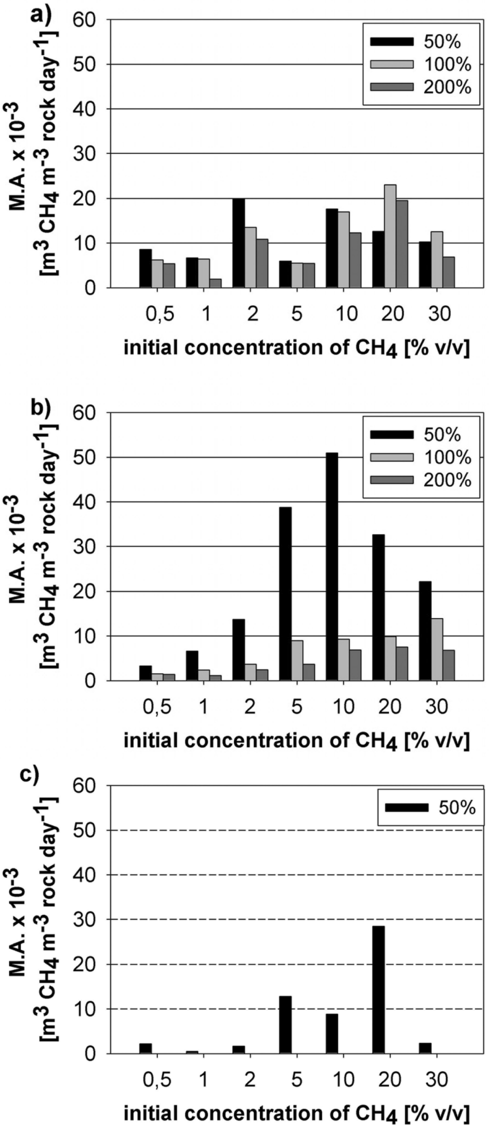

Figure 1. Methanotrophic activity in the most active rock material 2–3 years of dumping at a) 30, b) 20 and c) 10°C.

3.1.2 *Degree of weathering*

The initial characteristics of rock material acidity, grain distribution and size of pores play a significant role by determining the conditions of habitat for methanotrophic bacteria growth (Fig. 3).

A significant effect of dumping time was observed in a 2–3 years sample (pH ca. 7) which showed the highest values of methanotrophic activity, and in the oldest sample (10 years, pH < 3) (Table 1), in which the activity of methanotrophic bacteria was rather small.

3.1.3 *Availability of substrates CH_4 and O_2*

The availability of substrates is determined by the concentration of gases in the headspace and moisture, which restrains diffusion to microsites inhabited by bacteria. It was confirmed that the initial concentration of methane has a significant effect on methanotrophic

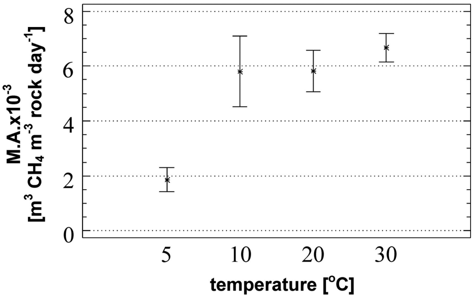

Figure 2. Effect of temperature on methanotrophic activity (means and standard errors – internals) (experimental set n = 280).

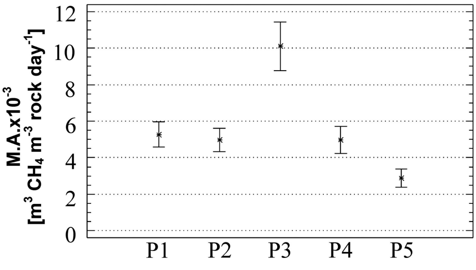

Figure 3. Effect of weathering degree (from 0 to 10 years) on methanotrophic activity (means and standard errors – internals) (experimental set n = 280).

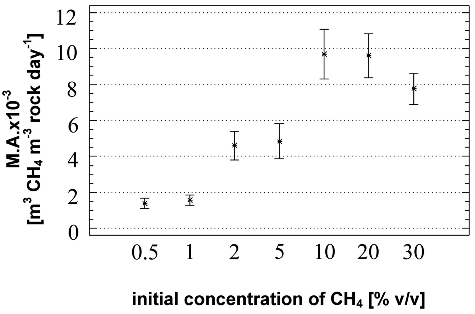

Figure 4. Effect of initial CH_4 concentration on methanotrophic activity (means and standard errors – internals) (experimental set $n = 280$).

activity (Fig. 4). Statistical analysis demonstrated three significant different groups of concentration ranges, 0.5–1%, 2–5% and 10–30% CH_4. The highest results were obtained during the incubation of rock material with an atmosphere enhanced with 10% CH_4.

The microbiological character of observed methanotrophic activity was confirmed by incubation of an autoclaved rock sample (1 h, 120°C) [Bender & Conrad 1995]. Autoclaved samples with added methane did not shown methanotrophic activity.

3.2 *Microscopic observation*

After the confirmation of methanotrophic capacity, active rock material was submitted to microscopic observation. The bacterial cells observed by us in a suspension of rock material were straight or curved rods with rounded ends, from 0.4–0.7 μm in width to 1,1–2 μm in length (Fig. 5). The cells occured singly and did not form chains, rosettes or colonies.

As is well known, methanotrophic bacteria differ in form, depending on their genus Methanotrophs of type I are short rods, usually occurring singly, some cocci or ellipsoids, type II – crescent-shaped rods, rods, pear-shaped cells, sometimes occur in rosettes and type X, cocci, often in pairs [Hanson & Hanson, 1996].

Presented on the microscopic pictures cells are similar in respect to form and size to the new acidophilic methanotrophs type II, *Methylocella palustris*, (0.6 to 1.0 μm wide and 1–2.5 μm long) observed by Dedysh [Dedysh et al., 2000]. However, our studied rock material has a pH close to neutral.

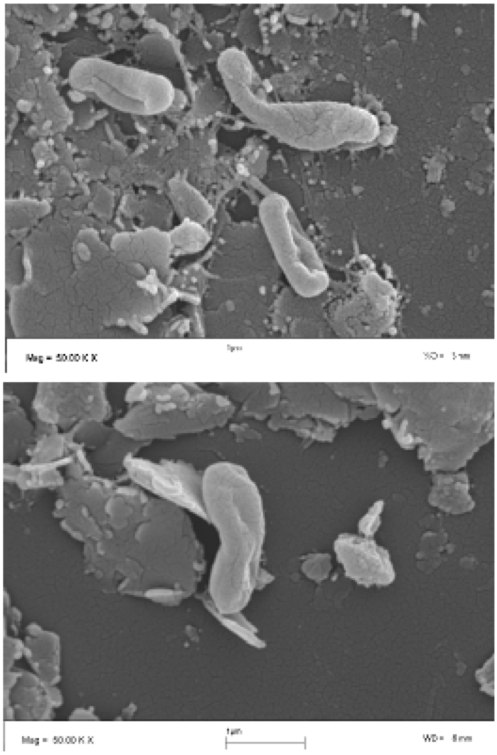

Figure 5. Cell morphology of bacteria inhabiting coal mine dump rock incubated under an atmosphere enriched with methane (Scanning Electron Microscope micrographs of active rock material, 50 000x).

4 CONCLUSIONS

On the basis of our experiments we find that:

1. The highest methane oxidation capacity was confirmed in samples having undergone 2–3 years of weathering. The methanotrophic activities observed in this rock material connected with each studied factor were significantly different from values characterized other samples. The lowest values occurred in combinations with the 10-years-old rock material, what is probably resulted from its high acidity, $pH < 3$.
2. Among tested temperature conditions, in the range 5–30°C, in all combinations of experiment only a temperature of 5°C has a significant effect on methanotrophic activity. The highest methanotrophic activity was observed at 20°C. The moisture effect, despite having no visible effect on the overall results, has a visible effect, especially in the most methanotrophic active, 2–3 years-old sample. The wetting degree of the material determines the availability of substrates, methane and oxygen from the atmosphere to the rock in which the methane oxidation is taking place. The most favourable concentration for methane consumption were 10% v/v CH_4.
3. The microbiological character of methane oxidation process in the tested rock material, was confirmed.

4. The presence of methanotrophic bacteria (by size and shape) was confirmed by SEM analysis of active coal mine rocks.

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Management of Pollutant Emission from Landfills and Sludge – Pawłowska & Pawłowski (eds)
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Aerobic stabilization of old landfills – Experimental simulation in lysimeters

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ABSTRACT: The effect of aeration on the reduction of landfill gas emissions and leachates, and biodegradation of deposited material in different stages of conversion of organic substances was investigated. The simulation of aerobic landfill processes was carried out in bench-scale lysimeters. Experimental studies showed that the aerobic waste stabilization was a very rapid process. During the course of one month the bed stabilized, reaching a significant reduction of nitrogen compounds, and easily biodegradable organic substances. The reduction of methanogenic potential of the landfill was even faster. The composition of gas at the outlet of the lysimeter changed and after only one day its content was similar to that of atmospheric air. It was also found that enhanced degradation of organic substance by advanced oxidation processes (ozonation and UV radiation with the addition of H_2O_2) contributes to increased reduction of pollutants in the leachates.

Keywords: Landfill, aerobic stabilization, methane oxidation, advanced oxidation processes.

1 INTRODUCTION

Landfilling is one of the most common ways of municipal solid waste (MSW) disposal in developing countries. Lately, the methods of landfill design, construction and operation have changed. Landfills have ceased being treated as only sites of waste disposal but are currently also perceived as special types of a bioreactor in which long-term anaerobic processes take place.

The technology of MSW landfilling causes a long-term environmental impact. For modern landfill strategies the sustainability of the landfill represents the main goal. To minimize the hazardous impact of old landfills on the environment induced by leakage of leachates and landfill gas emission, they are aerated in order to stabilize biodegradable substances and nitrogen-containing components and to reduce their methanogenic potential. One of the methods to quickly achieve stabilization is the implementation of an aerobic model of a landfill. During aerobic degradation of MSW, biodegradable materials are converted mostly to carbon dioxide and water. The primary goals of aerobic landfill systems are to enhance removal processes, achieve optimum waste stabilization, decrease concentrations of leachate contaminants, reduce methane production and waste mass subsidence (Mertoglu et al. 2006). Studies of aerobic biodegradation processes have demonstrated that the organic parts of the wastes can be degraded in a relatively short time compared with anaerobic degradation (Bilgili et al. 2006, Hudgins et al. 1999). There has been increasing interest in aerobic landfilling during recent years, and many pilot scale and field-scale studies have been recently undertaken (Bilgili et al. 2006, Borglin et al. 2004, Cossu et al. 2003, Das et al. 2002, He et al. 2006, Lee et al. 2002, Prantl et al. 2006, Read et al. 2001, Ritzkowski et al. 2006).

As one of the steps in the landfill leachate treatment Advanced Oxidation Processes (AOPs) are used. Both ozonation and UV radiation with O_3 or H_2O_2 (the photoassisted Fenton reaction) are applied for treatment of leachates from anaerobic landfills (Rice 1997, Kim et al. 1997). However, the impact of AOPs on biodegradation of leachates from aerated landfill has not been investigated.

The paper presents a comparison of the impact of aeration and enhancement of organic substance degradation by advanced oxidation processes (ozonation, UV radiation with the addition of H_2O_2) on the reduction of the landfill gas emissions and leachates, and biodegradation of deposited material in different stages of conversion of organic substances. The study was carried out in laboratory lysimeters.

2 MATERIALS AND METHODS

2.1 *Equipment*

Experiments were carried out in six laboratory lysimeters (L1–L6) with working capacity 15 dm^3. The lysimeters consisted of a glass cylinder of inner diameter 150 mm and height 850 mm, closed on top and bottom with stainless steel covers, equipped with pipes for leachate recirculation, sampling points, supply and removal of gases (Figure 1).

Advanced oxidation processes were performed in a 1 dm^3 batch reactor equipped with a low-pressure UV lamp and an ozonation set. The experimental set-up is shown in Figure 2. Ozone generated by an ozonizer of Polish construction (TU Lublin) was continuously supplied to the reactor through the gas distributor. The ozone monitoring devices were provided by BMT, Germany.

2.2 *Substrate*

In the simulation of a landfill process the lysimeters were filled alternately with layers of municipal solid waste and compost. The mixture of household waste contained: organic waste – 38% (vegetable and fruit – 10.9%; potatoes – 21.2%; bread – 2.3%; others – 3.6%), paper and cardboard – 25%, plastics – 17%, textiles – 5%, other wastes – 15% (Ledakowicz et al. 2004). The waste was shredded to 20–50 mm.

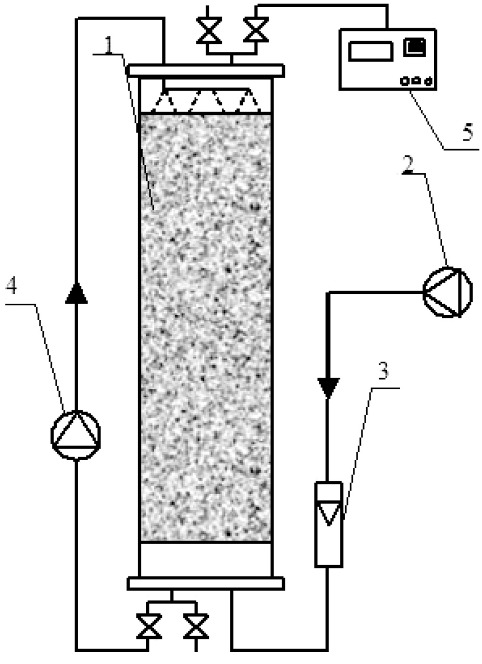

Figure 1. Schematic diagram of the lab-scale lysimeter with equipment: 1 – lysimeter, 2 – air pump, 3 – gas regulator, 4 – peristaltic pump for leachate, 5 – gas analyzer.

The bed was initially saturated with water by adding 3 dm^3 tap water to each lysimeter. A month after charging, around 200 ml of stabilized fermented sewage sludge was added to the lysimeters in order to initiate anaerobic digestion.

2.3 *Process parameters*

Initially the processes of anaerobic stabilization took place in all lysimeters (L2 about 4 months, L3 about 6 months, and L4, L5, L6 about 10 months). Then, after reaching an appropriate stage of conversion of organic substances in the lysimeters (L2 – acidogenic phase, L3 – initial methanogenic phase, L4, L5, L6 – final methanogenic phase), the investigation of the process of aerobic stabilization was started by continuously supplying air to the lysimeters at an aeration rate 0.013–0.015 L/min/kg waste. To determine the phases of waste degradation, the composition of outlet gases and leachates from the lysimeters was measured. To distinguish particular phases, the following criteria were assumed:

- acidogenic phase – COD > 10,000 mg O_2/dm^3, pH < 6, CH_4 < 30% vol., CO_2 > 50% vol.;
- initial methanogenic phase – COD > 10,000 mg O_2/dm^3, pH < 6, CH_4 > 30% vol., CO_2 > 50% vol.;
- final methanogenic phase – COD < 10,000 mg O_2/dm^3, pH > 6, CH_4 > 40% vol., CO_2 < 50% vol.;

Lysimeter L1 was not aerated and served as a control lysimeter in which anaerobic processes took place.

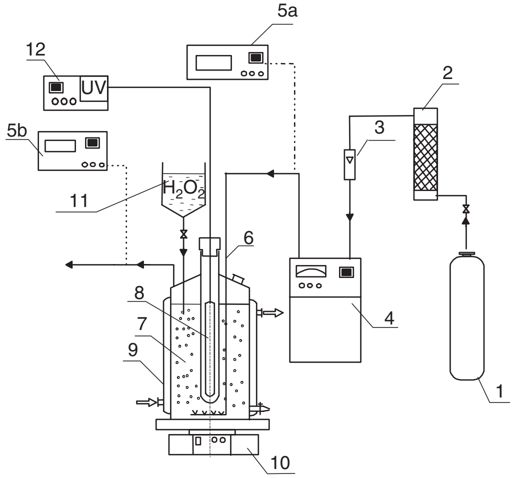

Figure 2. AOPs treatment set-up: 1 – oxygen cylinder; 2 – gas drier (P_2O_5); 3 – rotameter; 4 – ozone generator; 5a,b – ozone meters; 6 – gas inlet; 7 – photoreactor; 8 – UV lamp; 9 – heating jacket; 10 – magnetic stirrer; 11 – H_2O_2 dosimeter; 12 – UV lamp controller.

All leachates collected on the bottom of lysimeters were recirculated once a day. Processes in the lysimeters were carried out during 30 days at room temperature (around 20°C).

Leachates from two aerated lysimeters (L5 and L6) were also subjected to advanced oxidation processes (AOPs).

Leachates from lysimeter L5 were subjected to H_2O_2/UV AOPs on about the 20th day of the aeration processes. Hydrogen peroxide was supplied once in the amount of 0.033 g H_2O_2/g COD in leachates. The UV/H_2O_2 AOPs was applied during 3 hours for every 1 dm^3 of the leachates. After finishing AOPs the leachates were recirculated to the lysimeter L5.

Leachates from lysimeter L6 were ozonated. Ozone doses equal to 2 g O_3/g COD in leachates were used in the experiments. Ozone was supplied to the reactor through the gas distributor continuously until the required dose had been supplied. The absorbed ozone dose was calculated as the difference between the ozone concentrations in the gas between the inlet and outlet of the reactor (knowing the gas flow rate).

After finishing AOPs the leachates were recirculated to lysimeter L6.

2.4 *Analytical methods*

The following measurements were carried out on the leachates taken from the lysimeters:

- pH, (pH-meter WTW pH 540 GLP),
- redox potential (redox electrode, pH-meter WTW pH 540 GLP),
- BOD_5 (by the dilution method, APHA Standard Methods – Clescerl et al. 2005),
- COD (method 8000 Hach),
- VFA (according to the Polish Standard PN-75C-04616 using Büchi – Distillation Unit B-324),
- $N\text{-}NH_4^+$ (by the method of distillation in the Büchi device),
- TKN (according to the Polish Standard PN-75-C-04576-17 in the Büchi device),
- TOC (Coulomat 702 Li/C, Ströhlein Instruments, Germany).

The composition of gas being formed in this way (CH_4, CO_2 and O_2 content) was regularly measured (gas analyzer, LMS GasData).

The quality of the chemical analysis was checked by the use of standard solutions, such as potassium hydrogen-phthalate for the COD. The analytical errors were below 5%. The BOD_5 accuracy was much worse – possible errors could be up to 20%.

2.5 *Data analysis*

The data from each triplicate experiment were calculated to obtain the arithmetic mean values and standard deviations using computer programs. The arithmetic mean values ($n = 3$) were used for plotting the graphs.

3 RESULTS

Changes in the basic indices of organic load (BOD_5, COD, VFA), TKN, $N\text{-}NH_4^+$, pH, redox potential and changes in biogas composition with time were measured during the aerobic stabilization performance. Values of these indices at the beginning and after 30 days of aerobic processes for each lysimeter (L2–L6) are given in Table 1. For lysimeter L1 changes of these indices during 30 days of anaerobic processes since the moment of reaching the initial methanogenic phase in the reactor are presented.

3.1 *pH*

In the leachates from aerated lysimeters L3 – initial methanogenic phase, and L4 – final methanogenic phase, an increase of pH to 8.5–9.0 was observed. In lysimeter L2, in which aeration started in the acidogenic phase, the pH was maintained at the level of ca. 5.5. Figure 3 illustrates the changes observed in pH.

3.2 *BOD_5*

On the first 2 days of aeration a slight increase of BOD_5 in lysimeter L3 was observed, from then it was constant between the 2nd and 7th day of the process. An abrupt decrease between the 7th and 13th day was reported and after the 13th day there was a further gradual decrease to 300 mg O_2/dm^3. In the case of lysimeter L4 the BOD_5 values changed in a slightly different way: on the first two days of the aerobic processes there was a small increase, and then, between the second and seventh day, an abrupt decrease was observed. After the 7th day the BOD_5 decreased gradually to 16 mg O_2/dm^3. In the case of lysimeter L2 the values of this index decreased only slightly. Changes in BOD_5 are shown in Figure 4.

The highest degree of BOD_5 reduction was obtained in lysimeter L3. It was 99.0%, while the lowest one was 17.6% for L2.

3.3 *COD*

On the first 7 days of aeration a small decrease of COD in lysimeter L3 was observed. Subsequently, between the 7th and 13th day of the process a sharp drop occurred. After the 13th day there was a gradual decrease to 5490 mg O_2/dm^3. In the case of lysimeter L4 the values of BOD_5 changed in the following way: on the first two days of the aerobic processes a slight growth was reported, next between the 2nd and 7th day the level was relatively constant, between the 7th and 13th day there was a sudden decrease and after

Table 1. Load indices of leachates from lysimeters at the beginning and end of tested processes (averaged values).

	L1 (initial meth. phase – control)		L2 (acid. phase)		L3 (initial meth. phase)		L4 (final meth. phase)		L5 (final meth. phase – UV/H_2O_2)		L6 (final meth. phase – O_3)	
Index	Start	After 30 days	Start	After 30 days	Start	After 30 days	Start	After 30 days	Start	After 30 days	Start	After 30 days
BOD_5 [mg O_2/dm^3]	31,000	24,300	34,000	28,000	31,000	300	120	16	90	50	170	3
COD [mg O_2/dm^3]	52,500	40,300	62,800	55,400	58,100	5490	1230	1160	1290	1260	3800	625
TKN [mg N/dm^3]	770	480	880	840	680	210	59	50	43	53	38	14
N-NH_4^+ [mg N/dm^3]	520	400	510	540	500	22.0	11.4	4.2	2.7	4.3	9.3	0.9
VFA [mg CH_3 COOH/dm^3]	28,100	17,200	30,200	30,900	16,600	760	240	160	450	150	2000	30
TOC [mg C/dm^3]	950	800	23,200	10,800	16,500	2000	600	470	430	340	1000	130
pH [−]	5.54	5.52	5.23	5.43	5.25	9.14	7.19	8.76	6.98	8.81	7.23	8.69
Redox [mV]	−23	−37	−8	193	−37	54	34	179	51	188	47	173

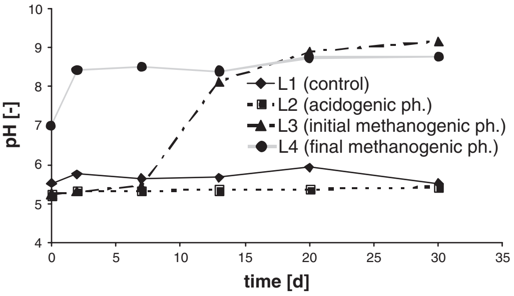

Figure 3. Changes of pH in leachates from the lysimeters L1–L4.

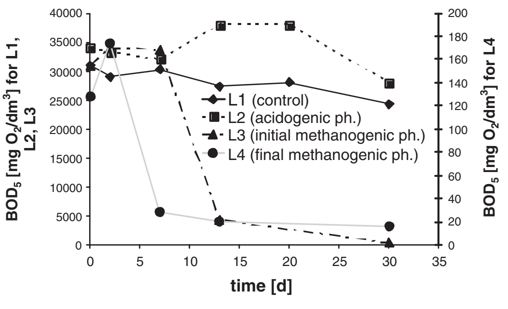

Figure 4. Changes of BOD_5 in leachates from the lysimeters L1–L4.

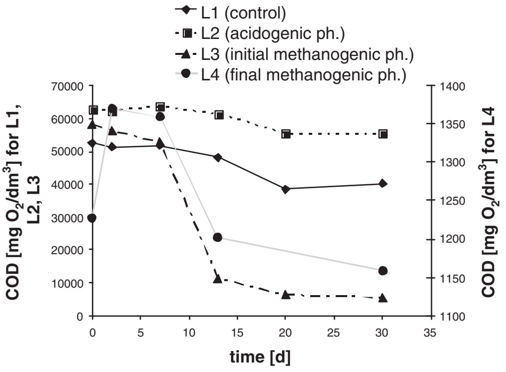

Figure 5. Changes of COD in leachates from the lysimeters L1–L4.

13 days the decrease continued to the value of 1160 mg O_2/dm^3.

In lysimeter L2 there was a slight stepwise decrease of COD. Figure 5 presents the obtained results.

The highest level of COD reduction was attained in lysimeter L3. It was 90.6%, and the lowest one – 5.7% was in L4.

3.4 *VFA*

It was found in the investigation that VFA content in lysimeter L2 oscillated on the same level, i.e. 28,000–33,000 mg CH_3COOH/dm^3. Initially in lysimeter L3

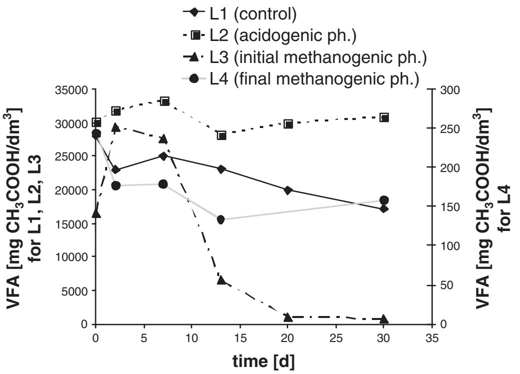

Figure 6. Changes of VFA in leachates from the lysimeters L1–L4.

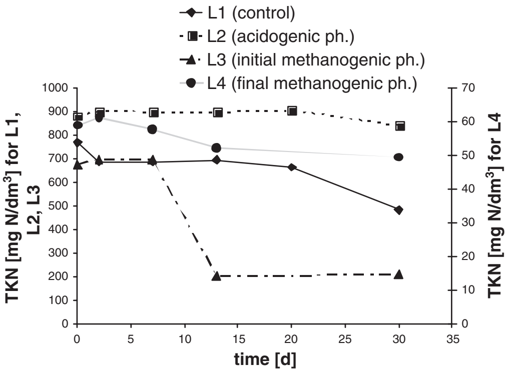

Figure 7. Changes of total nitrogen in leachates from the lysimeters L1–L4.

an increase of the VFA index was observed, next between the 2nd and 7th day of the process the index remained on a similar level, and between the 7th and 13th day a sharp decrease and after the 13th day a further gradual decrease was reported to attain the value of 760 mg CH_3COOH/dm^3. In the leachates from lysimeter L4 from the beginning to the end of the aeration process the content of VFA was gradually decreasing to reach the final value of 160 mg CH_3COOH/dm^3. These changes are shown in Figure 6.

The highest degree of VFA reduction equal to 95.4% was obtained in lysimeter L3 and the lowest – 0% in L2.

3.5 *Total nitrogen*

The initial concentrations of total nitrogen in lysimeters L1, L2 and L3 were 700–900 mg N/dm^3, and for lysimeter L4 60 mg N/dm^3. Between the 7th and 13th day of aeration, the total nitrogen decreased rapidly in lysimeter L3. In other lysimeters L2 and L4 the concentrations decreased only slightly (Figure 7).

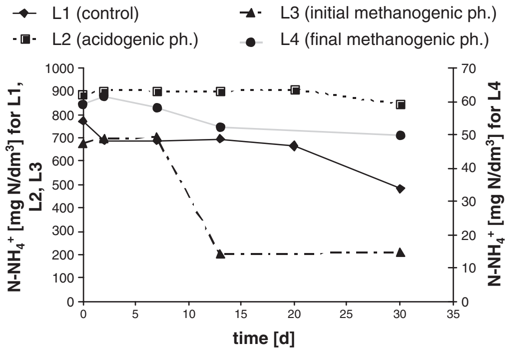

Figure 8. Changes of ammonia concentration in leachates from the lysimeters L1–L4.

The highest reduction of total nitrogen concentrations was attained in lysimeter L3 – it amounted to 68.8%, while the lowest 4.6% was obtained in L2. In L4 the reduction was 16%.

3.6 *Ammonium nitrogen*

At the beginning of aerobic stabilization the content of ammonium nitrogen in lysimeters L2 and L3 was around 500 mg N/dm^3, in lysimeter L4 it was much lower – 11.4 mg N/dm^3. Most probably this was due to a low content of ammonium nitrogen in the wastes which were charged to this lysimeter, since this nitrogen is not used by bacteria during anaerobic landfill processes.

A rapid decrease of ammonium nitrogen concentration was reported in lysimeter L4 on the first 2 days of the process, while in L3 between the 7th and 13th day. In lysimeter L2 no large changes were observed (Figure 8).

The highest level of reduction of ammonium nitrogen concentrations was obtained in lysimeter L3 – it was 95.6%, and in L4 a 63.4% reduction was reached.

3.7 *Biogas composition*

Aeration of the lysimeters started at the moment when the methane concentration in biogas for a particular lysimeter was: L2 – 0% vol., L3 – 60% vol. and L4 – 50%. Since the beginning of the aerobic process a decrease of methane content (L3 and L4) and carbon dioxide (L2, L3 and L4), and an increase of oxygen content (L2, L3 and L4) were observed. The composition of outlet gases in lysimeters L2, L3 and L4 resembled atmospheric air after just the first day of the process (Figure 9).

3.8 *Application of advanced oxidation processes*

The use of advanced oxidation processes enhanced waste biodegradation. In the lysimeter in which leachates were exposed to UV radiation in the presence of H_2O_2, the reduction of the indices of organic load of BOD_5, VFA and TOC was not high (Table 2). A better result was obtained in the case of ozonation. As presented in Table 2, the degrees of reduction were higher in comparison to lysimeter L4. Moreover, the biodegradability of leachates (as the ratio of BOD_5/COD, Figure 10) from the lysimeter L6 after implementation of ozone increased a little and enabled subsequent degradation.

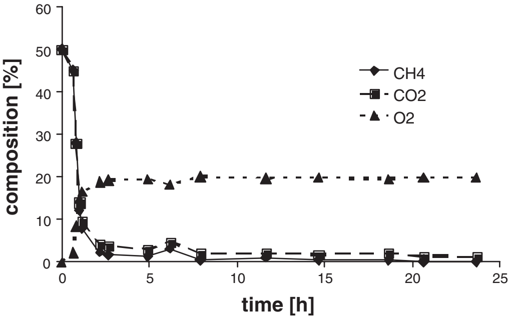

Figure 9. Changes of outlet gas composition for the lysimeter L4.

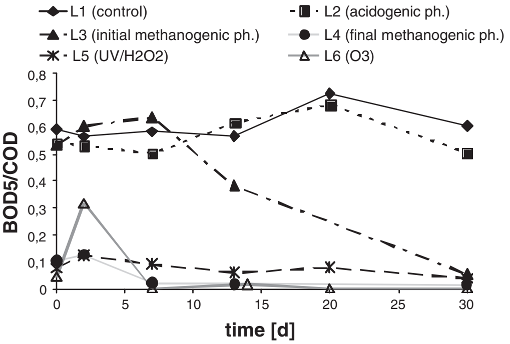

Figure 10. Changes of biodegradability in leachates from the lysimeters L1–L6.

4 DISCUSSION

The simulation of aerobic landfill processes was carried out in lysimeters with a bed stabilized anaerobically until reaching either the acidogenic phase or initial or final methanogenic phases. After starting the aeration processes, intensive aerobic processes caused a rapid biodegradation of the organic load. Experiments performed during this work showed that the aerobic waste stabilization was efficient only when aeration started at initial and final methanogenic phases – which is shown in Figures 4 through 8. Aerobic stabilization of landfills which starts in the initial or final methanogenic stage is quicker than stabilization processes in anaerobic conditions. In experiments carried out in anaerobic lysimeters by Ledakowicz et al. (2004) stabilization was obtained after about 150 days (from the beginning of the methanogenic phase), while for aerobic processes, in around 30 days the bed managed to stabilize, reaching a significant reduction of organic load indices.

By the significantly accelerated metabolism of aerobic microorganisms, aerated lysimeters show a fast reduction of organic leachate compounds. In particular, easily degradable organic compounds are rapidly reduced after starting the aeration (i.e. BOD_5 – 87–99%, COD – 91%, TOC – 23–88%). Additionally, the concentrations of the inorganic nitrogen compounds are noticeably reduced under the influence of aeration as well (reduction of N-NH_4^+ concentration – 63–96%). The reduction of this index is particularly important because ammonium resp. ammonia (NH_4^+/NH_3) are the most relevant compounds in the leachate with respect to the aftercare phase, as the NH_4^+-leachate concentrations decrease only over very long periods of time – several decades up to centuries (Ritzkowski et al. 2003). The biodegradability of leachates in lysimeter L3 (represented as a BOD_5 to COD ratio) initially increased, and next decreased significantly to the level of around 0.05 (Figure 10), which means that these leachates are very resistant to biodegradation. Curves illustrating changes in the values of particular indices for leachates from the

Table 2. Degree of organic load reduction in leachates from lysimeters after 30 days of aerobic stabilization.

Index	L1 (initial meth. phase – control) (%)	L2 (acid. phase) (%)	L3 (initial meth. phase) (%)	L4 (final meth. phase) (%)	L5 (final meth. (phase – UV/H_2O_2) (%)	L6 (final meth. phase – O_3) (%)
BOD_5	22	18	99	87	51	98
COD	23	12	91	6	3	83
TKN	37	5	69	16	0	63
N-NH_4^+	23	0	96	63	0	91
VFA	39	0	95	35	67	98
TOC	16	53	88	23	21	87

lysimeters are similar to the ones obtained by Cossu et al. (2003) in laboratory tests carried out in plexiglass columns packed with mechanical-biological pre-treated waste.

The reduction of a landfill methanogenic potential was even faster. The composition of gas at the lysimeter outlet changed and after the first day already resembled that of the atmospheric air. Curves that illustrate changes in the gas composition shown in Fig. 9, are similar in nature in each lysimeter. Investigations carried out by Heyer et al. (2001) during in situ aeration of the landfill in Kuhstedt (Germany) 14 years after closure, revealed that the methane content in the landfill gas decreased from around 50% to less than 1.5% during ca. a month since starting the aeration. In biogas samples taken from the landfill gas system installed in the landfill in Modena (Italy), around 10% methane was found after ca. 50 h of periodic aeration (Cossu et al. 2001).

The use of advanced oxidation processes yielded very good results only for ozonation, which is reflected by high degrees of reduction of particular indices for lysimeter L6 (Table 2). When these results are compared with the ones obtained in lysimeter L4, where aeration processes started also in the final methanogenic phase, it can be observed that the load of hardly biodegradable leachates can be still reduced to a very low level. However, in the lysimeter in which leachates were exposed to UV radiation with the addition of H_2O_2, the reduction of indices of organic load was lower than in lysimeter L4.

5 CONCLUSIONS

Experimental studies showed that the aerobic waste stabilization was a very rapid process. During one month the bed was stabilized reaching a significant reduction of organic load indices. In the case when aeration started in the acidogenic phase, no acceleration of the bed stabilization was achieved. Implementation of aeration in lysimeters is therefore recommended at the stage of methanogenic phase when methanogenic consortia of bacteria have already degraded carbon and nitrogen sources available for their biodegradation potential. However, the change from anaerobic to aerobic conditions, shows that there is still place for aerobic utilization of the biodegradation potential of aerobic consortia. Under aerobic conditions, the biodegradation of the leachates proceeded further reaching a reduction of organic load $>90\%$.

It was found that the application of advanced oxidation processes (especially ozonation) contributed to an enhanced reduction of the organic load in the leachates from aerated lysimeters. The application of leachate ozonation resulted in a very high degree of reduction of organic compounds. The reduction was higher by 12–73% as compared to a lysimeter in which no AOPs were applied and aeration processes started in the final methanogenic phase.

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Pathway of POPs in the waste, wastewater and landfill leachate

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Toxicity, fate and impacts of phenolic compounds in anaerobic municipal solid waste

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ABSTRACT: Of the wide range of potentially toxic/inhibitory compounds identified in landfill leachate, a significant proportion is phenolics, such as phenol, chlorophenols, dimethyl phenol, cresols and nitrophenols. Despite the anaerobic conditions to which these compounds are likely to be exposed, for example, in landfill sites or groundwater, few studies have addressed the toxicity, fates and impacts of these compounds, particularly in mixtures. We developed a standardised method for the assessment of anaerobic toxicity and by use of this test protocol identified that the toxic effects of 2-component mixtures of phenol, o-cresol and p-cresol were concentration dependent, such that at $1000\,\mathrm{mg\,l^{-1}}$ of each compound the effects were less than additive, while at lower concentrations the effects were synergistic. These results have practical implication in assessing the environmental toxic effects of xenobiotic mixtures.

Keywords: Anaerobic, phenolics, toxicity, interactive effects, synergy.

1 INTRODUCTION

The presence of phenols in the environment is of great concern due to their potential toxicity and recalcitrance (Brent and Herricks 1998, Bruce *et al.* 2001). Phenol is widely used in the production of many synthetic organic compounds such as agrochemicals and phenolics are present in the wastewaters of a variety of industries. For example, one coal conversion wastewater was found to contain phenol ($2150\,\mathrm{mg\,l^{-1}}$), *m-/p*-cresol ($710\,\mathrm{mg\,l^{-1}}$), *o*-cresol ($220\,\mathrm{mg\,l^{-1}}$), *p*-cresol ($420\,\mathrm{mg\,l^{-1}}$) and various dimethylphenols ($250\,\mathrm{mg\,l^{-1}}$) (nakhla and suidan 1995). Several studies have examined the resultant contamination of groundwaters: for example Harrison *et al.* (2001) reported that the long-term release of phenolic compounds into groundwater from a coal tar distillation plant in the uk had produced a plume about 500 m long, that contained mainly phenol, *o*-, *m*- and *p*-cresols and dimethylphenols. Borehole analyses within the plume demonstrated concentrations of phenol $\leq 2480\,\mathrm{mg\,l^{-1}}$, *o*-cresol $\leq 1450\,\mathrm{mg\,l^{-1}}$, and *m-/p*-cresols $\leq 750\,\mathrm{mg\,l^{-1}}$. In other contaminated groundwaters reported concentrations were much lower, and in a creosote-contaminated groundwater, phenol, *o*-cresol, and *m*-cresol concentrations were, respectively, 2, 0.65 and $0.78\,\mathrm{mg\,l^{-1}}$ (Flyvbjerg *et al.* 1993). While such low concentrations are individually below any likely toxicity threshold, the possible toxic effects of mixtures need to be evaluated. In landfill leachates, a wider range of phenolics has been identified (Table 1), due presumably to the diverse nature of municipal solid waste.

Many studies have examined the toxic effects of single compounds on the anaerobic degradation process (for example, Fang & Chan 1997, Vallecillo *et al.* 1999, Tepe *et al.* 2006). Few studies have evaluated the toxic effects, whether aerobic or anaerobic, of mixtures. In the broadest study so far reported Nirmalakhandan *et al.* (1994) examined a QSAR (Quantitative Structure-Activity Relationship) technique for predicting the toxicity of a two-component mixture. The IC_{50} value of single compounds was experimentally determined, and mixtures then formulated that were predicted to cause 50% inhibition. Deviations from the predicted inhibition were used to identify effects that were synergistic (more than additive) or antagonistic (less than additive), rather than simply additive. This study, however, utilised a commercial bacterial inoculum and only determined toxicity under aerobic conditions, as did the study of Mowat and Bundy (2002) who developed a mathematical algorithm to compute the combined toxicity of mixtures of metal contaminants using toxicity data for the individual components of the mixture. The Microtox® bioassay was used to experimentally obtain the toxicity data for a suite of metals (Pb, As, Cd, Cu, Hg, Zn, Cr). Results from binary and ternary metal

Table 1. Potentially toxic organic compounds found in leachate.

Substance	Concentration ($\leq$mg/l)	Substance	Concentration ($\leq$mg/l)
Benzene	0.61–3.8	Dibromoethane	0.19
Toluene	0.55–41	Dimethylphenol	200
Phenol	12.5–300	2-Chlorophenol	200
Ethylbenzene	0.27–2.2	Nitrophenol	200
Dichloroethane	0.18–34	Dinitrophenol	100
Trichloroethane	0.49	Methyl chlorophenol	200
Dichloroethylene	0.15–7.7	Methyl dinitrophenol	100
Trichloroethylene	0.15–7.7	Chlorobenzene	4.62
Tetrachloroethylene	0.59	Dichlorobenzene	0.52
Xylene	3.3	Dichloromethane	17

combinations indicated that additive, synergistic, and antagonistic effects were possible. Biosensors were used by Strachan *et al.* (2001) to demonstrate both antagonistic and synergistic effects of herbicides in fresh water. While Renard *et al.* (1993) investigated the anaerobic toxicity of a mixture of polychlorinated compounds, the toxicities of the component compounds were not addressed, limiting prediction of the effects of related but not identical mixtures.

Although the Anaerobic Toxicity Assay (ATA) (Owen *et al.* 1979) has been adopted by several workers, there have been few attempts to optimise and standardise experimental conditions by investigating the effects of experimental parameters on the results obtained (e.g. temperature, test medium, quantity and source of inoculum). However, biodegradability studies have demonstrated that, for example, the source of inoculum may have significant effects (Moreno-Andrade and Buitrón, 2004). In the first phase of this study, therefore, a range of operating parameters were examined for their effects on sensitivity, reproducibility, ease of use, and microbial activity.

Since methanogenesis is a complex process mediated by several trophic groups, the toxicity effects of an organic compound may be targeted towards one or several of these groups. While inhibition of any of them will impact on resultant methane production, accumulation of specific intermediates may be used to identify the most sensitive step. For example, Holmes *et al.* (2002) used this technique to demonstrate that in an anaerobic association isolated from landfill, Sulfate Reducing Bacteria were more sensitive to the inhibitory effects of *o*-cresol than methanogens. Most studies on anaerobic toxic inhibition have, however, used decrease in methane production as the most sensitive and accessible indicator of inhibition (Renard *et al.* 1993). In this study methane production from anaerobic batch cultures supplemented with phenolic compounds, singly or in combination, was measured and used to derive the concentration that reduced cumulative methane production by 50% (IC_{50} value).

2 MATERIALS AND METHODS

2.1 *Municipal Solid Waste (MSW) source and preparation*

Month-old pulverised MSW samples were taken from Shewalton landfill site (Irvine, Ayrshire) and stored in tightly sealed polythene bags at 4°C in the dark. Prior to use, the MSW was handsorted to remove larger ($\geq$5 mm) pieces of glass, wood, metal and plastic, and shredded manually and thoroughly mixed.

2.2 *Development of standardised test*

Cultures of refuse were prepared (in triplicate) in 500 ml bottles. For the investigation of the influence of

1. Type of suspending medium, 10 g (dry weight) of refuse were added to 200 ml of distilled water, 6 mM phosphate, or mineral medium (Coutts *et al*, 1987);
2. Addition of microorganisms enriched from decomposing refuse, portions of an actively methanogenic culture of refuse (100 g of refuse in 1000 ml of distilled water) which had been incubated at 30°C for more than 6 months were used to supplement cultures of refuse in distilled water (total volume 200 ml) containing various concentrations of 2,4-DCP;
3. Added quantities of MSW, three different weights (2.5, 5.0, and 10 g (dry weight)) of autoclaved MSW were included in the cultures supplemented with 20 ml of an actively methanogenic culture (*see* 2 above);
4. Incubation temperatures, two were tested (30°C and 37°C);
5. Inoculum storage, MCW samples were stored at 4°C for periods between 0–12 months and their methane potential then assessed.

All cultures, with the exception of test 4, were incubated at 30°C. The cultures were made anaerobic by flushing oxygen-free nitrogen into the headspace. The pH, concentration of volatile fatty acids in the culture medium, and the cumulative production of methane during the course of incubation were determined. In this paper, only the effects on methane production are presented.

2.3 *Toxicity testing in batch cultures*

To 10 g sorted MSW in triplicate bottles (500 ml), 200 ml of the appropriate solution was added, to give final concentrations of 0, 100, 200, 400, 800, and 1000 mg l^{-1} phenol, *o*-cresol or *p*-cresol. To other bottles, mixtures (phenol/*o*-cresol, phenol/*p*-cresol, *o*-cresol/*p*-cresol) were added to give final concentrations of 100, 200, 400, 500 and 1000 mg l^{-1} of each compound. Bottles, closed with subaseals, were incubated at 30°C.

2.4 *Analysis*

2.4.1 *Methane*

Headspace methane concentrations were determined by use of a GC (Perkin Elmer 8700) fitted with a flame ionisation detector. The sample was separated on a metal column (2 m × 2 mm internal diameter) packed with 5% neopentyl glycol sebacate and 1% H_3PO_4 on Chromosorb W-AW (mesh 80–100). The temperatures of the injector, oven and detector were 200, 80 and 210°C, respectively, and oxygen-free nitrogen (OFN) (40 ml min^{-1}) was the carrier gas. Triplicate 50 μl culture gas samples were injected and peak areas compared to those of pure methane (British Oxygen). Methane concentrations were converted to molarity at STP. After sampling, bottles were overgassed with OFN for 5 minutes.

3 RESULTS AND DISCUSSION

3.1 *Development of standardised test*

It was evident that cumulative methane concentrations did not significantly differ with the suspending medium, and that over the incubation periods nutrients in the MSW were not limiting (Figure 1). Subsequent tests were therefore prepared in distilled water.

The mean values of A_v were calculated for inoculated cultures to which 2.5, 5, or 10 g of refuse (dry weight) were added. The results are shown in Figure 2. The production of methane in the presence of 2.5 g refuse appeared to be stimulated by 0.1 mM 2,4-DCP, indicating possible hormesis, the stimulation of metabolic activity at low or sub-lethal concentrations of toxic substances (Christofi *et al*. 2002).

At the concentrations of 2,4-DCP where toxicity was observed (0.52 mM and 1 mM), the mean A_v increased as the quantity of refuse increased. This effect was caused possibly by increasing amounts of 2,4-DCP being adsorbed to the refuse at the higher quantities of refuse; the more refuse that is present, the greater the organic content, which results in more binding sites and, possibly, a lower extent of inhibition. The concentration of 2,4-DCP in the liquid phase of these cultures decreased rapidly within 3 days of incubation (data not shown).

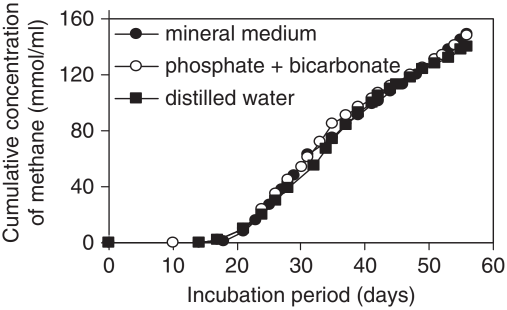

Figure 1. Cumulative methane produced in triplicate cultures prepared with various media.

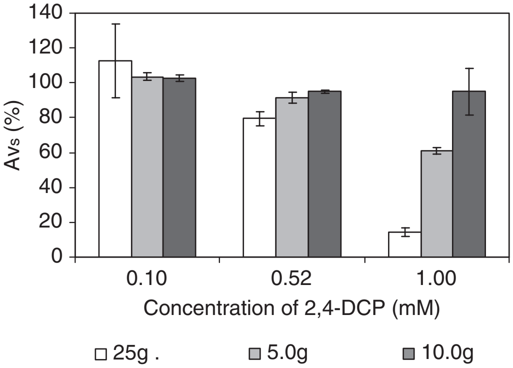

Figure 2. Mean A_v of supplemented cultures containing various concentrations of 2,4-dichlorophenol (2,4-DCP) and various quantities of MSW. A_v is defined as the ratio of methane produced in toxicant-challenged cultures compared to control cultures, over the steady methane production phase.

The mean values of A_v observed for cultures that contained 0.52 mM and 1.0 mM 2,4-DCP and 2.5 g of refuse were significantly lower than those for cultures containing these concentrations of 2,4-DCP and 10 g of refuse [$0.0025 > P > 0.0005$ and $P < 0.0005$, respectively; one tail-tests (data collected when the rate of production of methane was steady)].

These results suggest that the quantity of refuse used in an assessment of toxicity has a significant influence on the value of A_v. At the same concentration of the toxicant, the extent of inhibition increased when smaller quantities of refuse were used,

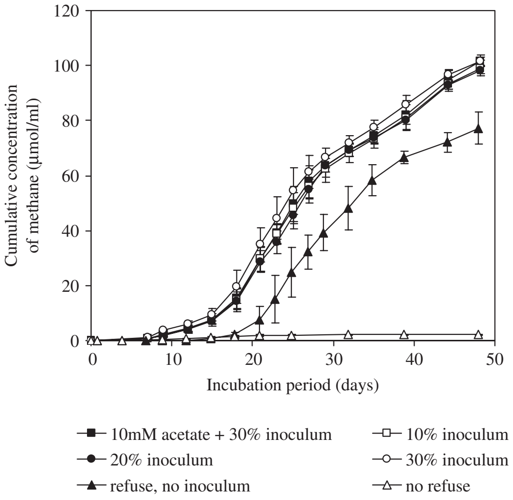

Figure 3. Cumulative production of methane in non-augmented and augmented cultures.

even although the cultures received the same quantity of actively methanogenic inoculum. Therefore, to simulate the degradation of refuse in landfills, the utilisation of the highest practicable quantity of refuse is advisable. The quantity of refuse used also will depend on the total volume of liquid. From the results of this investigation, for 200 ml of liquid, 10 g (dry weight) of refuse is recommended.

Figure 3 shows the production of methane by cultures augmented with a methanogenic inoculum. With the exception of the cultures that did not contain refuse, the un-inoculated cultures started to produce methane approximately one week later than did the inoculated cultures. The total amount of methane produced by un-inoculated cultures at the end of incubation clearly was lower than the others. Moreover, the variation among replicates of the total amount of methane produced by inoculated cultures was much smaller than that of the un-inoculated ones (data not shown). The amount of methane produced by cultures with 30% inoculum was not significantly different from that produced by cultures with 20% and 10% inocula. It appeared that there was a sufficient quantity of nutrients available when cultures were inoculated to the extent of 10%. The addition of 10 mM acetate did not affect the production of methane. The amount of methane produced by 30% inoculated cultures containing 10 mM acetate was similar to that of the other inoculated cultures. Therefore, these findings suggest that a sufficient amount of nutrients was provided by 10 g of refuse.

Only a very small amount of methane was produced by cultures with a 30% inoculum that did not contain refuse (Figure 3), possibly because of either the insufficiency of nutrients, such as N, P, and K, in the medium or the absence of refuse. The activity of oxygen scavengers present in the refuse maintains the anoxic condition of the cultures, while refuse itself provides nutrients and a large surface area for attachment of the microorganisms.

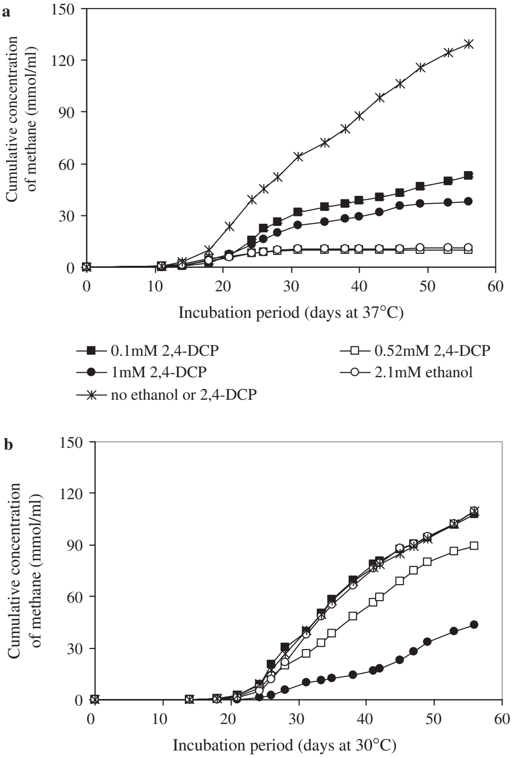

Figure 4. Cumulative methane production in cultures incubated at (a) 30°C and (b) 37°C.

Extensive attachment of microorganisms to surfaces characteristic of landfill sites was demonstrated by Jones *et al.* (1994). The results obtained here illustrate the importance of assessing toxicity in the presence of the material that is to undergo anaerobic degradation, i.e. landfilled MSW in this study. Consequently, it was concluded that cultures supplemented with an actively methanogenic inoculum at 10% of the total volume of the culture were suitable for use in a toxicity test, and this quantity of inoculum was used to supplement all of the cultures described in experiments 4 & 5.

At 30°C, inhibition of methanogenesis was DCP concentration-dependent (Figure 4(a)), such that the greatest % inhibition was recorded with 1 mM 2,4-DCP. No inhibition was recorded with 0.1 mM DCP. A very different pattern, however, was observed in cultures incubated at 37°C, a temperature at which mesophilic activity was expected to be greater than

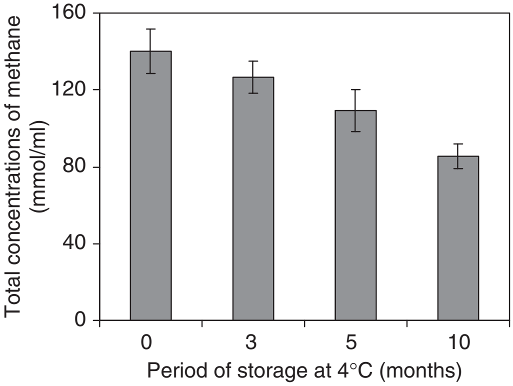

Figure 5. Cumulative methane from MSW stored for periods between 0–12 months.

at 30°C. Indeed, in these cultures in which methane was produced, the lag phase was shorter than at 30°C (Figures 4 (a) and (b)), and in cultures amended with neither ethanol nor DCP cumulative methane concentrations on Day 56 were 130 ± 34 μmol/ml, compared to 109 ± 11 μmol/ml at 30°C. The cultures supplemented with ethanol did not produce methane in significant amounts (Figure 4(b)). In the later stages of the incubation, the pH of these cultures decreased to 4.95 and acetate accumulated to between 75 and 87 mM. Methanogenesis was presumably inhibited by the low pH values (Christensen and Kjeldsen, 1989).

Cultures supplemented with 0.52 mM 2,4-DCP also did not produce significant amounts of methane (Figure 4(b)). The concentration of acetate increased in a similar fashion to that recorded in control cultures supplemented with ethanol. Rather surprisingly, in cultures supplemented with 0.1 mM and 1 mM 2,4-DCP significant amounts of methane were produced (Figure 4(b)), although at both concentrations, two of the three replicate cultures did not produce methane. In the two replicate cultures supplemented with 0.1 mM 2,4-DCP that did not produce methane, the net concentration of acetate increased to between 55.0 and 69.0 mM. In the culture containing 1 mM 2,4-DCP that produced methane (one of the three replicates), the concentration of acetate increased in the early stage of incubation, and then it decreased to approximately 1 mM on day 35. However, after day 35 the net concentration of acetate increased again, to 27 mM and remained at this concentration until the end of incubation. The increase in the concentration of acetate in the later stage coincided with the reduced production of methane by this culture after day 31 (Figure 4(b)).

Even although only one of the three replicate cultures produced methane, it was clear that, at 1 mM 2,4-DCP, the activities of fermentative bacteria and acetogens were inhibited most extensively, and that this inhibition was responsible for the slower production of acetate in all of the cultures during the first two weeks of incubation [compared with the cultures supplemented with 0.52 mM and 0.1 mM 2,4-DCP, and with the cultures supplemented with ethanol].

This experiment was repeated four times, and it was evident that when cultures containing 2,4-DCP were incubated at 37°C, the results were not reproducible. The refuse used in all investigations was from the same batch excavated from the landfill. The effects might have been due to the combined influences of increased incubation temperature, the heterogeneity of the refuse, and the size of particles of refuse. The interaction of the groups of organisms involved in anaerobic biodegradation, in which organic acids are intermediates, is such that the degradative process is vulnerable to the effects of overproduction of these VFAs. The inhibition of methanogens at low pH is well known (Barlaz *et al.* 1990). At 37°C, In the presence of a highly active acidogenic population, or elevated concentrations of readily degradable organic substrates such as ethanol, the relatively rapid generation of VFAs might result in inhibition of the acid-sensitive methanogens. Also, the small size of particles of refuse that were used might have facilitated contact between the substrates and the microorganisms and caused a more rapid rate of hydrolysis of polymeric molecules in the refuse and a more rapid production of organic acids. At an incubation temperature less than optimal (for example, 30°C), because the rate of production of VFAs might be slower, the proliferation of the slower-growing methanogenic population might have been enabled. Although the refuse used in these experiments was homogenised, undoubtedly there were slight variations in the MSW added to the various replicate cultures. Landfilled MSW is heterogeneous. The effects of these slight variations, in terms of generation of VFAs, might be amplified at 37°C, possibly resulting in significant variations in the production of methane by the various replicate cultures. Paradoxically, the addition of a low concentration (0.1 mM) of the potentially inhibitory DCP enhanced methane production (Figure 4(b), possibly by selectively inhibiting fermentation and acetogenesis, minimising imbalances in microbial activities.

Therefore, it was concluded that 37° C was not a suitable incubation temperature for the assessment of toxicity of 2,4-DCP to the anaerobic microorganisms of landfilled MSW in which aqueous ethanol was used as the solvent for the toxicant.

A lower temperature (30°C) afforded results that were more reproducible and easy to interpret. The total concentration of methane decreased as the period of storage of refuse at 4°C increased. The amount of methane produced by refuse that had been stored for 3 months was not significantly different from that of refuse that was used within 2 weeks of excavation (0.20 > P > 0.10), while the concentrations of methane produced by refuse that had been stored for 5 and 10 months before use were significantly lower than that produced by refuse that was used within 2 weeks of excavation (0.025 > P > 0.0125 and 0.0025 > P > 0.0005, respectively; one-tail tests). These results suggest that the activity of microorganisms in the refuse declined with time of storage at 4°C, and that refuse that had been stored for longer than 5 months might give misleading results in a test of toxicity. The reduction of the activity of microorganisms in the refuse might be caused by the exposure of microorganisms to small amounts of O_2. The problem of changes in the activity and numbers of microorganisms in refuse that has been stored at 4°C is difficult to overcome. Freezing (and thawing) of the refuse might reduce the numbers of microorganisms due to crystallisation of water and lysis of cells. Utilisation of pure cultures might solve this problem because, under these conditions, cultures are easier to standardise and control. However, results obtained from toxicity tests with respect to anaerobic degradation of landfilled refuse that use single organisms would not reflect the effects of toxicants on the complex interactions of the various groups of microorganisms involved.

As a result of these studies, future toxicity tests on the interactive effects of phenolic compounds were undertaken in triplicate cultures

- that were incubated at 30°C;
- that used distilled water as the suspending medium;
- which were inoculated with 10 g of pulverised and shredded MSW, stored for less than 3 months at 4° C, in 200 ml total volume; and
- to which 10% (of total volume) of an actively methanogenic augmentation was made.

3.2 *Toxicity testing in batch cultures*

As expected, phenol was less inhibitory than either *p*- or *o*-cresol, with no evidence of inhibition of methane production at concentrations ≤ 800 mg l^{-1} (Figure 6a).

As a result it was not possible to identify the concentration that induced 50% inhibition (the IC_{50}) although it was certainly more than 1100 mg l^{-1}. Similar results have been previously reported: Watson-Craik and Senior (1989) used a multi-stage continuous culture system to segregate the components of a methanogenic association isolated from MSW, and reported that when challenged with phenol, methane production was only inhibited at concentrations ≥ 8 mM (752 mg l^{-1}). Analyses indicated that hydrogenotrophic methanogenesis was more sensitive than acetoclastic methanogenesis.

Of the two cresols tested, *o*-cresol was more inhibitory, with an IC_{50} value of 700 mg l^{-1} (Figure 6b), compared to 1000 mg l^{-1} for *p*-cresol (Figure 6c). Progressive inhibition was recorded at *o*-cresol and *p*-cresol concentrations ≥ 125 and 400 mg l^{-1}, respectively. Very few studies have addressed the effects of a range of cresol concentrations on anaerobic degradation. Fedorak and Hrudey (1984) challenged sludge-inoculated cultures with *p*-cresol (200, 400, 600, 1000 and 2000 mg l^{-1}), and reported inhibition only at concentrations ≥ 1000 mg l^{-1}. In studies in which a multi-stage continuous culture system was challenged with *o*-cresol (Holmes *et al.* 2002) the segregated

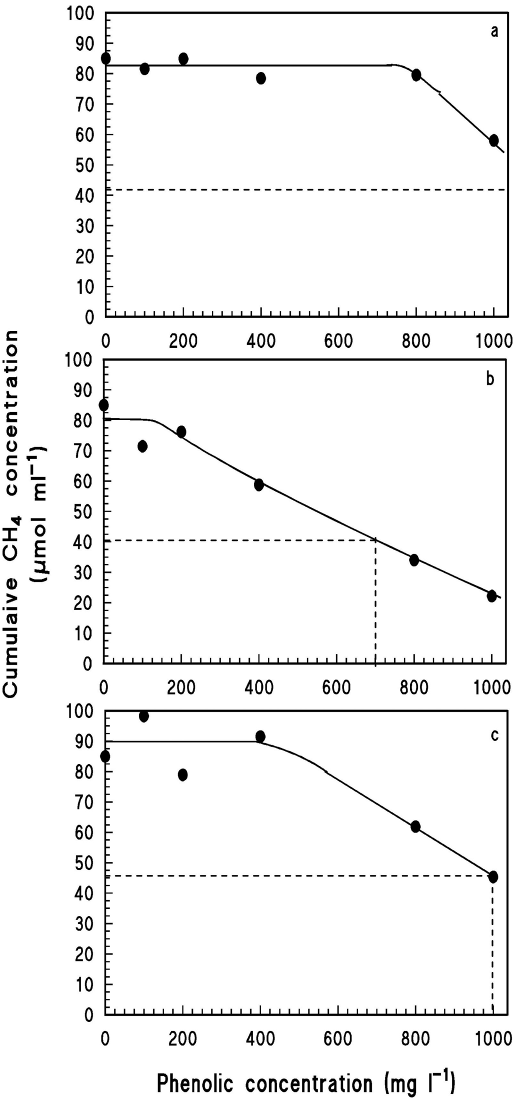

Figure 6. Cumulative methane concentrations (µmol ml^{-1}) in triplicate anaerobic batch cultures supplemented with a range of phenol (a), *o*-cresol (b) or *p*-cresol (c) concentrations.

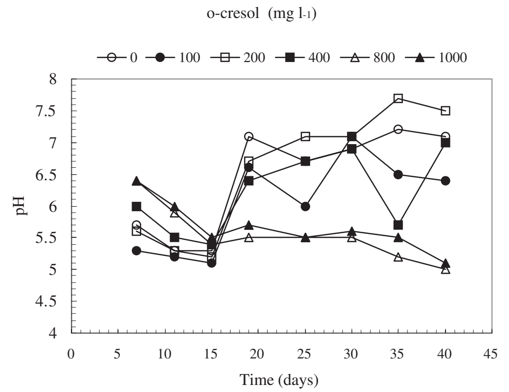

Figure 7. Changes in pH in anaerobic batch cultures supplemented with a range of *o*-cresol concentrations from 0–1000 mg l^{-1}.

methanogens were not inhibited at 6 mM (648 mg l^{-1}) although methanogenesis was completely inhibited at 20 mM (2160 mg l^{-1}). The IC_{50} value was not identified. Kennes *et al.* (1997) reported progressive inhibition of sludge-inoculated (from a fish cannery wastewater treatment plant) anaerobic batch cultures at *p*-cresol concentrations $\geq$200 mg l^{-1}.

pH analyses (Figure 7) suggested that inhibition largely focused on the methanogens, since, in bottles supplemented with *o*-cresol at concentrations $\geq$800 mg l^{-1}, pH values were $\leq$5.1 by Day 39, while in those supplemented with concentrations $\leq$400 mg l^{-1}, final pH values ranged from 6.4–7.5. VFA analyses confirmed the accumulation of intermediate acids, but indicated, however, that there was selective inhibitory action of the cresols on VFA turnover. When, for example, the VFA analyses of phenol-supplemented and *o*-cresol supplemented bottles were compared, it was clear that while analyses of the key intermediates (acetate, butyrate and propionate) on Day 11 were similar, by Day 40 there were significant differences between the bottles (Table 2). In bottles supplemented with *o*-cresol concentrations $\geq$400 mg l^{-1}, butyrate accumulated, although net propionate concentrations were lower, possibly reflecting inhibition of decarboxylation of butyrate to propionate (Gourdon *et al.* 1988).

Propionate concentrations were higher in cultures supplemented with phenol concentrations $\geq$800 mg l^{-1}. A similar accumulation was noted by Pullammanappallil et al (2001), who reported that in an anaerobic digester, which was deliberately inhibited by the addition of phenol, propionate accumulated. This was attributed to the metabolism of phenol, and the authors suggested that propionic acid may be an effect rather than a cause of inhibition of the anaerobic digestion process, as is generally assumed. Nevertheless, in the present study, net accumulation of VFAs was recorded in even the most methanogenically inhibited bottles, suggesting that methanogenesis was more inhibited that acidogenesis.

Table 2. Volatile fatty acid analyses of bottles supplemented with either phenol or o-cresol.

	VFA concentration (mg l-1)					
	Acetate		Propionate		Butyrate	
	Day 11	Day 40	Day 11	Day 40	Day 11	Day 40
Control	1782	bd	296	669	748	bd
Pentanol						
100	1632	120	474	747	985	84
200	Bda	66	925	1065	1830	bd
400	1758	90	703	1147	1152	bd
800	2184	78	518	1302	1941	bd
1000	1692	78	696	1532	1127	863
o-cresol						
100	1620	bd	311	2094	739	bd
200	2058	72	688	1665	1109	bd
400	1470	492	488	1672	809	1029
800	1488	78	392	400	1091	660
1000	1128	78	562	200	1065	308

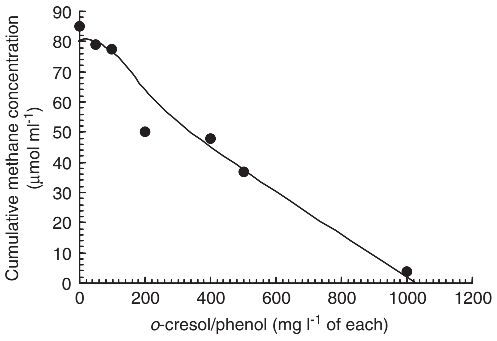

Figure 8. Cumulative methane concentrations (µ mol ml^{-1}) in triplicate anaerobic batch cultures.

Each 2-component mixture of the phenolic compounds comprised equal concentrations of the two compounds. The IC_{50} values for cultures supplemented with phenol/*o*-cresol, phenol/*p*-cresol and *o*-cresol/*p*-cresol were 460, 825 and 630 mg l^{-1}, respectively (Figures 8, 9 and 10).

From the values of the IC_{50} values of the individual compounds, where the order of inhibition was *o*-cresol > *p*-cresol > phenol, the *o*-cresol/*p*-cresol mixture might have been expected to be the most inhibitory. However, it was clear that the inhibitory effects were not simply additive.

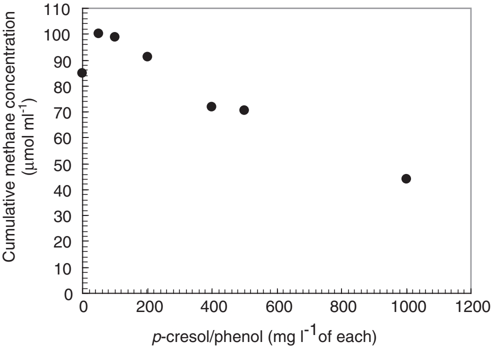

Figure 9. Cumulative methane concentrations (µ mol ml^{-1}) in triplicate anaerobic batch cultures supplemented with a mixture of *p*-cresol and phenol concentrations.

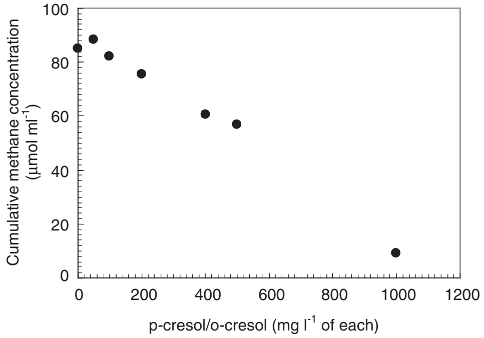

Figure 10. Cumulative methane concentrations (µmol ml^{-1}) in triplicate anaerobic batch cultures supplemented with a mixture of *p*-cresol and *o*-cresol concentrations.

In mixtures in which the concentrations of phenol were below levels that would not be inhibitory when added alone, inhibition was greater than would be expected from the other component. For example, in cultures challenged with 400 mg l^{-1} of either phenol or *o*-cresol, methane production was inhibited by 0 and 25%, respectively (Figure 6). However, in cultures challenged with 400 mg l^{-1} of each of phenol and *o*-cresol, cumulative methane production was reduced by 43.8%.

Conversely, at 1000 mg l^{-1}, at which both *o*-cresol and *p*-cresol were $\geq$50% inhibitory, the mixture of compounds was less than 100% inhibitory. A similar pattern was recorded with mixtures of phenol/*p*-cresol and *o*-cresol/phenol. The reasons for this were not clear, although since phenol exerts its toxic effects at the cell membrane by uncoupling of oxidative phosphorylation (Escher *et al.* 1999) it is possible that a combination of adsorption of phenolics to MSW surfaces, protection of the microbes attached to surfaces and saturation of cellular uptake sites was implicated.

In practical terms, the effects of mixtures of low concentrations of phenolics are likely to be of more importance, since even in grossly contaminated groundwater systems, only limited volumes of the plume are likely to contain concentrations in excess of 1000 mg l^{-1} (Williams *et al.* 2001). Moreover, the differing toxicities of individual phenolic compounds are likely to complicate the prediction of the effects of mixtures. It was clear from this study that concentrations of phenol below the toxicity threshold could contribute to the overall toxicity of a mixture of compounds. Simple analyses of groundwater or leachate composition may not be sufficient basis for the prediction of toxicity.

ACKNOWLEDGEMENT

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Presence of EDCs (Endocrine Disrupting Compounds) in landfill leachate and municipal wastewaters

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ABSTRACT: During the last decade, concerns regarding the occurrence of endocrine disrupting compounds (EDCs) in the environment have rapidly increased worldwide. Main EDCs are commonly used industrial chemicals, pesticides and pharmaceuticals. Another important source of EDCs consists in industrial processes by-products. Municipal/industrial solid waste disposal leads to the presence of significant quantities of EDCs in landfills, hence leachate can be enriched of them. Wastewater treatment plants effluents are also considered to be a significant source of EDCs. In the paper, literature data concerning the occurrence of main EDCs in landfill leachate and sewage are reported. Mechanisms of removal in conventional biological plants and the role of chemical oxidation in enhancing the overall removal of EDCs are also briefly discussed.

Keywords: Chemical oxidation, EDCs, landfill leachate, municipal sewage, treatment plants.

1 INTRODUCTION

During the last decade, concerns regarding the occurrence of endocrine disrupting compounds (EDCs) in the environment have rapidly increased worldwide. EDCs include a heterogeneous group of substances, which in general interfere with endocrine system directly or indirectly by means of an agonistic or antiagonistic action (Fent, 2001; Wright and Welbourn, 2002). EDCs are suspected to impair the function of hormones in the human body, even at trace level. In literature it has been reported that chronic exposure to such compounds can cause unpredicted and unknown effects (among the dozens of works, see Wright and Welbourn, 2002; Lintelmann et al., 2003; Lee et al., 2004).

Main EDCs are commonly used industrial chemicals, such as synthetic detergents, flame retardants, additives for plastics and paints (alkyl phenol etxhoxylates, polybrominated biphenyl ethers, polychlorinated biphenyls, phthalates, organotin compounds), pharmaceuticals and pesticides (natural and synthetic steroids, organochlorinated insecticides, triazines). Another important source of EDCs consists in industrial processes by-products, such as polynuclear aromatic hydrocarbons, polychlorinated dioxins and furans.

Municipal/industrial solid waste disposal leads to the presence of significant quantities of EDCs in landfills, hence leachate can be enriched of them. Literature reports several cases of EDCs occurrence in landfill leachates and in effluent from leachate treatment facilities. Hence, the presence of EDCs in leachate should be taken into serious account, since their environmental fate is still not clear. In many Countries (as in Italy) it is allowed to dispose leachate in municipal wastewater treatment plants: efforts are now underway to study proper removal processes.

Municipal sewage and municipal wastewater treatment effluents are considered to be a major source of pollution, as well, due to the documented presence of such compounds also at relevant concentrations.

This paper discusses literature data about EDCs occurrence in landfill leachate and in municipal sewage. Their fate in a wastewater treatment plant and, more generally, in the environment (based on chemical, physical and toxicological characteristics) is also discussed, as well as the role of chemical oxidation in combined biological-chemical processes.

2 PARAMETERS AFFECTING EDCs BEHAVIOUR

Before presenting results of a literature survey on EDCs in landfill leachate and municipal wastewater, it is important to point out some relevant chemical-physical and toxicological properties affecting their behaviour in the environment (USEPA (a) and (b), Wright and Welbourn, 2002; Schwarzenbach et al., 2003):

- Henry's Law Constant (H): an estimate of the extent of chemical partitioning between air and water at equilibrium. A larger value indicates that the chemical is more likely to volatilise.

- water solubility (γ_{sat}): the maximal concentration of a substance solved in pure water at a given temperature.
- *n*-octanol/water partition coefficient (K_{ow}): the distribution of a given substance between *n*-octanol and water at equilibrium. Octanol serves as a model for the lipid part of animal tissue (namely fish). Generally, the K_{ow} is a good indicator of the tendency of a substance to move from water to lipid, thus its tendency to move from the aqueous environment into biological membranes.
- Organic carbon partition coefficient (K_{oc}): an estimate of the extent of chemical partitioning between organic carbon and water at equilibrium. A larger value indicates that the chemical is more likely to remain bound to soil or sediment. This parameter is useful for the description of the adsorption of a chemical substance to suspended matter in surface water. The K_{oc} value increases with increasing hydrophobicity of a compound, i.e., the higher K_{oc}, the stronger is the adsorption to suspended matter or water. K_{oc} correlates with the octanol/water partition coefficient K_{ow}. The partition coefficient can be therefore a good descriptor of the bioconcentration.
- Bioaccumulation factor (BF): the ratio of the concentration of a given compound or element in an organism (in this case, the tissue of fish) to its concentration in the immediate environment, measured in the field and thus incorporating food chain as well as direct sources.
- No-Observed-Adverse-Effect Level (NOAEL): the highest exposure level at which there are no biologically significant increases in the frequency or severity of adverse effect between the exposed population and its appropriate control; some effects may be produced at this level, but they are not considered adverse or precursors of adverse effects.
- No-Observed-Effect Level (NOEL): an exposure level at which there are no statistically or biologically significant increases in the frequency or severity of any effect between the exposed population and its appropriate control.
- Lowest-Observed-Adverse-Effect Level (LOAEL): the lowest exposure level at which there are biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group.
- Lowest-Observed Effect Level (LOEL or LEL): in a study, the lowest dose or exposure level at which a statistically or biologically significant effect is observed in the exposed population compared with an appropriate unexposed control group.
- Reference Dose for Chronic Oral Exposure (RfD): an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from a NOAEL, LOAEL, or benchmark dose, with uncertainty factors generally applied to reflect limitations of the data used. Generally used in EPA's noncancer health assessments.
- Drinking Water Unit Risk: the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 μg/L in water. The interpretation of unit risk would be as follows: if unit risk $= 1.5 \times 10^{-6}$ μg/L, 1.5 excess tumors are expected to develop per 1,000,000 people if exposed daily for a lifetime to 1 μg of the chemical in 1 liter of drinking water.

Based on chemical, physical and toxicological characteristics, the fate of EDCs in a wastewater treatment plant and, more generally, in the environment, can be predicted.

Table 1 shows some important properties of main organic EDCs found in leachates. Substances with evidence or evidence of potential endocrine disruption (accordingly with DL n. 3883, 1999; European Commission, 1999; European Commission, 2001) are listed. Pharmaceuticals, estrogens, phytoextrogens and personal care products (e.g. parabens and their esthers) are omitted, because literature data concerning leachate are insufficient, although their ubiquitous presence in the environment and their fate and behaviour (in most cases leading to toxic effects) are widely documented. Several metals are suspected to behave as endocrine disruptors as well: based on environmental and toxicological studies, aluminium, cadmium, mercury and lead can be cited (European Commission DG ENV, 2000).

Very low Henry's Law constants indicate the scarce tendency to volatilise of these compounds, hence their persistence in the hydrosphere and geosphere, as a consequence of their specific application field. On the contrary, HCHs and HCs are appreciably volatile.

As expected, compounds scarcely soluble in water (low γ_{sat} values) show a relevant affinity with *n*-octanol (high log K_{ow} values).

Most of listed compounds are characterised by log K_{ow} values in the range 3–7: they are extremely dangerous for fish and mammals, since they are significantly hydrophobic (they can accumulate in fat tissues) but, at the same time, the extent of their hydrophobicity does not prevent their transfer into aqueous media (e.g. blood) thus their mobility within an organism. Moreover, by comparing log K_{ow} and BF values, it appears a direct proportionality: the former, in fact, is an estimation of the tendency of a substance to move from water to lipid, and the latter is an experimental measure of the same phenomenon for a group of organisms (it has to be noted that *n*-octanol is used as

Table 1. Chemical, physical and toxicological characteristics of main organic EDCs found in landfill leachate.

Group	Substance	Henry's Law constant° unitless	γ^{*}_{sat} μg L^{-1}	log K°_{ow} unitless	K°_{oc} Lkg^{-1}	BF° Lkg^{-1}	$RfD^{\#}$ $mgkg^{-1}d^{-1}$	Drinking water unit $risk^{\#}$ per μgL^{-1}
Biphenyls	PCBs	$<3.0 * 10^{-2@}$	277°	6.29	$4.5 * 10^{4}$	$5.8 * 10^{4}$	–	$1 * 10^{-5}$
	PBDEs	$<8.5 * 10^{-3\c{c}}$	<130	>5.74	–	–	–	–
PCDD	2,3,7,8- TCDD	$2.0 * 10^{-3}$	0.0013	6.80	$1.5 * 10^{5}$	$3.4 * 10^{4}$	–	–
PCDF	2,3,7,8-TCDF	$6.3 * 10^{-4}$	0.42	6.53	$8.1 * 10^{4}$	$2.1 * 10^{4}$	–	–
Pesticides	Aldrin	$1.8 * 10^{-3}$	17°	6.5	$1.1 * 10^{5}$	$2.0 * 10^{4}$	$3.0 * 10^{-5}$	$4.9 * 10^{-4}$
	Atrazine	$9.7 * 10^{-8}$	$138000^{\wedge}$	2.61	$2.3 * 10^{2}$	$9.8 * 10^{0}$	$3.5 * 10^{-2}$	–
	Benthiocarb	$1.1 * 10^{-5}$	28000°	3.4	$2.7 * 10^{3}$	$8.3 * 10^{1}$	$1.0 * 10^{-2}$	–
	p,p′-DDT	$3.4 * 10^{-4}$	3.4	6.91	$2.2 * 10^{5}$	$4.2 * 10^{4}$	$5.0 * 10^{-4}$	$9.7 * 10^{-6}$
	p,p′-DDD	$2.7 * 10^{-4}$	90	6.02	$1.5 * 10^{5}$	$8.6 * 10^{3}$	–	$6.9 * 10^{-6}$
	p,p′-DDE	$1.7 * 10^{-3}$	24	6.51	$1.5 * 10^{5}$	$2.1 * 10^{4}$	–	$9.7 * 10^{-6}$
	2,4-D (2,4-Dichlorophenoxyacetic acid)	$1.5 * 10^{-6}$	677000°	2.81	$2.9 * 10^{1}$	$3.2 * 10^{0}$	$1.0 * 10^{-2}$	–
	Dieldrin	$4.1 * 10^{-4}$	250°	5.2	$1.1 * 10^{4}$	$2.0 * 10^{3}$	$5.0 * 10^{-5}$	$4.6 * 10^{-4}$
	Endosulfan (α/β)	$2.7 * 10^{-3}$	450°	3.83	$2.2 * 10^{4}$	$1.8 * 10^{2}$	$6.0 * 10^{-3}$	–
	Endrin	$2.6 * 10^{-4}$	250°	5.2	$1.1 * 10^{4}$	$2.0 * 10^{3}$	$3.0 * 10^{-4}$	–
	γ-Hexachlorocyclohexane	$2.1 * 10^{-4}$	$25000^{\wedge}$	4.14	$3.4 * 10^{3}$	$3.1 * 10^{2}$	$3.0 * 10^{-4}$	–
	Malathion	$2.0 * 10^{-7}$	143000°	2.36	$3.1 * 10^{1}$	$1.3 * 10^{1}$	$2.0 * 10^{-2}$	–
	Methyl parathion	$4.1 * 10^{-6}$	$100000^{\wedge}$	2.86	$5.2 * 10^{2}$	$3.2 * 10^{1}$	$2.5 * 10^{-4}$	–
	Propoxur	$5.9 * 10^{-8}$	1860000°	1.52	$4.4 * 10^{1}$	$3.0 * 10^{0}$	$4.0 * 10^{-3}$	–
	Simazine	$3.9 * 10^{-8}$	$28000^{\wedge}$	2.18	$1.5 * 10^{2}$	$4.6 * 10^{0}$	$5.0 * 10^{-3}$	–
	Triadimefon	$3.3 * 10^{-9}$	71500°	2.77	$5.2 * 10^{3}$	$2.7 * 10^{1}$	$3.0 * 10^{-2}$	–
	Trifluralin	$4.2 * 10^{-3}$	184°	5.34	$9.7 * 10^{3}$	$2.6 * 10^{3}$	$7.5 * 10^{-3}$	$2.2 * 10^{-7}$
	2,4,5-(Trichlorophenoxyacetic Acid)	$1.9 * 10^{-6}$	278000°	3.31	$4.9 * 10^{1}$	$3.2 * 10^{1}$	$1.0 * 10^{-2}$	–
PAHs	Fluoranthene	$3.6 * 10^{-4}$	220	5.16	$7.09 * 10^{4}$	$1.9 * 10^{3}$	$4 * 10^{-2}$	–
APEs	Ethoxy nonylphenol	–	3020	4.17^{*}	–	–	–	
	Nonylphenol	$1.0 * 10^{-7@}$	$6350^{\S}$	$5.76^{\S}$	$6.1 * 10^{4\S}$	–	–	–
	Nonylphenol ethoxycarboxylate	–	–	–	–	–	–	–
	4-ter-octylphenol	–	12600	4.12^{*}	–	–	–	–
Phthalates	Butylbenzylphthalate	$5.2 * 10^{-5}$	$8300^{\wedge}$	4.73	$9.36 * 10^{3}$	$8.8 * 10^{2}$	$2 * 10^{-1}$	–
	Di-n-butylphthalate	$7.4 * 10^{-5}$	$43650^{\wedge}$	4.45	$1.46 * 10^{3}$	$5.8 * 10^{2}$	$1 * 10^{-1}$	–
	Di(2-ethylhexyl) phthalate	$1.1 * 10^{-5}$	$270^{\S}$	$7.6^{\S}$	$1.65 * 10^{5}$	$3.1 * 10^{2}$	$2 * 10^{-2}$	$4 * 10^{-7}$
	Di-ethylphthalate	$2.5 * 10^{-5}$	$1080000^{\S}$	2.42	$1.26 * 10^{2}$	$1.5 * 10^{1}$	$8 * 10^{-1}$	–
Organotins	Tributyltin	–	$748^{\S}$	$4.76^{\S}$	$1.50 * 10^{4\S}$	–	–	–
Phenols	Bisphenol A	$3.7 * 10^{-10}$	120000	3.32	$7.52 * 10^{4}$	$7.2 * 10^{1}$	$5 * 10^{-2}$	–
	4-tert-butylphenol	–	$7.8 * 10^{6\wedge}$	$3.14^{\wedge}$	–	–	–	–
	2,4-dichlorophenol	$9.0 * 10^{-5}$	4500000°	3.06	$7.2 * 10^{2}$	$1.8 * 10^{1}$	$3.0 * 10^{-3}$	–
	Ethylphenol	–	$6.6 * 10^{7\wedge}$	$2.50^{\wedge}$	–	–	–	–
	Pentachlorophenol	$1.0 * 10^{-6}$	$70800^{\wedge}$	5.12	$3.38 * 10^{3}$	$7.0 * 10^{2}$	$3 * 10^{-2}$	$3 * 10^{-6}$
HCs and CHCs	Hexachlorobenzene	$7.0 * 10^{-2}$	$28^{\wedge}$	5.73	$3.4 * 10^{3}$	$5.2 * 10^{3}$	$8.0 * 10^{-4}$	$4.6 * 10^{-5}$
	Styrene	$1.1 * 10^{-1}$	310000°	2.95	$5.2 * 10^{2}$	$3.7 * 10^{1}$	$2.0 * 10^{-1}$	–
	Tetrachloroethylene	$7.2 * 10^{-1}$	206000°	3.4	$1.1 * 10^{2}$	$8.3 * 10^{1}$	$1.0 * 10^{-2}$	–
	1,2,4-Trichlorobenzene	$5.8 * 10^{-2}$	$166000^{\wedge}$	4.02	$7.18 * 10^{2}$	$2.5 * 10^{2}$	$1 * 10^{-2}$	–
	1,1,1-Trichloroethane	$7.0 * 10^{-1}$	$9.8 * 10^{6\wedge}$	2.49	$4.86 * 10$	$1.6 * 10$	–	–

a model substance for fish fat tissues). High values of both parameters contribute to biomagnification, that is the increase in concentration at successive trophic levels in a food chain.

Values of K_{oc} are in agreement with $\log K_{ow}$ and γ_{sat}, since all of them deals with lipophylicity.

As far as drinking water unit risk is concerned, only a few values are available, most of which, referring to pesticides: their high toxicity can be clearly explained with their low specificity. Moreover, the higher the drinking water unit risk, the lower the RfD value. It is worth to be noted that phthalates are characterised by high RfD values despite their recognized endocrine effect. Anyway, it should be remembered that experimental doses are obtained based on laboratory tests carried out on different *taxa*, thus affecting their direct transferability to human beings.

3 EDCs IN LANDFILL LEACHATE AND MUNICIPAL WASTEWATER: A LITERATURE REVIEW

3.1 *Alkylphenol ethoxylates (APEOs)*

These compounds are mainly used as non-ionic surfactants and can occur also in laundry detergents and personal care products. Water solubility increases with increasing number of ethoxy groups. Toxicity in aquatic environment is higher with lower number of ethoxy groups and with greater length of the hydrophobic chain: thus, derivatives are more toxic than original compounds (ethoxylated). Biodegradation of APEs (in the environment or in WWTPs) leads to compounds with estrogenic activity and a tendency toward bioaccumulation. Alkylphenols only exhibit estrogenic activity if the alkyl chain is in the *para* position; moreover, alkylphenols with alkyl chains having less than four C-atoms are inactive (Lintelmann et al., 2003).

Leachate. Nonylphenol was detected in landfill leachate at a concentration of 2.8 µg/L by Behnisch et al. (2001) and octylphenol was detected in appreciable concentrations by Shiraishi et al. (1999).

Wastewater. Nonylphenol was detected in wastewater at a concentration of 57.64 µg/L (Planas et al., 2002), 1.4 µg/L (Fuerhacker et al., 2001), 32–122.3 ng/L (Jiang et al., 2005), 2.75–10.2 µg/L (Fauser et al., 2003), 0.32–25.0 µg/L (Lee et al., 2005), <240–19000 ng/L (Vethaak et al., 2005), 2.82–5.95 µg/L (Palmquist and Hanæus, 2005, in grey water), 2.30–5.23 µg/L (Palmquist and Hanæus, 2005, in black water). The amount of 4-*t*-octylphenol was assessed to be 167–301 ng/L (Espejo et al., 2002), 0.88 µg/L (Auriol et al., 2005), 85–611.1 ng/L (Jiang et al., 2005), 0.01–3.56 µg/L (Lee et al., 2005), <270–13000 ng/L (Vethaak et al., 2005), 0.08–0.16 µg/L (Palmquist and Hanæus, 2005, in grey water), 0.09–0.28 µg/L (Palmquist and Hanæus, 2005, in black water). Espejo et al. (2002) also reported values for NP_{1-18} from 1010 to 6790 ng/L. As far as ethoxylated compounds are concerned, Planas et al. (2002) determined C_6-NP1EO (42.70 µg/L), C_6-NP2EO (39.69 µg/L) and NPnEO, where $n = 0$–2 (140.03 µg/L). Fytianos et al. (1997) and Vethaak et al. (2005) measured concentrations of NPnEO ranging from 1180 to 1620 µg/L, and, <820–125000 ng/L. Palmquist and Hanæus (2005) determined the concentration of each ethoxy nonylphenol (up to 9 ethoxy units) and octylphenol (up to eight ethoxy unit), both in grey and black water: highest values were reached, as expected, in grey water, with the range 2.75–61.4 µg/L for NPnEO and 0.08–4.74µg/L for OPnEO. Non-ionic surfactants were expressed as BiAS by Fuerhacker et al. (2001) who found the range 770–2210 µg/L.

3.2 *Phenols*

Phenols (substituted and chlorinated) are employed as preservatives, antioxidant additives, oils, plastic materials. Bisphenol A is one of the most widespread chemical substances and an EDC of particular concern. Due to significant water solubility, low Henry's Law constant and appreciable K_{oc} and $\log K_{ow}$ values, BPA is mainly transported by water in the environment, is persistent and is adsorbed by organic matter. It can be degraded by acclimatised microorganisms (Lintelmann et al., 2003). Due to its relatively low hydrophobicity, BPA tends to elute easily from plastics and rapidly move into the aqueous environment. Several Authors studied the occurrence and analytical methods for improving the detection of BPA, but clear concentrations values are scarcely reported.

Leachate. Asakura et al. (2004) postulated that, due to its relatively low hydrophobicity, BPA tends to elute easily from plastics and rapidly move into the leachate: this would explain the observed decrease of the concentration in the leachate with passing years. Furthermore, Urase and Miyashita (2003) showed that, in leachates, BPA is mainly in the dissolved form rather than bound to macro-molecular organic substances.

BPA was detected by Yamamoto et al. (2001) in leachate from 7 hazardous waste landfills in concentrations ranging from 1.3 up to 17200 µg/L. Plastic wastes have been considered as the main responsible for the presence of this compound in leachate. Behnisch et al. (2001) also detected BPA, but at much lower content (0.13 µg/L). Concentrations ranging from 0.07 to 228 µg/L where found by Asakura et al. (2004) in two MSW landfill sites in Japan. Paxéus (2000) reported a concentration range between 4 to 136 µg/L. As pointed out by Urase and Miyashita (2003), factors affecting the amount of BPA in landfill leachates are still unclear (plastic wastes and high-pH environment should favour the presence of

BPA in leachates, while biodegradation is also effective, in particular in organic-rich sites, where the concentration of BPA could decrease with time.

As far as other phenolic compounds are concerned, Paxéus (2000) measured concentrations of ethylphenol and pentachlorophenol equal to, respectively, 0.1–67 μg/L, 0.1–0.2 μg/L.

Wastewater. Lee et al. (2005) detected 0.02–2.40 μg/L while Jiang et al. (2005) 378–890 ng/L and Vethaak et al. (2005) 250–5620 ng/L.

3.3 *Organotins(OTs)*

Organotins are widely employed as heat and light stabilisers in PVC (MBT, DBT), molluscicides, agricultural pesticides (TPhT) and antifouling agents on ships (TBT). They are highly bioaccumulable and adsorbable onto particulate matter; they readily bind to sediments, sludge and soils and are slowly biodegradable (being biocides, they exhibit toxicity).

Leachate. Waara et al. (2003) report concentrations of tenths of ng/L of OTs (among which monobutyltin, dibutyltin, tributyltin) in landfill leachate.

Wastewater. Voulvoulis et al. (2004) detemined the concentration of TBT (expressed as 0.006–14.439 mg/L of Sn), DBT (expressed as 0.015–0.337 mg/L of Sn), MBT (expressed as 0.019–14.921 mg/L of Sn) and MPhT (expressed as 0.009–3.517 mg/L of Sn) in sewage. Palmquist and Hanæus (2005) surveyed OTs in municipal sewage, finding 252–3000 ng/L of DBT, 20–21 ng/L of DOT, 431–990 ng/L of MBT, 29–100 ng/L of MOT, 209–287 ng/L of TBT in grey water and 21.1–96.2 ng/L of DBT, 16.4–35.5 ng/L of MBT, up to 8.4 ng/L of MOT and up to 3.8 ng/L of TBT in black water.

3.4 *Biphenyls (PCBs and PBDEs)*

The hydrophobic PCBs are classified as Persistent Organic Pollutants (POPs). The higher the degree of chlorination, the higher hydrophobicity and sorption tendency, while the lower the biodegradability and water solubility. They tend to undergo to bioaccumulation and biomagnification. PBDEs constitute one class of brominated flame-retardants that have been synthesised globally for the past 30 years. They are used in a variety of consumer products such as electrical appliances, building materials, and textiles in order to retard their combustion. Recently they have gained increased attention as "Emergent Chemicals" because of their persistence in the environment, potential bioaccumulation, due to high lipophilicity and resistance to degradative processes, and potential toxicity.

Leachate. PCBs were detected by Yoshikawa et al. (1999) and by Behnisch et al. (2001) in some landfills in Japan, in concentrations varying from less than 1 pg/L up to 46 ng/L. The presence of PCBs in leachate was attributed to incineration ash disposed in the landfills. A correlation between the presence of PCBs and dioxins in the leachate has been also pointed out by Yoshikawa et al. (1999). Relatively low levels of chlorinated organic compounds (in comparison with other EDCs) may be attributed, at least partially, to the reductive dechlorination of hazardous compounds during the acid formation and methanogenic phases within the landfill (Reinhart and Pohland, 1991).

Presence in landfill leachate of PBDEs is reported by Waara et al. (2003) in concentrations of 2.6–4.3 ng/L.

Wastewater. In general, PCBs in WWTPs are thought to derive from leachate inflow. Anyway, Palmquist and Hanæus (2005) found tetra BDE (0.066–0.24 μg/L), penta BDE (0.170–0.76 μg/L) penta BDE 99 (0.120–0.64 μg/L) in grey water and BDE (0.034–0.053 μg/L), penta BDE (0.086–0.12 μg/L) penta BDE 99 (0.059–0.095 μg/L) in black water. Similar considerations can be drawn for polichlorinated dibenzo-dioxins (PCDD) and –furans (PCDF).

3.5 *Phthalates*

Phtalates are ubiquitous because of their massive use: they are commonly employed to provide flexibility to rigid polymers. They are also used in paper and paperboard manufacturing as defoaming agents, in capacitors as dielectrics, as food preservatives, in detergents, as insect repellents, etc.. A tendency to persist in the environment and bioaccumulate in organisms is the main contributory factor to their priority status. Phtalic acid esters are almost insoluble in water, nevertheless, they can be solubilized by interaction with fulvic and humid acids.

Leachate. Among plasticisers found in leachate, phtalates are the most common. Several Authors reported their occurrence in landfill leachates (*inter alia*: Yamamoto et al., 2001; Jonsson et al., 2003; Marttinen et al., 2003). Phtalic compounds were recovered in leachate of Swedish landfills by Öman (1999) at concentrations varying from 1 to 31 μg/L. Higher concentrations were detected for di-(2-ethylhexyl)phthalate (DEHP). Asakura et al. (2004) also found that DEHP was the most occurrent among the monitored phtalates in two MSW landfills in Japan, its concentration ranging from 9.6 to 49 μg/L; butylbenzylphthalate (BBP), di-n-butylphthalate (DBP) and di-ethylphthalate (DEP) were detected at concentrations ranging from 0.7 to 7.8 μg/L, 3 to 15 μg/L and 1 to 8.4 μg/L, respectively. Paxéus (2000) reported the following concentrations for DEHP, BBP, DBP and DEP, respectively: 97–346 μg/L, 1–2 μg/L, 2 μg/L, 4 μg/L. Concentrations detected by Baun et al. (2004) are the following: BBP 2 μg/L, DEHP 1–3 μg/L, DEP, 60 μg/L. DEHP and DEP are the substances most commonly linked to MSW.

Wastewater. Several Authors reported phthalates occurrence in sewage: *inter alia*, Fauser et al. (2003) measured the following types of phthalates: DEHP (5.85–44.3 μg/L), DPP (up to 0.14 μg/L), DBP (up to 0.28 μg/L), BBP (0.05–0.53 μg/L); Vethaak et al. (2005) found 390–6200 ng/L of DMP, 41–44 μg/L of DEP, <380–51000 ng/L of DBP, 1–6700 ng/L of DPP, 560–4900 ng/L of BBP, <13–100 μg/L of DEHP. López-Jiménez et al. (2005) analysed DBP, BBP and DEHP, finding 6.6–62 μg/L, 0.5–1.2 μg/L and 1.1–2.9 μg/L, respectively; Palmquist and Hanæus (2005) made a monitoring of grey and black water, obtaining the following results: up to 9.0 μg/L of BBP, 8.4–160 μg/L of DEHP, 1.8–9.4 μg/L of DBP and 4.2–38 μg/L of DEP in grey water. In black water the concentrations were remarkably lower (a few μg/L).

3.6 *Other compounds of major concern in landfill leachate*

PCDD/PCDF. Polichlorinated dibenzo-dioxins (PCDD) and –furans (PCDF) are enclosed in the POP list. The number of chlorine atoms affects vapour pressure and water solubility (inversely correlated with the number of chlorine atoms). PCDD/F accumulate in aquatic organisms and in food chain, because of their affinity for lipids and resistance to biodegradation.

PCDD and PCDF were detected by Behnisch et al. (2001) at concentrations of 21 and 8.7 pg/L, respectively, in the leachate of a landfill containing residues from incineration (about 20% of total wastes being constituted by flying ashes). Yoshikawa et al. (1999) also found similar concentrations (up to 16 pg TEQ/L) of PCDD/F in leachate from 13 landfills in Japan: higher amounts were detected in landfills where incineration ashes were disposed of. Other Authors found much higher (of even more than one order of magnitude) concentrations of dioxin TEQ (Shiraishi et al., 1999). It was observed that relevant concentrations were detected for younger landfills. Furthermore, dioxins are mainly present in the particulate (even more than 90% with respect to the total amount measured), due to the scarce water solubility of these compounds.

Pesticides. Insecticides and herbicides are frequently recorded in MSW landfill leachate (*inter alia*: Christensen et al., 2001; Kjeldsen et al., 2002; Waara et al., 2003; Slack et al., 2005). Most of them are persistent in anaerobic landfill conditions. Among pesticides exerting endocrine disrupting effects, Baun et al. (2004) detected atrazine (0.16 μg/L), simazine (2.3 μg/L) and propoxur (2.6 μg/L); benthiocarb was found by Yasuhara et al. (1997), atrazine and simazine by Christensen et al. (2001) and Kjeldsen et al. (2002).

Polynuclear Aromatic Hydrocarbons (PAHs). PAHs are very lipophilic: water solubility and thus hydrophilicity diminish with increasing number of aromatic rings. They are classified as POPs. Owing to their high hydrophobicity, PAHs should accumulate in the organism, but as a result of metabolisation and excretion, a biomagnification is not observed. Naphthalene and related compound contamination of leachate is commonly reported (Reinhard et al., 1984; Yasuhara et al., 1997). PAHs were detected by Gade et al. (1996) in the leachate of the Raindorf landfill (Germany) in which hazardous wastes were disposed. Concentrations up to 4 μg/L were recorded in the leachate and concentrations above 1 mg total PAH/kg of dry substance were detected in the disposed wastes. A concentration of 10 μg/L of total PAHs is reported by Waara et al. (2003). Paxéus (2000) found concentrations variable from 1 to 6 μg/L of fluoranthene.

Hydrocarbons (HCs) and Chlorinated Hydrocarbons (CHCs). HCs and HCHs include a huge amount of compounds and, being commonly employed in almost every field of human activity, they (together with degradation products) are widely found in leachate. Types and concentrations differ across leachates, depending on waste composition and landfill age and management processes. Chlorinated aliphatic compounds (e.g. 1,1,1-trichloroethane and tetrachloroethylene) have been found in a large number of Danish landfills (Kjeldsen et al., 2002) in contrast with results of Baun et al. (2004) (5.48 μg/L of 1,1,1-trichloroethane and 2.19 μg/L of tetrachloroethylene), who postulated possible microbial degradation (via dechlorination). Concerning styrene, which can derive from impurities in petroleum based products and wastes, Paxéus (2000) detected concentrations in the range 0.1–11 μg/L, while Baun et al. (2004) from 0.1 to 11 μg/L.

3.7 *Other compounds of major concern in municipal wastewater*

Natural and synthetic hormones. Hormones are highly responsible for estrogenic activity exerted by influents and effluents both in vitro and in vivo conditions. Their fate and behaviour are influenced by chemical structure and physico-chemical properties: for instance, phenolic ring in E1 and E2 can bind to the acceptor sites of the estrogen receptor, resulting in disrupting activity. Humans and animals excrete hormones mainly in a conjugated form; the deconjugation can occur in the environment, leading to a reactivation of these substances or to the transformation into a different estrogen (i.e.: mestranol into EE2).

Plenty of Authors have detected hormones in sewage, WWTP effluent and water bodies: Auriol et al. (2005) report 1.8–115 ng/L for E1, <0.3–30.4 ng/L for E2, <0.25–381.5 ng/L for E3, 3–7.1 for EE2; while

Lee et al. (2004) cite a concentration up to about 140 ng/L for E1 and E2 and up to about 15 ng/L for EE2. Lee et al. (2005) found <0.001–0.054 μg/L of E1 and <0.001–0.022 μg/L of E2, respectively. Johnson et al. (2005) found 16–90 ng/L of E1, and Jiang et al. (2005) detected 57–81 ng/L of E1, 132–224 ng/L of E2, 72.4–123.5 ng/L of EE2 and 36-71.7 ng/L of 16α-hydroxysterone. Vethaak et al. (2005) detected 20–130 ng/L of E1, <0.3–5.9 ng/L of EE2, <0.7–15 ng/L of 17α-estradiol and 17–150 ng/L of 17β-estradiol.

4 POSSIBLE FATE OF EDCs IN WASTEWATER TREATMENT PLANTS AND ROLE OF CHEMICAL OXIDATION

In many Countries landfill leachate is sent to municipal wastewater treatment plants (WWTPs) and, as previously shown, EDCs occurrence in municipal sewage has been widely documented anyhow. In Italy, accordingly with the Legislative Decree 152/99, municipal WWTPs are allowed to receive liquid wastes (that is landfill leachate or in general wastes from industrial activities, driven by truck to the treatment facility) provided that the two following conditions are satisfied: 1. wastes are compatible with the plant and the biological process; 2. plant residual capacity (to be determined on the basis of actual influent loading) is not exceeded. For the assessment of these conditions, a methodological approach, which takes into account several involved technical aspects, has been proposed by Bertanza and Collivignarelli (2004).

The mass balance of a generic organic compound in a WWTP is determined by mineralisation to CO_2 and water, stripping/volatilisation, biosorption onto the sludge or release to receiving waters (in this case, the substance can be either unmodified, or transformed into a more hydrophilic but often still persistent form). An attempt of predicting the extent of occurrence of these phenomena can be based on the knowledge of the chemical-physical characteristics of a substance (e.g. the Henry's Law constant, *n*-octanol/water partition coefficient K_{ow}, the organic carbon partition coefficient K_{oc}). Biodegradability data in real conditions are not easy to be found. In many studies, in fact, the global removal of a substance is reported without the assessment of contribution of various processes (in particular biosorption and biotransformation). Actually, literature data concerning EDCs removal are not easily comparable, due to different treatment conditions adopted, sampling procedures and analytical methods. Besides, mass balance calculations can be affected by variability of wastewater characteristics with time, very low concentration of these compounds, small number of collected data (due to high cost and analytical difficulties) etc.; moreover, biodegradation products must be also taken into account.

Although removal potential of many EDCs by conventional WWTPs is recognised (see for instance the review of the Authors: Bertanza and Pedrazzani, 2006), transformation products and their fate should be carefully considered, for possible impacts on receiving water ecosystems and in case of sludge reuse in agriculture. Actually, in order to reach very low concentrations, in comparison with threshold levels for estrogenic activity, a further treatment is necessary. Even if positive results have been achieved by tertiary chemical oxidation, technical-economic suitability of this process is still to be fully demonstrated, in particular when complete mineralisation or, at least, transformation into innocuous by-products is to be guaranteed (as stated also by Auriol et al., 2005). As a consequence, chemical oxidation (whose advantage with respect to other processes like activated carbon adsorption is indeed its capacity of transforming instead of transferring harmful compounds) may be an interesting and feasible solution in case the aim of removing micropollutants can be coupled to another scope, requiring tertiary treatment (e.g. disinfection, color removal). In particular, since municipal WWTPs are in many cases provided with final disinfection, in our opinion, this stage (whose primary objective is the reduction of microbiological activity) may be optimised in order to control EDCs discharge into the environment. From this standpoint, processes like ozonation and UV (coupled with H_2O_2 dosage) may be taken into consideration.

Preliminary results of experiments carried out by the Authors show, for instance, that the oxidation of the effluent of a full scale WWTP by means of UV/H_2O_2 process leads to the removal of 4- para – nonylphenol, accordingly with a first order kinetic with rate constant variable between 0.05 and 0.20 min^{-1} (depending on tested treatment conditions). This means that, while achieving a very high disinfection efficiency within a few minutes (5 log units for *E. coli* in 1 min) by means of UV irradiation, in order to achieve a significant removal of the target compound (e.g. 90%) a higher retention time (>10 min) and H_2O_2 additional dosage (e.g. 10 mg/L) is required. These data can be a useful starting point for assessing the technical-economic feasibility of this solution. Finally, as stated above, the issue of by-products should be carefully taken into account.

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Management of Pollutant Emission from Landfills and Sludge – Pawłowska & Pawłowski (eds)

Changes in the Polycyclic Aromatic Hydrocarbons (PAHs) content in an urban waste composting process

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ABSTRACT: The ever increasing quantity of urban waste forces society to seek new possibilities and new technologies for transforming wastes into reusable material. Composts made from municipal waste are real sources of biomass, however they often contain many harmful or toxic compounds. In this work variations in the concentration of Polycyclic Aromatic Hydrocarbons (PAHs) during the maturing of compost were analyzed. Urban waste from MUT-DANO technology was investigated in two periods: i) during winter-autumn and ii) late spring-winter periods. High fluctuations of PAH concentrations were observed. Their concentrations ranged from 0.4 to 15.7 mg/kg dw. It was also observed that meteorological conditions during the ripening of compost had a real impact on the concentration of PAHs.

Keywords: Compost, municipal waste, PAHs.

1 INTRODUCTION

Environmental pollution resulting from industry and transport development and other human activities are the most important reasons for interest in contamination of the natural environment. Improved living standards and the development of technology causes a systematic increase in municipal waste production. In parallel, a growing amount of waste is subject to recycling (especially industrial waste) but only about 2% of municipal wastes is being recycled at present. Thus, it is necessary to control the content of inorganic and organic substances in waste and in products made during waste transformation processes, as some of them might be harmful or toxic to both human health and the environment. Especially worthy of note are organic compounds because of the growth in their production and emission and the rapid development of analytical procedures leading to ever lower limits of their detection (Biziuk 1996, Ouyang 2006, Sibielska 2003). This work especially is focused on persistent organic pollutants (POP's) i.e. a group of organic compounds very dangerous for humans and the environment. Such materials are mostly anthropogenic with a strong sorption nature, low solubility in water and long period of decay. Typical for this group of compounds are polycyclic aromatic hydrocarbons (PAHs). Polycyclic aromatic hydrocarbons never exist as single compounds but always in a mixture. The presence of one PAH compound in an environmental sample always indicates the presence of other PAHs compounds (Bojakowska 2003). Polycyclic aromatic hydrocarbons present in the natural environment could originate from natural and anthropogenic sources. The main natural sources are geochemical reactions in degraded biological material – the crude oil or bituminous shale maturation process and natural pyrolysis processes during volcano eruptions, forest fires and production as a result of transformation of humic substances in soil (Amir 2005, Atanassova 2004, Bojakowska 2003, Chen 2004, Lage 2005, Moretto 2005, Nadal 2004, Tang 2006, Thiele 2002, Verdin 2005, Wilcke 1999). The most important anthropogenic sources are combustion of fossil fuels, crude oil and wood processing and also waste utilization (Amir 2005, Atanassova 2004, Bojakowska 2003, Moretto 2005, Nadal 2004, Verdin 2005, Wilcke 1999).

PAHs are lipophilic organic compounds, so plants and animals can easy accumulate them in their tissues. As a result, the concentration in tissues can be much higher than in the local environment (Bojakowska 2003). In Poland investigations focused on PAHs content in composts from urban wastes are rarely reported. In this work we have undertaken an attempt to bridge that gap. And so, in this paper we report on changes in the polycyclic aromatic hydrocarbon content of composts during their maturation as a function of a number of their fundamental chemical characteristics.

2 MATERIALS AND METHODS

This work focuses on compost resulting from the utilization of urban waste. Material used in the studies was produced in a composting factory using the MUT-DANO biological system (available for non-sorted wastes) in Katowice (Poland). The waste originated mainly from large scale urban agglomerations. Sampling was repeated eight times over a 30-day period in two experimental series. The first sample was taken from a container of fresh compost – just after the rotary reactor. Samples were taken from the surface (5 cm) and at depths of 50–70 cm from compost piles located in the open. Samples were collected and transported in dark glass containers. Investigations (Figure 1) were carried out in two series; i) series A covered compost produced in the winter. The last samples of this series were taken from autumn wastes, Series B covered compost samples collected from late spring (May) to early winter (December). For the complete characterisation of compost material, analyses were carried out according to quality standard BN-89/9103-09. The PAH analyses were performed using GC-FID. In each sample sixteen compounds from the PAHs group recommended by the US-EPA were quantified: naphthalene (NAPH), acenaphtylene (ACY), acenaphtene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaANT), chrysene (CHR), benzo(b)fluoranthene (BbFLA), benzo(k)fluoranthene (BkFLA), benzo(a)pyrene (BaPYR), indeno(1,2,3-cd)pyrene (IPYR), dibenzo (a,h)anthracene (DahANT), benzo(g,h,i)perylene (BghiPER).

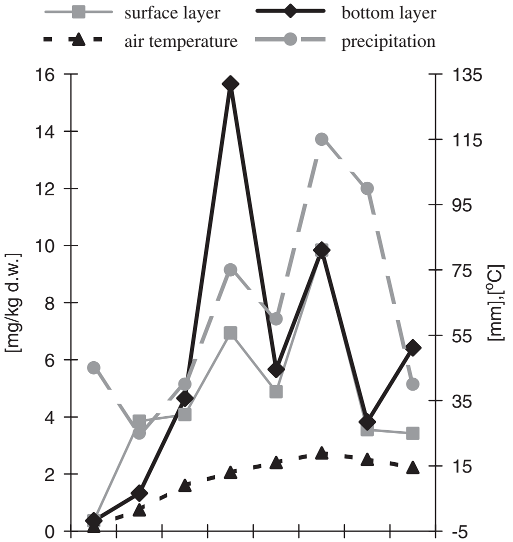

Figure 1. Dependence of changes in the sum of PAH's in series A, on air temperature and precipitation during the period of the experiments.

Fresh samples (10 g) were dried over anhydrous Na_2SO_4 and extracted with hexane (Chempur HPLC-grade) in fexIKA®apparatus for 5 hours. Extracts were evaporated under an inert gas stream and purified on alumina (Aldrich) glass columns. Concentrated eluates were analyzed using GC (Varian series 3800; 30 meters ZB-5 column; injector temperature 250°C; detector 300°C). The initial oven temperature program was 100°C, held for 2 min, and increased to 300°C at a rate of 5°C/min. The final temperature of 300°C was held for 10 min. Carrier gas (He) was set at a constant flow of 1 ml/min. The detection limit was 0.1–0.5 ng per individual compound. Qualified standards (2000 μg/ml of each analyte; LGC Promochem Corporation, Teddington, UK) were used for calibration. A statistical test LSD was used to identify differences in PAHs contents. Correlation coefficients of PAHs content were computed for the linear model $y = ax + b$. Ratios for selected PAHs were calculated according to references: ANT/(ANT+PHE), BaANT/(BaANT+CHR) for the separation of those of petrogenic and pyrogenic origin and FLA/(FLA+PYR), IPYR/(IPYR+BghiPER) for detection of those derived from petrogenic, liquid fuel combustion and solid fuel combustion processes.

3 RESULTS AND DISCUSSION

Analysis of compost basic parameters showed that the content of glass and ceramics (mean content 3.43 and 5.10% for series A and B respectively) and zinc (2223 and 2416 mg/kg dw. for series A and B respectively) could drastically reduce its value as compost (Table 1). The rest of the parameters could qualify this material to first – the best class according to standard BN-89/9103-09.

Samples from series B had a higher content of organic matter, organic carbon and Kjeldahl nitrogen in comparison with series A samples due to start of the vegetation period and plant growth. PAH concentrations in compost samples differed between the surface and deeper layers of the compost pile, as well as between the experimental series. Winter time (series A) samples (processed in February) had low contents of PAHs (0.368 mg/kg dw.). During the ripening of material in the piles, the PAHs content rose to a maximum in the fourth month (May) of the maturation process when it reached 15.66 mg/kg dw. and 6.94 mg/kg dw in the surface and deeper layers, respectively. After six months, the concentrations dropped to 4.88 and 5.66 mg/kg dw. in the surface and bottom layers. In the bottom layer concentrations of PAHs are stable. Over the six month period concentrations rose to 9.83 mg/kg dw. in both layers. If we compare the dynamics of the content of PAHs in the compost pile with atmospheric conditions, a parallel exists between PAHs content and the amount of atmospheric precipitation (Figure. 1). With the rise in the quantity of precipitation, the PAHs content in the investigated material also rose. Comparable results of total PAHs concentration (2.296–17.008 mg/kg dw.) were obtained in an investigation of the products of Upper Silesia compost plants (Wiśniowska 2005).

Table 1. Characteristics of compost samples from A and B* experimental series ($n = 9$).

	Series of samples			
	A		B	
Parameter	Mean	SD	Mean	SD
pH in H_2O	8.0–9.1	–	6.9–8.3	–
Grain size [mm]	<15	–	<15	–
Humidity [%]	34.73 ± 3.8	4.88	36.5±28.3	21.25
Organics [%]	45.60 ± 3.3	4.35	51.8 ± 16.3	12.26
TOC [%]	15.70 ± 1.1	1.39	19.9 ± 2.9	2.18
Kjeldahl N [%]	0.87 ± 0.18	0.23	1.0 ± 0.13	0.10
P_2O_5 [%]	1.20 ± 0.00	0.00	1.1 ± 0.16	0.12
K_2O [%]	0.63 ± 0.03	0.035	0.6 ± 0.03	0.02
Glass [%]	3.43 ± 1.81	2.35	5.1 ± 2.61	1.96
Cd [mg/kg]	3.37 ± 0.97	1.26	3.8 ± 0.69	0.52
Cr [mg/kg]	40.36 ± 14.3	18.61	41.3 ± 2.7	2.00
Cu [mg/kg]	179.5 ± 40.4	52.55	186.5 ± 137.4	103.2
Ni [mg/kg]	39.59 ± 1.8	2.28	23.9 ± 9.0	6.77
Pb [mg/kg]	150.6 ± 24.9	32.45	261.9 ± 84	63.02
Zn [mg/kg]	2416 ± 278	361.2	2223 ± 359	269.9

n – number of samples; *Series A: winter to early autumn; Series B: late spring (May) to early winter.

When little or no precipitation occurred, the PAHs concentration dropped. In the A series a statistically important correlation ($r = 0.85$) between PAHs content in the surface layer of the pile and the quantity of precipitation was observed. Similar correlations between temperature and PAHs content on the surface ($r = 0.81$) and between temperature and PAHs content in bottom layer of the pile ($r = 0.61$) were noted. The main PAHs in this series of samples were: benzo(b)fluoranthene, benzo(k)fluoranthene, and fluoranthene (Table 2). The spring series of compost samples (series B – processed in May) had a low content of PAHs (0.783 mg/kg dw.), similar to series A. However, one month after the piles were formed the PAHs concentration rose drastically (over 10-fold), to 7.98 mg/kg dw. and from that point until the fourth month of maturation (August) the content dropped. The maximum of PAHs content in series B was observed in the sixth month (October) 11.93 mg/kg dw. in the surface layer and 10.05 mg/kg dw. in the bottom layer of the pile (Figure. 2). The main compound in this series of samples was fluoranthene with a mean content of 1.3 mg/kg dw. In series B no clear dependence of PAHs concentration on atmospheric precipitation was observed. The PAHs production is especially clear in oxygen deficient conditions – the PAHs content rises with no offshore source of these pollutants (Thiele 2002), thus it is very important to mix piles to ensure oxygen access. We focused on benzo(a)pyrene as its content in the A series was strongly correlated with

Table 2. Average content of PAHs for A and B series ($n = 32$) [mg/kg dw.].

	A				B			
	Min	Max	Mean	SD	Min	Max	Mean	SD
NAPH	–	0.115	0.039 ± 0.015	0.042	–	0.041	0.010 ± 0.006	0.016
ACY	<0.001	0.031	0.013 ± 0.003	0.008	–	0.026	0.013 ± 0.003	0.008
ACE	0.001	0.163	0.045 ± 0.014	0.039	0.007	0.215	0.071 ± 0.025	0.068
FLU	0.003	0.172	0.050 ± 0.016	0.045	0.007	0.156	0.075 ± 0.016	0.043
PHE	0.010	1.680	0.380 ± 0.147	0.408	0.025	1.423	0.512 ± 0.133	0.369
ANT	–	0.289	0.084 ± 0.028	0.078	0.011	0.160	0.070 ± 0.017	0.047
FLA	0.011	2.233	0.626 ± 0.191	0.528	0.072	2.457	1.318 ± 0.163	0.452
PYR	–	1.734	0.473 ± 0.148	0.409	0.035	1.805	0.852 ± 0.188	0.521
BaANT	–	0.946	0.299 ± 0.103	0.285	0.054	0.657	0.376 ± 0.059	0.164
CHR	0.004	1.541	0.601 ± 0.195	0.539	0.081	0.694	0.571 ± 0.085	0.236
BbFLA	–	1.921	0.698 ± 0.213	0.590	0.013	1.082	0.458 ± 0.098	0.272
BkFLA	–	2.094	0.729 ± 0.235	0.651	0.026	1.136	0.528 ± 0.104	0.288
BaPYR	–	1.749	0.563 ± 0.210	0.582	0.058	1.053	0.446 ± 0.095	0.263
IPYR	–	1.642	0.443 ± 0.191	0.528	–	3.038	0.821 ± 0.321	0.888
DahANT	–	0.793	0.114 ± 0.078	0.215	–	0.713	0.158 ± 0.071	0.196
BghiPER	–	0.575	0.140 ± 0.055	0.152	0.034	0.986	0.487 ± 0.093	0.259
$\sum$ 16 PAHs	0.369	15.658	5.292 ± 1.41	3.914	0.783	11.928	6.495 ± 1.17	3.251

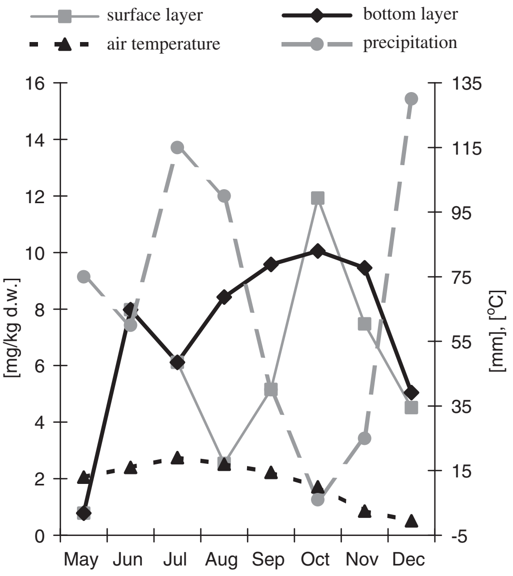

Figure 2. Dependence of the changes in the sum of PAH's in series B, on air temperature and precipitation during the period of the experiments.

the amount of atmospheric precipitation ($r = 0.58$ and 0.72 for surface and bottom layers, respectively) and, similarly to the B series, its maximum content was observed six months after formation of the compost pile. In samples from the B series a negative correlation between the amount of precipitation and PAHs content ($r = -0.42$ and -0.56 for the surface and and bottom layers, respectively) was observed. However, in the case of some compounds (ACE, FLU, PHE, ANT) the correlation between PAHs content and quantity of precipitation in the first fourth months was relatively strong ($r = 0.31 - 0.66$).

Calculated analysis of variance (LSD) did not show statistically important differences ($p < 0,05$) either between the PAHs content in surface and bottom layers of pile or for the experimental series A and B. In the surface layers of both sampling series lower concentrations of PAHs in comparison with bottom samples were observed. The cause could be a result of photo-oxidation processes on the surface of the pile and higher level production of PAHs by microbiological decomposition of organic material inside piles. Absence of light and anaerobic conditions also show degradation. (Bojakowska 2003, Tang 2006, Wilcke 1999). Some PAHs ratios could contain information about the sources of PAHs. Relatively high values of calculated ratios of particulate PAHs content, show that the highest quantities of determined compounds are of pyrogenic origin, from liquid fuels and biomass or coal burning processes (Brandli 2005).

4 CONCLUSIONS

In all investigated samples of compost, PAHs were detected. Their concentration ranged from 0.4 to 15.7 mg/kg dw. and were higher than quantities in soils reported by other authors (Wilcke 2004, Thiele 2001). Hence, use of the investigated composts as a soil fertilizer can cause risk of pollution. The maximum percentage of benzo(a)pyren in total PAHs content was relatively high – 17,8%. In sample series A a statistically important correlation between PAHs content and the quantity of precipitation was found. In addition, in the first four months of composting a similar correlation for some other compounds (eg. ACE, FLU, PHE, ANT) of series B was found. Two maximum PAHs concentrations peaks were observed – in the fourth (only in series A) and sixth months (both series) after the piles were formed. However, statistical LSD tests found no differences between compost samples, in surface layer concentrations were on average 10.8 mg/kg dw. lower than in samples taken from the bottom of the pile. This could be a result of photo-oxidation on the surface and microbial enzymatic production in the bottom of piles. No clear tendency in PAHs concentration during the compost maturation process was found. Ratios of certain PAHs indicate that most of determined compounds originate from pyrogenic processes, and arrive with dry or wet precipitation at the compost material.

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Transformation pathways of polychlorinated dibenzothiophenes (PCDTs) in landfill leachates

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ABSTRACT: This study investigates possible pathways for the degradation of chlorinated dibenzothiophenes. We propose that under conditions of limited oxygen availability, which are typical in landfill sites, the transformation from chlorinated dibenzothiophenes to chlorinated dibenzofurans, via pathways similar to the Van Afferden route, is possible.

Keywords: Chlorinated dibenzothiophenes, transformation pathway, landfill leachate.

1 INTRODUCTION

During research to determine the polychlorinated dibenzothiophene content of landfill leachate, an interesting phenomenon was observed. In one sample analyzed immediately after it had been obtained from the landfill, and in the same sample re-analyzed 32 days later, a significant decrease (of 40.2%) was observed in its 2,3,7,8-TCDT content, and an increase (of 28.5%) was observed in its 2,3,7,8-TCDF content [Czerwinski et al., 2007]. This suggests that tetrachlorodibenzofuran is produced as result of condensation of other compounds (e.g. chlorophenols) and/or through tetrachlorodibenzothiophene oxidation.

It is well known that microorganisms play a primary role in the degradation of persistent pollutants, such as polyaromatic hydrocarbons (PAHs) [Bressler et al., 2000; van Herwijnen et al., 2003; Eibes et al., 2006] and heterocyclic compounds [Alves et al., 1999; Constantini et al., 1996; Di Gregorio et al., 2000; Kropp et al., 1998; Yamazoe et al., 2004]. Dibenzothiophene degradation pathways have been studied by many authors, but only two important pathways are fully accepted. The first of these pathways, proposed by Kodama [van Herwijnen et al., 2003] is presented in Figure 1. In the case of 2,3,7,8-TCDT, however, the carbon 2 atom is blocked by chlorine, and thus this pathway does not work.

The reaction cycle identified by Van Afferden [*2000*] is shown in Figure 2.

Similar reactions can occur for chlorinated derivatives of dibenzothiophenes, but their kinetics depend on the degree of chlorination of the benzene rings in the dibenzothiophene molecule. Therefore, the reaction mentioned above should be the slowest for octachlorodibenzothiophene. Using the reaction cycle shown in Figure 2, and the fact that the SO_2 group can be easily split off and form a diol, we suggest that as a result of consecutive stages of the reaction cycle (in which a water molecule splits off), another cyclization occurs with the generation of an appropriately-chlorinated dibenzofuran molecule. This is shown in Figure 3.

Occurrence of this reaction cycle may explain the high concentrations of polychlorinated dibenzofurans and low concentrations of polychlorinated dibenzodioxins in environmental samples [Czerwiński et al., 2007; Nakai et al., 2007].

2 MATERIALS AND METHODS

In order to verify our hypothesis concerning the proposed reaction cycle, two kinds of waste samples were selected: coal ashes with a high sulfur concentration (7.8%) and scraps of car tires, which are a potential source of the polychlorinated dibenzothiophenes in landfill leachate.

The samples were placed in beakers filled with a solution of acetonitrile in water, where initial TOC was 100 ppm, to extract dibenzothiophenes and other analytes into the solution. After 10, 21, 30 and 40 days, 100 ml of supernatant was extracted with two doses (5 ml each) of dichloromethane. The extract was evaporated under a nitrogen stream to the volume of 2.5 ml, and purified using size exclusion chromatography (SEC) on Brezee 1525 liquid chromatograph equipped with Envirogel columns (Waters).

Similar curves to those presented in Figure 4 were also observed for dibenzothiophenes substituted with five chlorine atoms. Concentrations of highly chlorinated dibenzothiophenes were too low to measure.

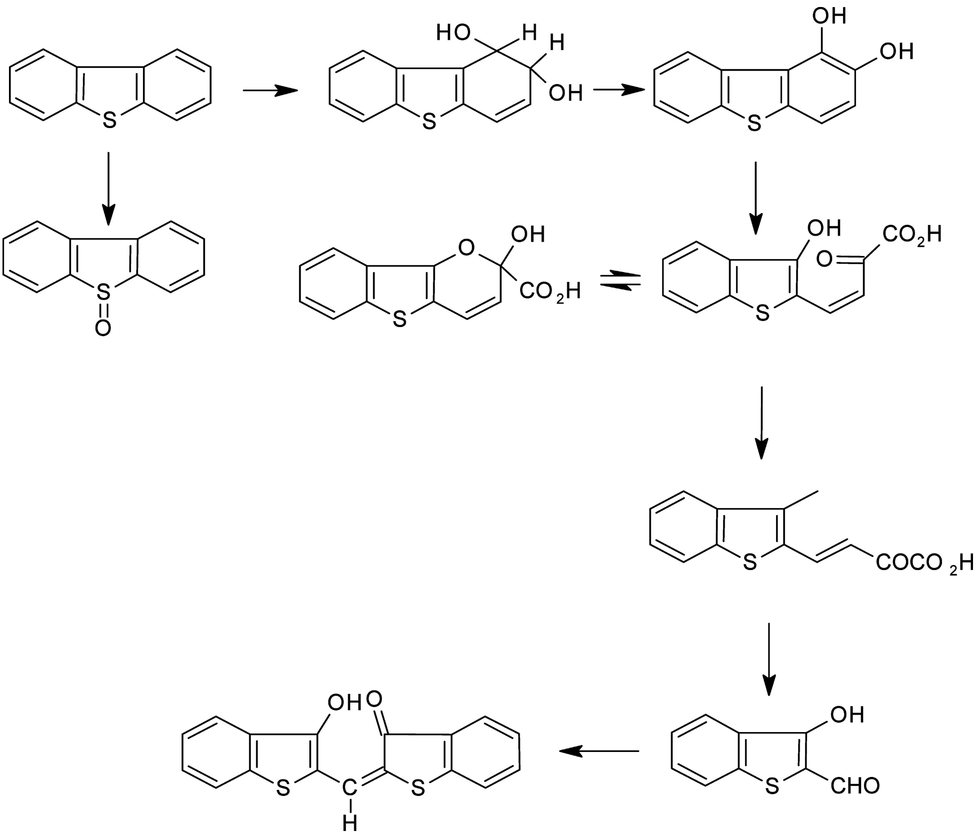

Figure 1. Oxidative degradation of dibenzothiophene via Kodama pathway [van Herwijnen et al., 2003; Seo J-S., 2006].

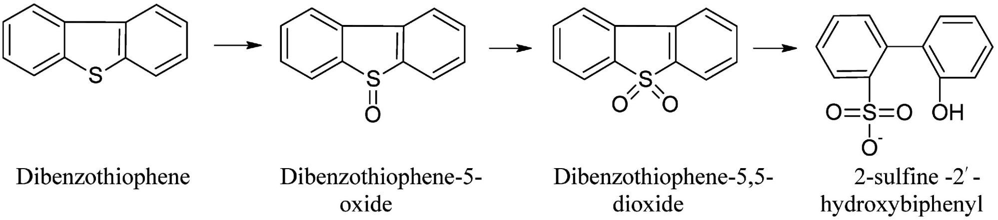

Figure 2. Oxidative degradation of dibenzothiophene via Van Afferden pathway [Van Afferden, 2000; Bressler & Fedorak, 2000].

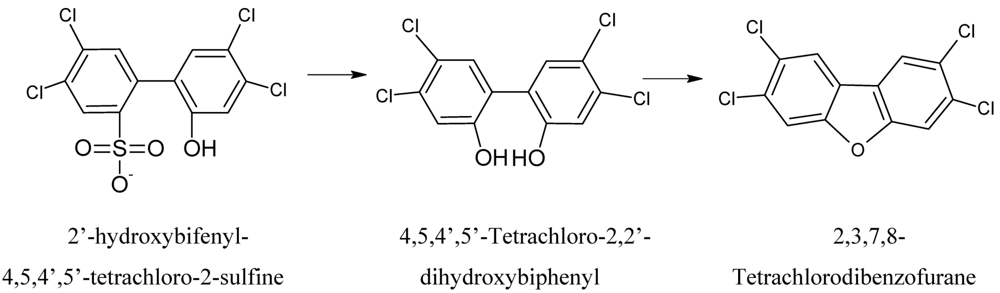

Figure 3. Proposed transformation pathway from tetrachlodihydroxybiphenysulfine to tetrachlorodibenzothiophene.

Table 1. GC-MS system conditions.

The operation conditions of the chromatograph					
Injector	PTV (splitless mode) @ 320°C				
Capillary column	RTx Dioxin (Restek) 60 m × 0.25 mm $d_f = 0.18$ μm				
Oven temperature programming	60°C (0.5 min hold) ramp 15°/min to 260°C than ramp 5°/min to 320°C, 5 min hold				
Carrier gas	He (99,9996%) @ 40 cm/s				
The MS operating conditions					
The ion source temperature	250°C				
The transfer line temperature	275°C				
Scanning mode I: Full Scan	50.0–550.0 amu				
Collision gas	He (99,9996%) @ 2 ml/min				
Scanning mode II: MS/MS	MS/MS for dibenzothiophenes, SIM for other compounds				
Monitored ions					
	tetra	penta	hexa	hepta	octa
Dibenzothiophene	322	356	390	426	460
	253.0–263.0	288.0–298.0	322.0–332.0	357.0–367.0	391.0–401.0
Dibenzotiophene-5,5-dioxide	354	389	412	448	482
Dihydroxybiphenyl	324	359	392	428	462
Dibenzofurane	306	341	374	410	444

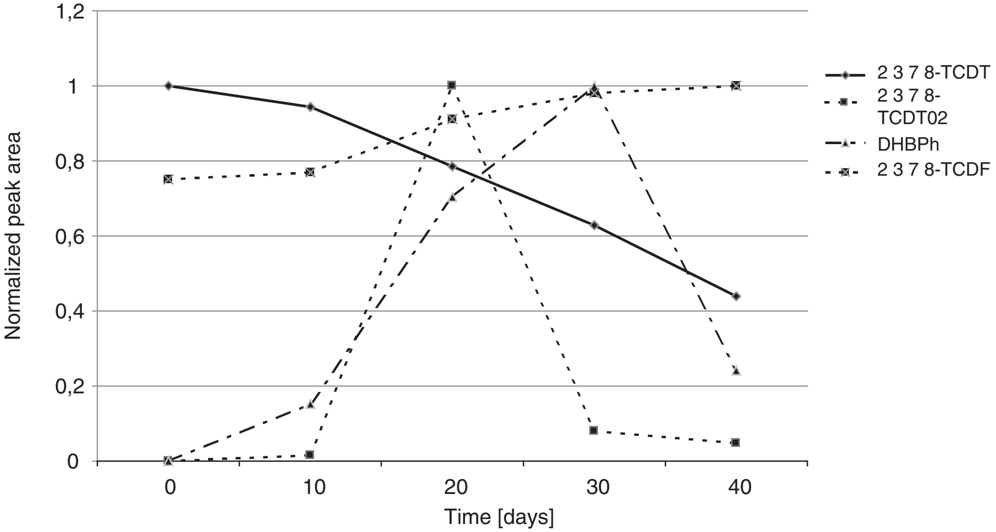

Figure 4. Concentration changes in non polar tetrachloro substituted products of 2,3,7,8-TCDT oxidation.

In the second part of the experiment, in which chlorinated dibenzothiophenes were extracted from tire scraps only, octachlorodibenzothiophene was present in the extract. Concentration changes were smaller than the measurement error. These results also suggest that the chlorine atoms in the 4 and 6 positions in the dibenzothiophene molecule blocked the oxidation of sulfur in the octachlorodibenzothiophene molecule. Due to a lack of ^{13}C-labeled chlorinated dibenzothiophene standards, we are unable to fully confirm the suggested reaction pathway at this time.

We used a GC–MS/MS system TraceUltra- Polaris Q (Thermo-USA) for final sample analysis.

3 RESULTS AND DISCUSSION

Peaks areas for the appropriate congeners of non polar compounds which can be analysed by GC-MS are shown in Figure 4. Peak area was normalized to the highest peek of selected compound.

The proposed reaction pathway also explains why concentrations of chlorinated dibenzofurans are significantly higher than concentrations of chlorinated dibenzodioxins in the landfill leachate.

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Degradation of endocrine disruptors in landfill leachates by ozonation

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ABSTRACT: Endocrine disruptors (EDs), their presence in the environment, and their influence on living organisms, constitute an important area of interest for many researchers all over the world. Thus the problem of ED removal or neutralization has become extremely crucial. The literature indicates that even slight concentrations of some compounds suspected of endocrine disruption can cause irreversible changes in certain organisms and their progeny. A significant number of these substances were identified in the effluent of wastewater treatment plants (WTP), which proves that the processes traditionally applied in WTP are not sufficient to remove EDs. This paper presents the research on oxidation of bisphenol A, tetrabromobisphenol A, and phenanthrene in simulated landfill leachates.

Keywords: Endocrine disruptors, oznonation, landfill leachate.

1 INTRODUCTION

Exposure to a great number of compounds which have a negative effect on humans occurs in everyday life, even if the presence of these compounds is not noticed. Synthetic chemicals are practically present everywhere – in herbicides, in food packaging (which contains phthalates which may disrupt the functioning of the reproductive system), and in cosmetics, clothes, babies' feeding bottles, textiles and computers [Lintelmann et al., 2003; Damstra et al., 2002; Yamamoto et al., 1999; Yamamoto and Yasuhara, 2001; Jiang et al., 2005]. During their production and use, such chemical substances are released into the environment and can move large distances in water and air due to natural transportation processes.

During the last ten years, many studies have been conducted to analyze the possible influence of chemical compounds on the hormonal system; these considered mainly the hormones such as estrogens and androgens which are active in reproductive processes. The most recent investigations have mainly focused on analyzing the influence of chemical compounds on the activity of the thyroid, pituitary, and other exocrine glands. It has also been established that some of the compounds destabilize the hormonal system, disturbing the activity of hormones secreted by glands – hence their classification as endocrine disrupters. A wide range of substances are found within this group of compounds, such as pharmaceuticals (some antibiotics and painkillers), steroids, hormones (17β-estradiol, estron and estriol), personal hygiene products, and surface active compounds (e.g. nonylphenol) [Brown et al., 2003].

Endocrine disrupters influence the endocrine system (internal secretion) in the following three ways:

- by causing undesirable biochemical reactions, through their simulation of natural hormones (e.g. estrogen and testosterone),
- by locking-out the hormonal receptors in cells, which curtails the activity of natural hormones,
- by disturbing particular stages in the synthesis, transportation, metabolism and discharge of hormones, thus altering the correct level of these in an organism.

Endocrine disruptors originate from several sources; for example, the pharmaceutical products such as antibiotics and painkillers enter the environment through domestic and industrial wastewaters. Many studies confirm that the elimination and degradation of such substances during treatment is difficult [e.g. Kot-Wasik 2004]. The relative estrogenic potency of selected estrogens is presented in Figure 1.

The annual production of bisphenol A (BPA) in Europe is around 930 kT, while in Poland it is about 10 kT. For tetrabromobisphenol A (TBPA) these data are unavailable. Because of their high levels of production, endocrine disruptors are also present in landfill leachates [Nascimito et al., 2003; Irmak et al., 2005; Christensen et al., 2001; Silva et al., 2004].

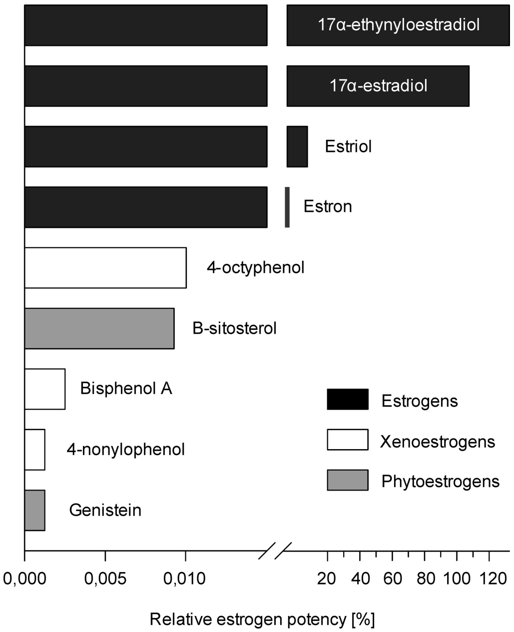

Figure 1. Relative estrogen potency of selected compounds with estrogen activity [based on Gutendrof & Westendorf, 2001].

2 MATERIALS AND METHODS

Leachates from three municipal landfills in Lubelskie province (Poland) were examined in the study. All landfills were of similar age, all were exploited, and in all the leachate was collected in the drainage system. The samples examined were collected from leachate wells.

In addition, to determine the removal efficiency of BPA, TBPA and phenanthrene (Ph), a simulated landfill leachate was prepared by dissolving examined substances in methanol. BPA and TBPA were obtained from ACROS Organics (Germany) and phenanthrene was obtained from Merck (Germany).

The removal tests were carried out in a specially designed glass reactor, where ozone was introduced. For each test, the reactor was filled with 2 dm^3 of ultra-pure water (from a Millipore system), then a sample containing the compound to be studied was added. In the bottom of the reactor an Akwatech diffuser was installed, which allowed the introduction of air (for mixing) or ozone (for oxidation). The flow of the gas was made possible by the water pump included in the system. The decomposition of the endocrine-disrupting compounds present in landfill leachates, under the chemical oxidation process of ozonation, was then studied. Samples were taken from the reactor after 5, 10, 15 and 30 minutes. Every time a volume of 100 ml of solution was taken for analysis. Each sample was prepared by adding 2 cm^3 of a hexane/isopropanol 95/5 v/v mixture, and shaken. Afterwards, about 1 ml of the organic phase was placed in a vial and analyzed using a gas chromatography–mass spectrometry (GC–MS) system (Table 1).

Table 1. Conditions used for gas chromatography–mass spectrometry (GC–MS).

GC: Trace Ultra (Thermo)	
Injector:	PTV (splitless mode) @ 320°C
Capillary column	RTx Dioxin (Restek); 60 m × 0.25 mm; $d_f = 0.18$ µm
Oven temperature programming	80°C (0.5 min hold); ramp 15°/min to 200°C; then ramp 5°/min to 310°C, 5 min hold
Carrier gas	He(99.9996%) @ 40 cm/s
MS: Polaris Q	
Ion source temperature	250°C
Transfer line temperature	275°C
Scanning mode	selected Ion Monitoring-SIM
Quantitation ion and (qualifiers)	
Phenanthrene	178(176)
Bisphenol A	213(228)
Tetrabromobisphenol A	529(527,531)

Table 2. Levels of selected endocrine disruptors in landfill leachate. BPA = bisphenol A; TBPA: tetrabromobisphenol A.

	Place of leachate origin	BPA content [µg/dm^3]	TBPA content [µg/dm^3]
1	Rokitno	117	18
2	Łęczna	34–67	2,3
3	Puławy	21	4,1

3 RESULTS AND DISCUSSION

The results of the GC–MS analysis for selected endocrine disruptors in landfill leachate are given in Table 2. The values obtained are similar to the levels reported by Christensen et al. [2001], Jiang et al. [2005] and Silva et al. [2004].

The efficiency of removal of BPA TBPA and phenanthrene, due to ozonation, is presented in Figure 2.

The problem of the presence of endocrine disrupters in the environment is a new topic in Poland, and most of the relevant literature is published in

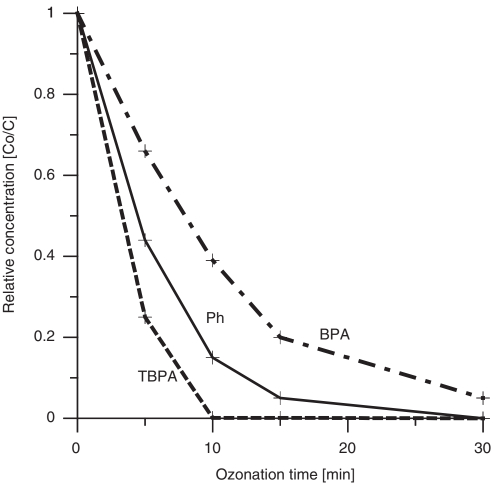

Figure 2. Removal efficiency of bisphenol A (BPA); tetrabromobisphenol A (TBPA) and phenanthrene (Ph) in simulated landfill leachate during an ozonation experiment. Co/C = Original concentration/measured concentration.

the English language. Polish scientists have, however, already started experiments related to endocrine-active compounds in the environment. This paper presents some techniques using advanced oxidation methods, and underlines the efficiency of ozone oxidation of endocrine disrupters. Conducted studies allowed to investigate the degree of phenanthrene, BPA and TBPA removal. These experiments confirm that the ozonation process is highly efficient in removing endocrine disrupters.

Based on literature reviews and experimental results we concluded that:

- Current methods of domestic wastewater treatment are not efficient enough to remove endocrine-active compounds.
- The ozonation process is an effective method of removing most of the endocrine-active substances from landfill leachates.
- The results of GC–MS analyses confirm high efficiency of ozonation process.
- It is reasonable to continue studies on the degradation of endocrine disrupters using oxidation methods.

The results obtained suggest that TBPA is a compound which is relatively easy to remove from landfill leachates. They also suggest that a first step in the degradation of TBPA is oxidative debromination (Figure 3). Tri- and di- bromosubstituted BPA were present in a first extract (after five minutes oznonation). Confirmation of degradation pathway of BPA due to presence of high polar products needs HPLC–MS system.

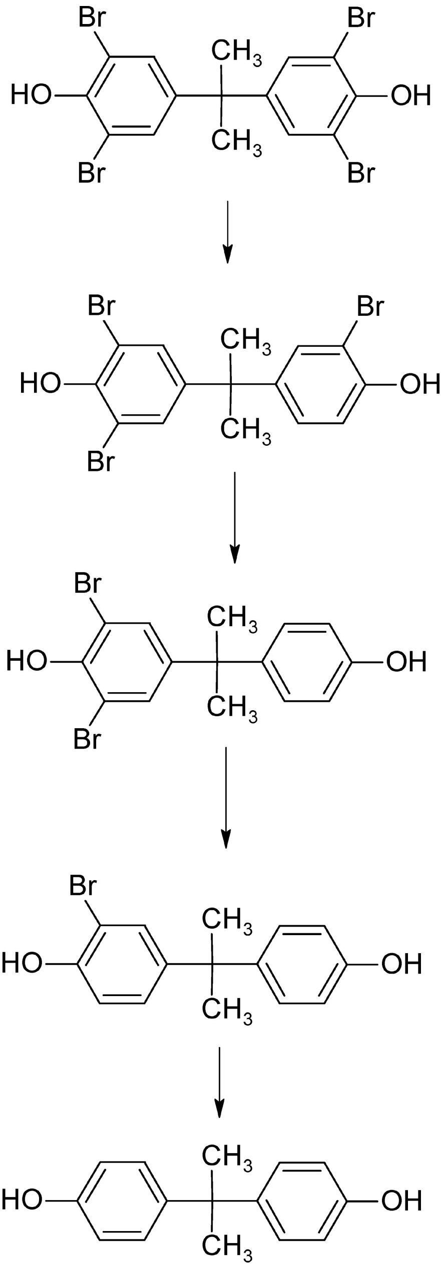

Figure 3. Proposed degradation pathway tetrabromobisphenol A (TBPA) during an ozonation experiment.

ACKNOWLEDGEMENTS

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Migration of heavy metals from waste disposal sites and sewage sludge

Management of Pollutant Emission from Landfills and Sludge – Pawłowska & Pawłowski (eds)

The migration of pollutants from the reservoir of copper mining waste

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ABSTRACT: In the paper we focused on the transport of heavy metals migrating with leachates from the reservoir of a copper mining waste to ground and surface water. Studies on soil and water chemistry have been carried out around the reservoir of post-flotation waste in the buffer zone (about 50 m from the reservoir) and outside it (up to 500 m distant). No effect of the cooper post flotation waste reservoir was found on increased accumulation of heavy metals in soils as compared to the values typical of this region. The reservoir is a source of contamination for ground and surface water. Water transports elements from the reservoir providing a pathway which enables them to enter element cycles in the environment.

Keywords: Heavy metals, migration, landfill.

1 INTRODUCTION

Landfill sites pose a definite environmental risk. The impact of a landfill site on the local environment depends on its content of toxic elements and substances, their mobility including solubility in water and susceptibility to release into the atmosphere in a gaseous or dust form as well as on safety measures which prevent migration of the pollutants from a landfill. A good insulation notwithstanding (bottom sealing, leachate draining and treatment, preventing dust formation, gas collection system), a landfill site will always constitute a source of pollution emitted to the environment.

Pollutants in the environment may be transported by different pathways. Air pollution in dust carrying heavy metals is deposited onto the soil surface, foliage and surface water. Metals rinsed by the precipitation water penetrate to the soil and to the groundwater causing their contamination.

Copper ore processing and enrichment generates large amounts of post-flotation waste. The waste displays a variety of mineralogical and physicochemical properties which depend on the ore composition and processing technology. In terms of chemical composition waste is of low environmental nuisance since it usually contains neutral compounds like silica, carbonates, silicates and aluminosilicates.

The post-flotation waste from the KGHM Polska Miedź (Polish Copper Mine and Smelting Industry) in the LGOM – Legnica-Głogow Copper Mining Region is mainly stored at the Żelazny Most (Iron Bridge) disposal reservoir. This has a surface of 15 km^2 and volume of 350 mln m^3 with perspectives for further extension of up to 1.1–1.2 mld m^3. From the storage reservoir the pollutants migrate with water to the ground resulting in groundwater contamination. The dried waste is easily removed from the reservoir extensive surface by wind thus carrying heavy metals in the dust. Stabilizing mixtures based on asphalt have been applied to prevent dust emission, though the mixtures bring about additional contamination by PAHs (polycyclic aromatic hydrocarbons).

Pollution of the environment around the reservoir has already been investigated by numerous authors. Results of these investigations have been periodically summarized by agencies servicing the exploitation of the local copper deposits (Czuba 1991, Mocek 1994, Basińska 1994, Chodak & Szerszeń 1995, *Assessment*... 1996). In our investigation we focussed on the transport of various elements including heavy metals migrating with leachate from the reservoir to the ground and surface water.

2 MATERIALS AND METHODS

The post-flotation waste from the KGHM Polska Miedź copper mine is disposed of in a semi-liquid state in the Żelazny Most reservoir which has no isolation from the ground. The waste is basically composed of quartz and contains small amounts of aluminosilicates. The Cu content in the waste fluctuates from 1000 to 2000 mg/kg, the Pb content is usually within the limits of 100–300 mg/kg, while the content of other heavy metals amounts to about some tens of mg/kg. Large amounts of sulphates and chlorides were found in water gathering above the sediments (*Assessment*... 1996).

The surface water was sampled in the girdle ditch surrounding the reservoir, in the water stream at the limit of the reservoir buffer zone and in the drainage ditches located both within and outside the reservoir buffer zone. The groundwater was sampled at the depth of below 80 cm under a rye field in the reservoir buffer zone.

Soil samples were taken around 50 m from the reservoir from a soil profile from the rye field, i.e. from the depths of 0–35 cm, 35–55 cm, 55–80 cm and below 80 cm. Around a profile soil samples were taken from no less than 20 sites at depths of 0–35 and 35–55 cm to derive average mixed samples. Similar average mixed soil samples of the ploughed layer were also taken from wheat, barley and potato fields in the reservoir buffer zone. Reference soil samples were taken from similar fields outside the reservoir buffer zone. Soil was classified as deluvial brown soil (Eutric Cambisols).

At the laboratory, the water samples were filtered and determinations were performed of pH, electrical conductivity and contents of 12 elements. Soils were analyzed for total contents of heavy metals, exchangeable cations and the chemistry of soil solutions. The total contents of metals (Cu, Zn, Pb and Ni) were determined using the FAAS method after soil extraction with a mixture of concentrated HCl and HNO_3 in the proportion of vol. 3:1 in the MDS–2000 microwave digestor. The contents of exchangeable cations in soil (Ca, Mg, K and Na) were determined by FAAS method after extracting with 1 M ammonium acetate.

Soil solutions were prepared in the laboratory by extracting the soil with deionized water at the soil: water ratio of 1:3, following a 10-day incubation at 25°C. After centrifuging, Ca, Mg, K and Na in the water extracts were determined using FAAS method. Chlorides and sulphates were determined by capillary electrophoresis.

3 RESULTS AND DISCUSSION

The reservoir of post-flotation waste affects the environment through base compression. This results in the infiltration of leachate into the ground and raises the groundwater level up to the point at which water spills over the surface. In addition, the drying surface of waste may easily be pulverised and blown away as dust. Thus, both water and dust carry pollution load. All elements entering the environment in an uncontrolled way are considered as pollution, and for the Żelazny Most reservoir it includes significant amounts of heavy metals, especially Sr and Ba. Moreover, the water in the reservoir contains large amounts of sulphates and chlorides.

A number of studies have been carried out around the disposal site, both in the buffer zone and outside, to provide evidence of environmental effects of the reservoir including its effect on water, soil, plants and animals. The infiltration of water from the reservoir was found to increase by 0.802 m^3/min over the period of five years (1990–1995) while the total mineralisation of groundwater increased from 496–5430 mg/dm^3 in 1990 to 2206–12674 mg/dm^3 in 1995. The salinity limit has been moved by about 100 m further from the reservoir. Water discharged to the nearest water stream was found to have the following contents of heavy metals: Cu 17–60, Zn 49–74, Pb 26–75, Ni 50–112 and Cd 15–21 mg/dm^3 (*Assessment*... 1996).

The majority of soils around the reservoir were developed from loams and have slightly acid or neutral pH, while the carbon content in the 0–35 cm layer is about 2.6% (Table 1). These soils are mostly managed for cereals and fodder plant cultivation.

We found that at the distance of around 50 m from the reservoir in the buffer zone, the soil contents of Cu, Pb, Ni and Zn are lower than the local background levels of the above elements established for the Legnica Gtogów Copper Mining Region (Tables 2, 3).

Table 1. Some characteristics of soil in distance 50 m from the reservoir.

	Soil texture						Exchangeable cations				Soil solution			
Depth cm	1.0–0.1	0.1–0.02	0.02– –0.002	<0.002	pH	$C_{org.}$ %	Ca mg/kg	Mg	K	Na	Ca mg/kg	Ma	K	Na
0–35	63	19	7	11	5.8	2.6	1700	26.6	34.4	4.2	148	2.1	10.2	1.3
35–55	42	20	18	20	6.4	1.4	580	11.3	24.8	4.4	15.1	0.7	4.8	1.1
55–80	42	20	16	32	6.4	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
>80	48	22	9	21	6.9	0.0	n.d.	n.d.	n.d.	n.d.	127*	9.7*	12.3*	5.8*

* – groundwater, concentration in mg/L; n.d. – no detected.

In soils not contaminated or contaminated only at the surface, heavy metal contents will usually decrease with the depth of soil profile. Higher metal contents in the upper part of the profile are explained by biological accumulation. The fact that the ploughed layer contains more heavy metals as compared to the parent bedrock is widely believed to be due to the biological accumulation of elements. Burt et al. (2003) noted that in smelter contaminated soils total Cu, Zn, Pb and Cd concentrations, as well as the more soluble (mobile) fractions were highest in surface horizons. It was found that the enrichment of the ploughed layer depends on trace element and may fluctuate within a wide range (Haiyan & Stuanes 2003). Our study has also shown that contents of all metals examined are higher in the ploughed layer than in the underlying horizons (Table 2).

The content of exchangeable basic cations in soils sampled within the distance of 50 m from the reservoir (Table 1) approximates their levels found in other arable soils of that type. Likewise, cation contents in soil solutions (Table 1), especially in the ploughed layer of the soils examined, do not differ from the values found in solutions of other arable soils.

Results of analysis of soil solutions sampled from the ploughed layer under three different cultures within the reservoir buffer zone indicate that cation contents in soil solutions depend on the type of culture (Table 4). Thus, it can be inferred that the values obtained are conditioned by the type of fertilisation. The respective values obtained for soil solutions sampled outside the reservoir buffer zone (Table 5) indicate that contents of Ca, Mg, K and Na are lower than within the buffer zone while contents of chlorides and sulphates remain similar (Tables 4, 5).

Table 2. Content of heavy metals in soil approx. 50 m from the reservoir.

Depth cm	Cu	Zn mg/kg s.m.	Pb	Ni
0–35	21.3	36.4	22.4	22.5
35–55	10.8	24.4	14.5	14.6
55–80	14.3	32.0	14.7	14.9
>80	14.2	32.1	11.5	14.4

Table 3. Mean total content of heavy metals in LGOM soils (n = 32).

Depth cm	Cu	Zn mg/kg d.m.	Pb	Ni
0–35	77.8	59.7	73.8	29.7
35–55	28.3	45.1	22.3	21.6
55–80	16.6	33.7	19.3	18.1
>80	12.9	28.9	15.4	14.9

The chemistry of the stream water sampled around 500 m from the reservoir was compared with that sampled within the area of the Puszcza Borecka Integrated Monitoring Station, situated in the region thought to be the least polluted at the country scale.

The electrical conductivity of water sampled from the girdle ditch surrounding the waste reservoir accounts for its high salinity, which conforms with expectations. Conversely, the conductivity of water sampled from a water stream at the limit of the reservoir buffer zone shows values several fold lower, although these values exceed, by about 10 times, the conductivity of water in streams from the unpolluted region (Ostrowska et al. 1994). The conductivity of groundwater in the vicinity of the reservoir is only about twice as high as that of the groundwater from an unpolluted region (Table 6).

The several fold higher salinity in the water stream running at the buffer zone limit as compared to that of the groundwater suggests that the quality of stream water is also conditioned by the direct inflow of water gathering above the sediments in the reservoir. This suggestion is corroborated by large amounts of Ba and Sr found in the streamwater. The Zn level in the leachate is not much higher than that found in water sampled from the water stream at the limit of the buffer zone while the content of Cu is higher by about 70 %, and the content of Pb is almost 20 times higher. Both, heavy metal content and electrical conductivity, are lower in the groundwater than in the surface water sampled from the water stream.

Table 4. Content of elements in soil solution in the ploughed layer in the buffer zone.

Culture	Ca	Mg	K mg/kg	Na	Cl	SO_4
Triticale	18.9	7.9	40.3	2.65	36.2	32.5
Barley	124	5.2	23.1	1.53	36.9	14.9
Potatoes	82.6	19.5	36.4	2.34	15.2	27.9

Table 5. Content of elements in soil solution in the ploughed layer under different types of culture outside the buffer zone.

Culture	Ca	Mg	K	Na mg/kg	Cl	SO_4
Sugar beat	46.4	0.61	3.07	0.12	72.0	34.4
Wheat	4.5	0.25	1.69	0.24	59.2	56.6
Rye	2.8	0.06	8.00	0.08	4.9	39.7
Barley	3.1	0.13	9.20	0.15	4.8	20.6
Potatoes	1.3	0.05	11.75	0.19	14.1	22.8
Soil A	5.5	0.21	14.26	0.08	5.8	22.9
Soil B	33.0	4.43	37.00	1.21	38.1	24.7

Soil A and Soil B – arable soils in unpolluted area, Soil A – sandy clay soil, Soil B – clay soil.

Table 6. Surface and ground water chemistry.

Sample place	Conductivity µS/cm	Ca mg/dm^3	Mg	K	Na	Cl	S-SO$_4$	Zn µg/dm^3	Cu	Cd	Pb	Ba	Sr
Leakage from reservoir	3890	465	259	20	3450	7200	690	325	14.5	0.2	35	119	10850
Stream – limit of BZ	900	244	463	8.7	605	1365	146	285	8.5	0.2	0.2	104	2250
Stream – UNP	40	64.7	7.4	0.5	3.3	6.2	4.7	3.0	1.0	<0.2	<0.2	n.d.	n.d.
Ground water – BZ	174	127	9.7	123	5.8	55	23	156	8.0	3.0	0.2	180	360
Ground water – UNP	92	9.5	2.0	1.0	2.5	3.5	8.0	40	3.0	0.5	0.8	20	20
Drainage ditch – BZ	n.d.	386	72	15	1085	2250	750	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Drainage ditch – outside BZ	n.d.	234	24	25	150	325	250	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

BZ – buffer zone; UNP – unpolluted area; n.d. – no detected.

A comparison of contents of all elements examined in the stream and groundwater sampled around 50–100 m from the waste reservoir with the respective values found in the unpolluted region points to significant differences to the disadvantage of the water around the reservoir. It can thus be said that the copper waste landfill constitutes a source of pollution for the ground and surface water. The water provides a carrier of elements from the reservoir and enables their incorporation into the element cycle in the environment. Significant differentiation was found in the chemistry of surface water, bottom sediments and aquatic plants investigated within the area subject to the impact of copper mining industry. For example, the Cu content fluctuated within the range of 0.2–17 µg/dm^3 in water, from about 10 to 350 mg/kg in sediments while from 10 to 217 mg/kg in plants. The Pb content varied from less than 1 µg/dm^3 in water to more than several hundreds mg/kg in sediments. Moreover, the sediments were found to contain significant amounts (up to 400 mg/kg) of Sr (Samecka-Cymerman & Kempers 2003). A considerable accumulation of Cu, Pb and Zn was also found in bottom sediments of the middle Odra River, in the deeper layers in particular (Ciszewski 2003), an observation which author links with the inflow of those elements from the copper mining area.

According to Van Hullebusch et al. (2003), the Cu contained in water is bound by organic substances resulting in unsoluble compounds which precipitate to the bottom. Xue et al. (2003) found that soil rich in organic matter accumulated more total Cu and Zn than mineral soil. More water soluble Cu and Zn fractions occur also in the organic soil. Soil organic matter is therefore a trap for these metals but it can be also a source of groundwater contamination.

It was shown that metals accumulated in bottom sediments may be mobilised by physical processes, as well as by physicochemical processes (Bolałek & Frankowski 2003, Caetano et al. 2003). The rate of metal release depends on the amount and form of a metal in the sediments (Bordas & Bourg 1998).

Dusts which, among other materials, carry a significant load of heavy metals also cause dispersal of the pollution from the copper waste reservoir into the environment (*Assessment*... 1996). In order to halt dust formation, stabilising mixtures based on asphalt have been applied. However, the latter constitutes an additional source of environmental pollution by aromatic hydrocarbons. Our pilot study has shown that the total content of PAHs is more than 10-fold higher in grain of wheat and triticale collected within the reservoir buffer zone than in those found in non-polluted regions. The sum of PAHs in the grain under study was 15 µg/kg while in the reference grain it was only 1.6 µg/kg. The contamination of the environment by substances used in waste stabilising was also reported by other authors (Baciocchi et al. 2003).

The pollution from landfill sites may enter and actually enters the trophic chain and accumulates in animal organisms as well as in humans. The heavy metal content in plants was studied to assess the impact of the copper waste reservoir. The results indicate that standard values were exceeded only in some percent of samples, especially those for Cu and Pb, as compared to levels found in plants growing in unpolluted regions (Mocek 1994). Simultaneously, the results of a study that was performed over the same time on the metal contents in tissues of animals bred within the impact of the waste reservoir indicate that the metal levels in the polluted region are much higher as compared to the metal contents in animal tissues from the unpolluted regions. For example, cow blood and milk were found to contain twice to three times more Cu, Pb and Zn than the tissues of the reference cows

Table 7. Mean concentration of heavy metals in cow blood and milk in µg/dm^3 (*Assessment*….1996).

	Under reservoir influence			Control		
	Mean	Min	Max	Mean	Min	Max
Blood						
Pb	162	98	226	59	30	72
Cu	1224	994	1403	765	660	909
Zn	1410	1120	1615	1050	920	1090
Milk						
Pb	55	49	71	35	20	49
Cu	125	95	143	55	30	68
Zn	5110	3450	6520	2780	1170	3980

(Table 7). Curzydło et al. (2001) investigated relationships between pollution levels in the system: soil-plant- animal in the vicinity of a steel mill and found that the exceedance of Pb content in the soil was two-fold, in grain almost five-fold while in goat liver it was ca. two-fold as compared to the respective control levels. It can thus be assumed that accumulation of pollution in living organisms, and in animals in particular, would constitute an indicator of pollution migration into the environment.

The range of impact of the waste reservoir depends on the pathways of pollution flow to the environment and on barriers retarding that transfer along the pathways. The main pollution carriers for the copper waste reservoir are water and air. Climatic conditions (precipitation, fog) may provide a barrier in the atmospheric pollution pathway efficiently acting with dusts less with gases (Wiktorowski 2001). The accumulation of respective metals in the soils depends on the soil sorption capacity, and especially on the content of organic matter, granulometric composition, especially soil coloids (Barton & Karathanasis 2003). Violante et al. (2003) have found selective heavy metals adsorption on iron and aluminium oxides in the sequence Pb > Cu > Zn > Co.

However, the metal sorption in the soil is restricted. Speir et al. (2003) in a four-year study of the migration of heavy metals following the application of waste-water sludge (100 t/ha) found that Pb and Cu migrate from the surface down the soil profile only in the fourth year. According to these authors the groundwater was enriched in Cu by 0.8–1.2% after adding 17–25 kg Cu with the sludge and in Zn by 19–27% after adding 70–103 kg Zn in the sludge. Model experiments carried out by Al-Subu et al. (2003) showed that Cu, Pb and Zn deposited with water onto the soil surface initially, are adsorbed and later washed down from the soil with a further inflow of these elements whereby the sorption intensity depends on soil properties.

The transfer of pollution with water in the environment depends upon the quality of stream bed and upon the flow rate. Albek (2003) found that the concentration of pollution load in water depends on the flow rate, though the major effect on the pollution transport rate is its interception. A significant role in the transfer of elements is the organic matter both via the accumulation in living organisms and adsorption on hydrous oxides of Fe, Mn and clays (Krupadam et al. 2003).

The results of our studies on heavy metal migration from the post flotation waste reservoir unequivocally indicate that the elements are transported with water and undergo biological and chemical sorption en route.

4 CONCLUSIONS

- The copper post flotation waste reservoir was found to have no effect on the increased accumulation of heavy metals in soils as compared to the values typical of this region.
- The post flotation waste reservoir is a source of contamination for ground and surface water. Water transports elements from the reservoir, providing a pathway enabling them to enter element cycles in the environment.
- Investigations made by various authors within the area of impact of the reservoir indicate that the number of exceedances of metal levels as related to the levels found outside the impact of the reservoir increase in the successive tiers of the trophic chain (air–soil–plant–animal). The highest metal accumulation was found in the latter tier of the chain, i.e. in animal organisms. It is worth noting that the relatively high accumulation of metals in the tissues of cows residing in the affected region may be mainly due to the fact that they consumed water from a local contaminated stream.

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Groundwater pollution by heavy metals from sludge processing: Hazard evaluation

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ABSTRACT: Vulnerability mapping on a planning scale in Germany is being achieved using the Hölting method. As investigations at our department have shown, the properties of soils in combination with land use have an important impact on vulnerability aspects. This is especially true for groundwater contamination aspects by heavy metals due to sludge processing as fertilizers under agricultural land use. Within this scope soil samples representative for large areas of the Rhine Basin nave been gained and investigated, considering organic matter, pH, clay mineralogy as well as CEC. Results show, that process parameters can be correlated to soil types respecting the actual land use. By coupling this area information with process parameters an area wide description of potential sorption capacity is possible. A comparison of results in hazard evaluation, using the classical method versus a new evaluation respecting sorption processes and land use aspects, considering the disposal of sludge, is presented.

Keywords: Groundwater vulnerability, hazard assessment, soil type, land use, sludge, GIS

1 INTRODUCTION

Various aspects of the vulnerability of groundwater vulnerability are gaining increasing importance especially in connection with the proposed regulations of the European Water Framework Directive. For the assessment of the vulnerability, in general the vadose zone is evaluated using different methods, such as DRASTIC (Aller et al. 1985; 1987), EPIK (Doerfliger et al. 1999), for karstic areas, GOD (Foster 1987), AVI (Aquifer Vulnerability Index) (Stempvoort et al. 1993) and many others (cp. Vrba & Zaporozec 1994, Magiera 2000). In Germany the so-called Hölting method (Hölting et al. 1995) is mainly applied. All these methods are based on a classification of different parameters that can be correlated over wide areas using gridding techniques in Geographic Information Systems (GIS). The results give useful information about aquifer protection on a planning scale.

In addition to such point or matrix based evaluation methods, numerical or mathematical modelling approaches exist, these however, suffer from necessity of having very specific parameters available for a wide area. In contrast, point and matrix based systems often are somewhat oversimplifying.

With regard to the German method, former investigations (Burchart et al. 2006, Wimmer & Burchart 2005, Wimmer, Leppig & Dietz 2001) have shown that soil and land use properties play an important role in the groundwater vulnerability assessment.

Therefore, in this work the focus has been placed on soil properties such as organic matter, pH, clay content and mineralogy as well as cation exchange capacity regarding vulnerability aspects.

2 MATERIALS AND METHODS

2.1 *Investigation area*

To carry out representative sampling for the development and application of an enhanced vulnerability method an area of about 100 km^2 has been chosen in the Lower Rhine Embayment (Fig. 1), Germany, with characteristic composition of soil occurrence regarding the entire Lower Rhine Basin, also reflecting the typical hydrogeological situation.

With respect to soil types four main types are representative of the area of investigation: Luvisol, Cambisol, Gleysol and Stagnic Gleysol, covering about 80% of the total area.

Lithologically, the area is dominated by Pleistocene terrace sediments, partially situated in the vadose zone, as well as periglacial sediments such as loess or aeolian sands or dunes. Furthermore, Holocene alluvial sediments occur, mostly in combination with little depth to groundwater. Older Oligocene sediments crop out in the eastern parts of the working area and are represented by silty fine sands. Here the depth to groundwater reaches maximum values of almost 30 m.

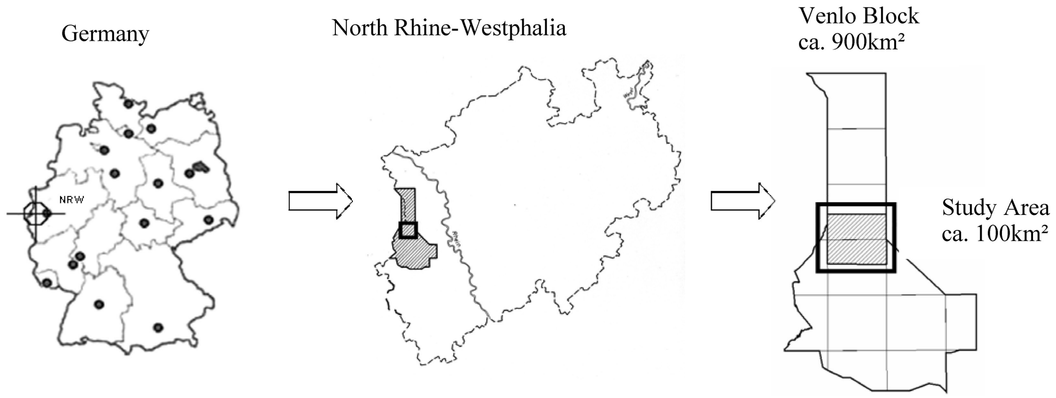

Figure 1. Main research site: Venlo Block (Lower Rhine Basin).

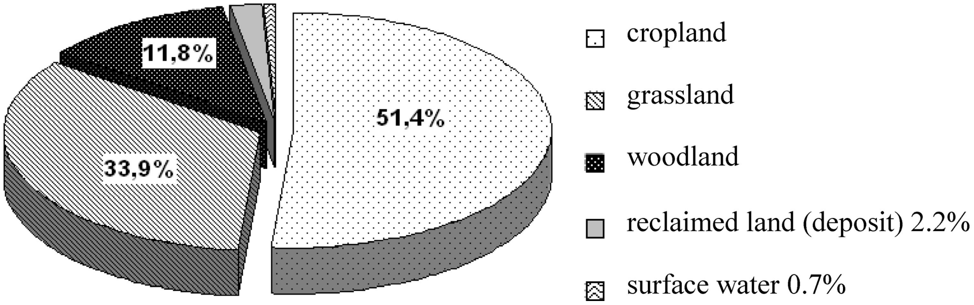

Figure 2. Distribution of land use in the study area.

Considering these constraints it is evident that the selected area is representative of the geohydrological, as well as of the pedological situation of the much larger Venlo Block again typical of the Lower Rhine Embayment.

2.2 *Soil sampling*

Prior to the main investigation a large scale soil sampling campaign was planned and executed. Sampling sites were chosen according to their prevailing soil type and land use. Land use was classified into three categories: woodland, cropland, and grassland. The distribution of land use is shown in Figure 2.

Over all, more than 100 samples were taken and subsequently analysed. In order to use corresponding data from a larger Bavarian sampling series conducted by the Bavarian Geological survey, sampling methods and results from lab analyses were compared beforehand. In general, probes were taken from the upper meter considering first the Ap-horizon, while in a second step an integrated sample was taken. For the measurement of soil moisture the uppermost 5 cm of the upper meter were sampled. Whereas the sampling was initially carried out using open cut cavities the sampling method was, after comparison of results, altered to sampling from 2.5″ drill holes. For saturated as well as unsaturated permeability tests, undisturbed probes were sampled from different depths, in 4″ metal tubes. Disturbed probes were stored in sealed plastic boxes; the natural water content was analysed the day following the sampling.

2.3 *Analysis of soil properties*

Parallel to and during the sampling campaign different soil parameters were analysed in the laboratory as well as during field tests. Whereas the field tests were limited to a saturated permeability test by means of a Guelph permeameter, laboratory analysis considered a much larger variety of parameters such as grain size composition, natural water content, saturated and unsaturated permeability, content of organic matter, pH, cation exchange capacity as well as clay mineralogy. The results of the clay mineralogy determinations were not available at the time of writing.

2.3.1 *Permeability evaluation*

In situ permeability tests were carried out with the Guelph permeameter (Fig. 3 (right)) at two different depths (0.3 m, 0.7 m). This method provided good results in soils with permeabilities as low as

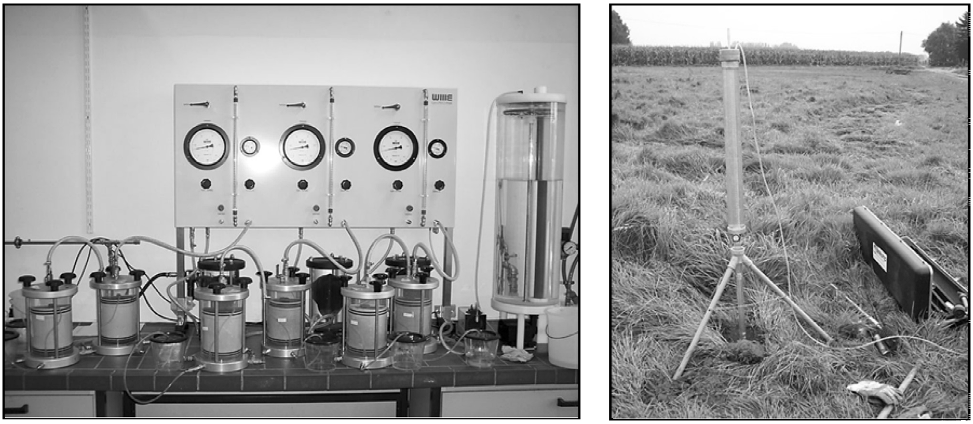

Figure 3. Permeability analysis: in the laboratory measuring saturated permeability (left) and (right) the field test realized with the Guelph permeameter for determining field saturated permeability.

10^{-7} m/s. More impermeable soils tend to prolong the duration of the experiment with the effect of overestimating marginal effects, resulting in even higher values for permeability. In the working area only Gleysols under agricultural land use (cropland) had permeabilities in this range ($<10^{-7}$ m/s).

In the laboratory, saturated permeability measurements were carried out in triaxial cells (Fig. 3 (left)) using a constant pressure head.

Unsaturated permeability was determined using a sand box and consecutively evaluating pF-curves using ceramic plates in negative pressure environment.

2.3.2 *Characterization of organic matter*

The amount of organic matter was analysed for the upper soil horizon (Ap) according to the German norm DIN 18128. The procedure was as follows: samples (ca.15g) were heated to 105°C, pulverized and subsequently heated to 550°C to constant weight. As a result, the amount of organic matter would be overestimated. Generally, the annealing was continued for ca. 2 hours. The difference in mass resulting from the annealing process represents the amount of organic matter in the upper soil horizon.

2.3.3 *pH measurement*

Measurement of the soil pH was carried out on an aqueous suspension according to EN 13037. In agriculture, pH measurement is often carried out in a $CaCl_2$ solution.

This results generally in a pH value that is decreased by 0.5 units. The pH was measured for the uppermost soil horizon Ap throughout all samples. The results are shown according to the soil type and land use.

2.3.4 *Determination of CEC considering copper-ions*

Finally, the cation exchange capacity was determined for 21 samples using a Cu (II)-triethylenetertamine solution. Samples were sieved to grain sizes <2 mm, treated with hydrogen peroxide and subsequently dried at 50°C. Subsequently, distilled water (50 ml) was added to a soil sample (1 g) as well as 1 ml of 0.1 M coppertriethylentetramine solution (0.1 M $CuSO4 \cdot 5H2O + 0.1$ M C6H18N4). The sample was then homogenized for 2 hours in an automatic jogger and afterwards centrifuged. The copper content of the remaining fluid was then analysed with ICP-OES (optical emission spectral analysis). The amount of exchanged cations can be derived by comparison with the initial copper concentration. Copper has a strong tendency to adsorb (Lambarki 2006). Therefore, other cations might be liberated during the copper sorption process. In unpolluted soil Na+ or K+ are the most probably released cations.

If the amounts of i) clay and silt and ii) organic matter in the sample are known, the results of the measurement can be compared with an estimation of CEC according to grain size analysis. In this case, the pH value has to be carefully adjusted due to its influence on the sorption process. We have conducted such a comparison.

3 RESULTS AND DISSCUSSION

The results of the analysis show clearly the impact of soil type and land use on the observed parameters. With regard to groundwater vulnerability, the impact of land use is sometimes even more important than the prevailing soil type. With regard to permeability it can be seen that the impact of land use is of the same order

Table 1. Values for water permeability according to soil type and land use.

		Permeability	
Soil type	Land use	Depth 0.3 m	Depth 0.7 m
Cambisol	Woodland	4.6·10-6	7.5·10-6
	Cropland	3.0·10-7	1.6·10-6
	Grassland	6.5·10-7	2.7·10-7
Gleysol	Woodland	3.4·10-7	2.2·10-7
	Cropland	2.6·10-8*	1.5·10-9
	Grassland	3.8·10-7	3.0·10-8
Luvisol	Woodland	1.1·10-6	1.6·10-6
	Cropland	6.2·10-8	2.9·10-7
	Grassland	2.2·10-7	no value

* single measurement only

of magnitude as the soil type. The results of Guelph permeameter tests at different depths, displayed in Table 1 (Burchart et al. 2006), show that under agricultural land use the field saturated permeability is often reduced in the Ap-horizon due to compaction of the upper part of the soils as a consequence of the recurrent use of heavy machinery.

Looking at the influence of land use on permeability, woodland always shows the highest values. Generally it is about 10 times higher than in the same soil under any other land use. For cropland permeability of the topsoil is generally lower compared to any other land use. Depending on the depth in which the infiltration tests were carried out, differences can be observed for the same locality. Besides grain size, the compactness of packing is responsible for the influence on soil permeability. Therefore, it can be expected that, with increasing depth, permeability values should drop or, at least, be stable. This can be observed for most of the field experiments. However, under agricultural land use (cropland) Cambisols as well as Luvisols show an about 5 times reduced permeability, again probably due to compaction by heavy machinery. A comparable conclusion, however, can not be made for Gleysols due to lack of data.

Gleysol shows, in an overall view, the lowest permeability values, followed by luvisol and cambisol with the highest values. This is also in accordance with granulometric analysis of soil samples in the laboratory (Kaspar 2006). However, considering the results in more detail, it appears that different soil types may have similar permeability with respect to land use (Table 1). Therefore it can be expected that the importance of land use is quite comparable in importance to the type of soil considering groundwater vulnerability aspects. With regard to sorption processes, the parameters pH, organic matter as well as clay content and mineralogy are of major importance. The results regarding these parameters are listed in Table 2 and 3.

Table 2. Results of laboratory analysis considering organic matter, pH and clay content sorted according to land use.

	Soil types				
Land use	Cambisol	Luvisol	Gleysol	Stagnic Gleysol	Mean value
Organic matter content [%]					
Cropland	2.61	3.33	2.68	3.30	2.98
Grassland	2.98	3.69	4.95	3.72	3.83
Woodland	4.44	8.26	8.74	4.38	6.45
pH value					
Cropland	6.24	6.60	6.13	6.03	6.25
Grassland	5.75	6.08	5.82	5.75	5.85
Woodland	3.70	3.18	4.77	3.34	3.75
Clay content [%]					
Cropland	8.20	13.2	7.00	11.0	9.85
Grassland	7.50	13.4	8.10	15.8	11.2
Woodland	12.5	16.5	7.60	17.8	13.6

Looking at the influence of land use on permeability, woodland always shows the highest values. Generally it is about 10 times higher than in the same Analysing these results shows that the content of organic matter relies on the type of soil as well on the land use. In the soil types studied the highest amounts of organic matter can be, as expected, observed under forestry land use with almost up to 9% of total mass. The lowest contents of organic matter in the investigated soils are found under agricultural land, especially cropland with only 3%.

In contrast to organic matter, pH values depend mainly on land use. Where agricultural use dominates, soils tend to be almost neutral. Under woodland, the pH decreases dramatically to values as low as pH 3.1 (mean: pH 3.75). This aspect is important because such low pH values prevent sorption of heavy metals to the soil.

On the contrary, the clay content is bound to the soil type. In our samples, the highest amounts of clay were found in Stagnic Gleysols followed by Luvisols.

On the basis if these results, a first step of developing a new method for vulnerability assessment has been undergone. Aiming, in a first step, at an enhanced vulnerability evaluation system, allowing a comparison of the new evaluation with the classical results of the Hölting method, a reclassification has to be undertaken. For the analysed parameters a repartition into 3 classes seems reasonable in order not to overinterpret the results from the laboratory test.

In the following the content of organic matter, the pH value as well as the amount of clay fraction is classified. In order to use this classification in an evaluation system each class is subsequently assigned a factor which will be applied in a new evaluation algorithm.

Considering sorption effects the content of organic matter has a major impact on vulnerability. It is however controlled by pH value due to the fact that

Table 3. Typical soil parameters (organic matter, pH, clay fraction) as a function of soil type and land use.

		Parameter			
Soil type	Land use	min.	max.	mean	stand. dev.
Organic matter content [%]					
Cambisol	Cropland	1.86	3.83	2.61	0.56
	Grassland	1.97	4.32	2.98	0.79
	Woodland	1.64	9.17	4.44	2.30
Luvisol	Cropland	2.72	3.75	3.33	0.36
	Grassland	2.70	4.87	3.69	0.79
	Woodland	7.43	9.23	8.26	0.74
Gleysol	Cropland	2.49	2.87	2.68	0.19
	Grassland	2.23	8.35	4.95	2.33
	Woodland	5.90	13.3	8.74	2.87
Stagnic Gleysol	Cropland	2.61	4.09	3.30	0.52
	Grassland	3.19	4.26	3.72	0.53
	Woodland	3.95	4.81	4.38	0.43
pH					
Cambisol	Cropland	5.22	7.15	6.24	0.61
	Grassland	5.20	6.61	5.75	0.61
	Woodland	3.16	4.48	3.70	0.49
Luvisol	Cropland	5.64	7.20	6.60	0.49
	Grassland	5.44	6.97	6.08	0.56
	Woodland	3.12	3.26	3.18	0.06
Gleysol	Cropland	5.87	6.40	6.13	0.26
	Grassland	4.72	6.82	5.82	0.79
	Woodland	3.39	5.84	4.77	0.93
Stagnic Gleysol	Cropland	5.05	6.71	6.03	0.67
	Grassland	5.34	6.17	5.75	0.41
	Woodland	3.20	3.45	3.34	0.10
*Clay content [%]**					
Cambisol	Cropland	2.5	14.0	8.2	
	Grassland	3.5	11.0	7.5	
	Woodland	6.0	18.5	12.5	
Luvisol	Cropland	10.1	16.0	13.2	
	Grassland	11.0	16.0	13.4	
	Woodland	12.0	21.0	16.5	
Gleysol	Cropland	3.0	11.0	7.0	
	Grassland	3.5	13.0	8.1	
	Woodland	4.5	11.0	7.6	
Stagnic Gleysol	Cropland	4.0	17.5	11.0	
	Grassland	11.0	20.0	15.8	
	Woodland	16.0	21.0	17.8	

* according to Kaspar (2006)

low pH values strongly inhibit sorption processes on whatever organic material is available.

Figure 4 shows a plot of cation exchange capacity versus pH value considering separately the contents of organic matter and clay.

The figure shows that sorption onto clay is almost independent of pH whereas, in contrast, sorption to organic matter is strong.

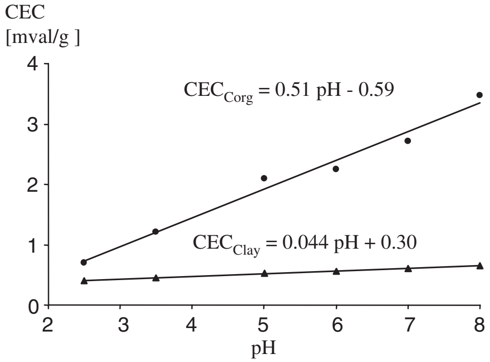

Figure 4. Cation exchange capacity in the Ap-horizon considering 0–4% org. content depending on pH according to Helling, Chesters & Corey 1964.

Table 4. Classification of organic content in the Ap-horizon and factorization.

Class	Content in mass [%]	Factorization f_{Corg}
A	≤3	1
B	3–5	1.5
C	>5	2

Table 5. Classification of clay content and factorization.

Class	Content in mass [%]	Factorization f_T
A	≤8	1
B	8–17	1.25
C	>17	1.5

Taking into account the guidelines on soil mapping (AG BODEN 2005) a classification of clay content as well as the content of organic matter has been undertaken taking into account these three classes (Tables 4 & 5).

Classification of content of organic matter considers the frequency of results in the samples. The proposed classification results in a normal distribution as shown in Figure 5.

For clay content the classification considers the different soil groups according to grain size composition. The 8% limit divides sandy soils and silty sand soils from those of higher content in silt and clay. The 17% barrier is the limit for loamy soils (AG BODEN 2005).

The values of factorisation of the clay content (Table 5) are somewhat lower than for organic material however the impact is permanent due to the fact that the coupling of CEC considering clays is much lower.

The pH value of the soil has a major impact.

As shown in Table 6 the pH value is classified according to the binding ability of heavy metals during

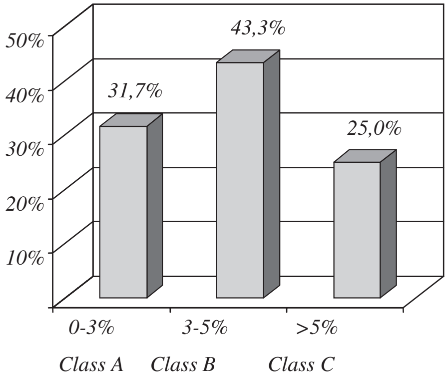

Figure 5. Distribution of classes of organic matter.

Table 6. Classification of pH value according to Gerstenberg & Smettan 2000 and factorization.

Class	pH value	Factorization f_{pH}
A	≤3	0
B	3–4.5	0.5
C	>4.5	2

Table 7. Results of CEC_{eff} evaluation according to laboratory analysis as well as granulometry (in $cmol_c/kg$).

Land use	CEC_{grains}	$CEC_{lab.}$
Cambisol		
Woodland	8.225	12.170
Cropland	8.128	13.048
Grassland	9.60	10.460
Luvisol		
Woodland	12.876	13.216
Cropland	12.383	13.078
Grassland	12.655	12.080
Gleysol		
Woodland	6.755	–
Cropland	12.548	16.258
Grassland	12.425	16.580
Stagnic Gleysol		
Woodland	10.106	13.806
Cropland	14.329	–
Grassland	21.079	–

sorption processes. For very low pH values this value equals zero, therefore the factor also has to be 0.

Globally, in this first step of development, the factorization is given in view of the possibility to compare the new approach to the existing system considering heavy metal sorption.

In view of a possible validation, cation exchange capacity can be calculated area wide on the basis of the results of the mentioned laboratory work. In addition to the described method measuring CEC with the help of coppertriethylentetramine, the CEC can be derived by analysing the granulometry of the soil sediment according to:

$$CEC_{eff(total)} = \sum [CEC_{pot(org)} \cdot pH_{Factor}] + CEC_{pot(grains)} \qquad (1)$$

where $CEC_{pot(grains)}$ equals:

$$CEC_{pot(grains)} = 0{,}5 \cdot Claycontent\ (\%) + 0{,}05 \cdot Siltcontent\ (\%) \qquad (2)$$

Comparing results of the experimental evaluation and the calculated effective CEC from grain size analysis (Table 7), it becomes obvious that laboratory values generally are between 23% and 38% higher if the clay content remains under 10%. The influence of inorganic material on CEC is hence less important than the impact of organic material. The problem in analysis may result from the incomplete oxidation of organic material during the addition of hydrogen peroxide. Hence, possibly the higher CEC results from residual organic substances.

Hence, possibly the higher CEC results from residual organic substances.

As a result of the analysis, considering copper with an atomic mass of 63,546 g/mol and an effective CEC of 20 $cmol_c/kg$ we calculate that a total mass of about 34 kg of copper ions per square meter of surface could be adsorbed (assuming a rooted depth of 1 m).

4 COMPARISON OF TRADITIONAL AND ENHANCED METHOD OF VULNERABILITY MAPPING

According to the conventional method after Hölting et al. 1995 the evaluation of groundwater vulnerability considers the following algorithm:

$$S = \left(B + \sum_{i=0}^{n} G_i \cdot M_i\right) \cdot W + Q + D \qquad (3)$$

where:

S = Point value overall vulnerability [–]
B = AWC of the soil [mm]
$\sum_{i=0}^{n} G_i \cdot M_i$ = Lithological propereties and thickness of the deeper subsoil [points/m · m]

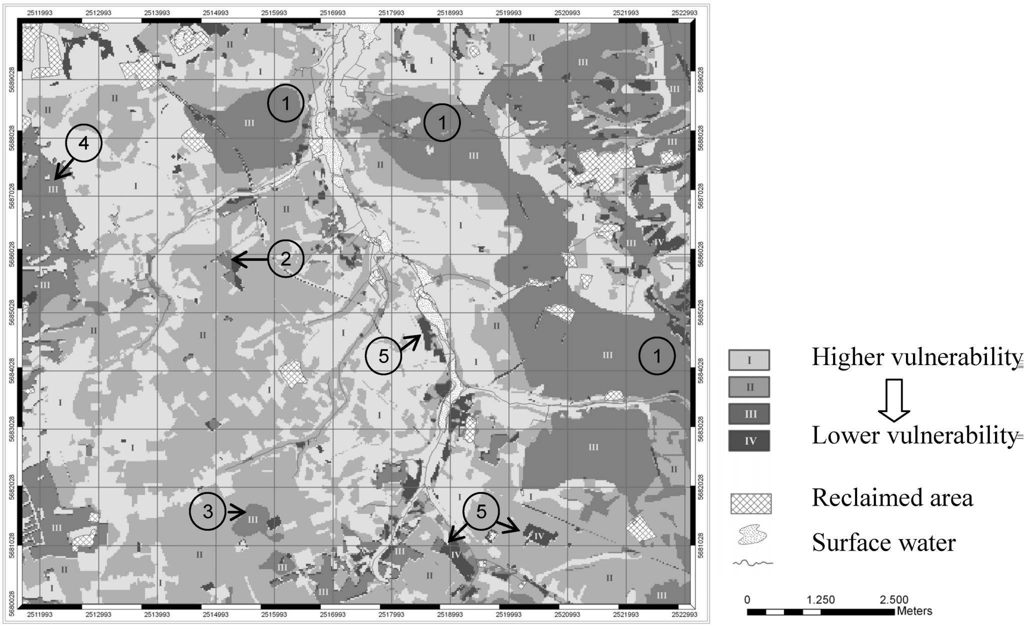

Figure 6. Map displaying the Bs1 value qualitatively classified according to vulnerability aspects. The classes I–IV are equal to those in Figure 7, so that results can be directly compared.

W = Annual seepage water [mm]
Q = Lump sum addition for perched aquifer situation [–]
D = Lump sum addition for artesian groundwater condition [–]

Considering this, the evaluation can be split into an assessment of the upper, pedological part of the vadose zone and the deeper geological underground. The present work only represents the situation of the upper soil in its pedological sense characterizing mainly the A and B horizon. Deeper "geological underground" stands for the part from the C-horizon down to groundwater level. Considering Hölting a *S*1 value can be calculated based on the classification of the available water capacity multiplied by the amount of annual seepage water (3).

$$\mathrm{S1} = \mathrm{B} \cdot \mathrm{W} \tag{4}$$

The depth employed corresponds to the rooted depth on which data is available at the geological survey NRW throughout North Rhine-Westphalia. To be able to conduct a comparison the S1 value according to Hölting is set at a base value.

Relying on this, the above mentioned factors for organic matter, pH value and clay content are allocated resulting in a new value called Bs1 (German "Boden" (=soil)), "s" for sorption and "1" for the upper part of the vadose zone considering only the A and B horizon. To complete the evaluation the following algorithm is used:

$$\mathrm{Bs1} = \mathrm{S1}[\mathrm{f_T} + (\mathrm{f_{Corg}} \cdot \mathrm{f_{ph}})] \tag{5}$$

Applying this to the area of investigation results in the following map (Figure 6) which can be compared to the traditional evaluation of S1, mapped in Figure 7.

Most striking is the clearly more structured result due to the new evaluation visible in Figure 6. A closer analysis shows that the structures rely partially on land use features on one hand but also on soil types on the other. A good example is given by the area marked as "1" in Figure 6. Here the rather rounded shape roughly follows the distribution of Luvisols.

Analysing this area in more detail shows that here a high $\mathrm{f_{pH}}$ factor (C) coincides with a medium $\mathrm{f_{Corg}}$ factor (B) to which a medium clay content (B) is added. The main land use in this area is cropland.

In contrast, the area designated with "2" shows an area rather influenced by land use. Typical are the rather edged forms delimiting class I and II. Both areas also are increased by a rather high factor whenever cropland tends to fall in class II, due to a higher clay fraction, whereas grassland remains in the initial class according to Hölting. The small difference of the factor Bs1 for these areas relative to land use shows that the primary evaluation according to Hölting also reached a level close to the next unit of classification. Typical for the area "2" is a Cambisol.

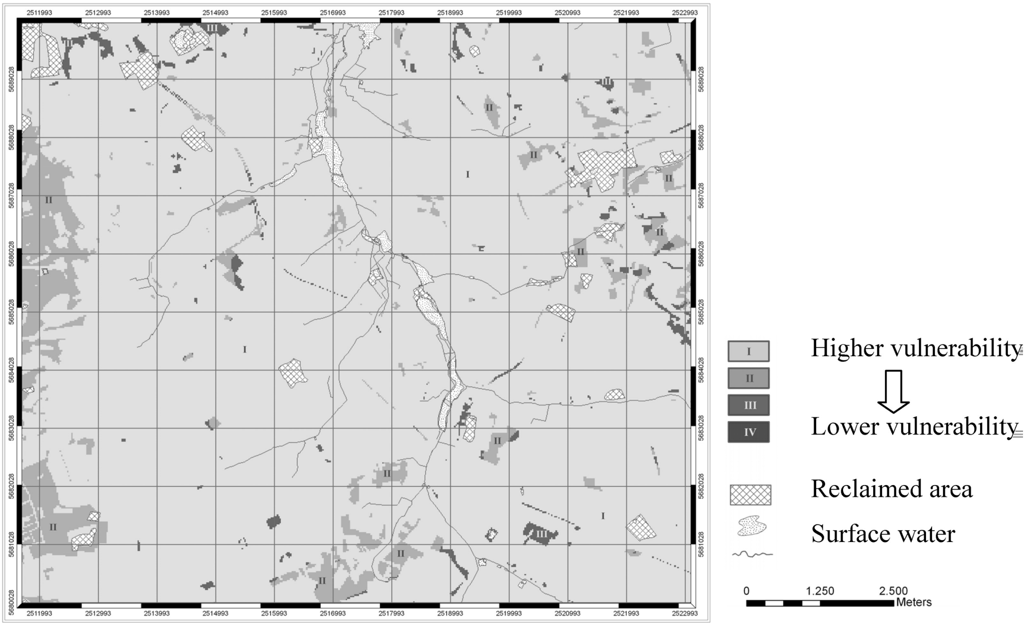

Figure 7. Map displaying the S1 value according to Hölting.

A very big difference in classification compared to the Hölting method, is shown by the areas designated with “3”. Here the occurrence of Stagnic Gleysols under cropland represents soils with a high sorption capacity (see Fig. 8) and thus possessing a high protection capacity against intruding heavy metal pollutants.

The western part of the study area is characterized by larger woodlands. Because the available water capacity under this form of land use is already rather high the primary S1 evaluation shows higher values (see Fig. 7). By comparing these areas designated with “4” they not only keep their relatively high protection status but also increase it by one class. Even though pH values are low, they have still to be classified in class B for f_{pH} thus enabling the higher content of organic matter to undergo sorption processes with intruding heavy metals. Realistically however, one has to realize that under woodland conditions the immission probability for heavy metals is rather reduced to direct deposition from the atmosphere since normally, under this land use, no sludge or fertilizer processing is observable.

Areas described as “5” represent mainly Gleysols. The value for Bs1 is, according to the evaluation algorithm, very high. This result is in agreement with laboratory analysis but contrasts with literature values considering low sorption capability for Gleysols. In the context of this work it has to be admitted that the sampling of Gleysol probes was, due to given circumstances, not simple. Therefore, the number of samples was rather low. However, the results from laboratory

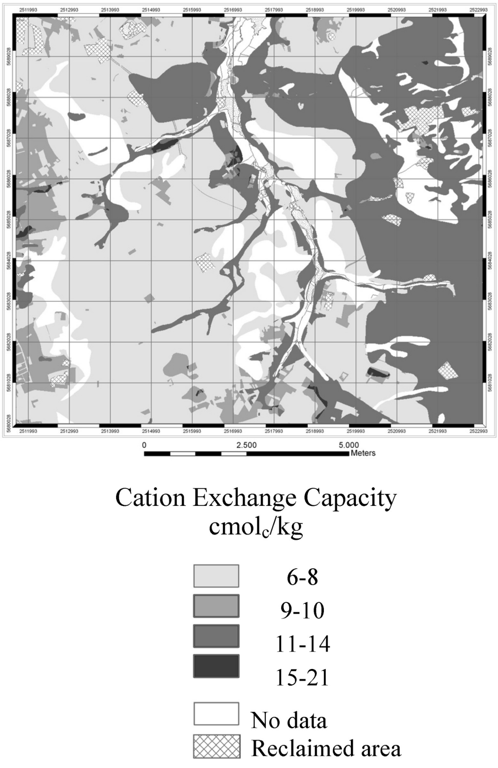

Figure 8. Map of the cation exchange capacity (no data areas correspond to other soil types than the investigated).

analysis are quite straightforward having no conspicuous deviations. A possible explanation might reside in the clay mineralogy and the differences of sorption capacities according to the type of clay minerals. This analysis is continuing though, unfortunately, the results cannot yet be integrated in the approach used so far.

5 VALIDATION AND CONCLUSION

Comparing the results of the enhanced vulnerability mapping considering the Bs1 value with the map of cation exchange capacity (Fig. 8) developed on the basis of the soil sampling and the laboratory results, a good correspondence of the results can be observed. The areas denoted as "1" and "3" (Fig. 6) with a higher Bs1 value compared to Fig.7 can also be found as areas with a higher cation exchange capacity according to laboratory analysis. The same is largely true for the areas numbered "2". It is also and especially true for areas described as "5". Here good agreement between model and laboratory evaluation can be observed. However, these results have to be verified as soon as further data become available. Overall, a validation of vulnerability mapping remains difficult. In this approach, the largely qualitative comparison of laboratory results vs. a modelled evaluation of Bs1 value (Fig. 7) shows good agreement. This would seem to demonstrate that the new evaluation method has considerable potential. This is especially true since the uniformity of the S1 evaluation, as applied so far, does not take into account observable sorption processes.

To integrate the results of the current research into a new evaluation method considering the entire vadose zone, it is important to couple percolation time to sorption processes. According to reflections considering retardation due to sorption processes this seems to be possible. Considering copper ions, the values for retardation are relatively high, which, in consequence, would lead to extremely low "percolation" times. This problem will be focussed upon in ongoing research work.

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The impact of a municipal landfill on the concentration of heavy metals in genetic soil horizons

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ABSTRACT: The impact of landfill sites upon the surrounding environment has been widely explored and a number of papers have been published on the topic. However, there are no data concerning mobility of pollutants in the soil environment. The object of this study is to determine the impact of landfill upon the soil genetic horizons around a landfill. In the research the total form of heavy metals (Cu, Cd, Zn, Cr, Co, Ni and Pb) were determined and five fractions determined by sequential extraction analysis.

Heavy metal forms determined in sequential extraction analysis show that the majority of metals (41% of total content fractions I-V) exist in chemically stable compounds, therefore they are not utilized by plants. Small amount of metals (7% of total content fractions I-V) exist in forms bound to carbonates (II fraction) and as metals of the exchangeable fraction.

Keywords: Landfill, heavy metals, speciation, soil profiles.

1 INTRODUCTION

Emission of particulate matter (transport of chemical substances), aerosols containing pathogenic bacteria and surface runoff of water from waste disposed to the landfills are considered major factors causing contamination of soils in areas adjacent to landfill sites. The emitted particulate matter may contain significant amounts of heavy metals, whose concentration in the aboveground air layer periodically exceeds permissible standards. Investigations of trace element content in particulate matter emitted from landfills to the atmosphere prove that the surrounding area is at risk of toxification (Ahmed 2001, Remon 2004).

Waste disposal is considered one of the critical factors causing environmental degradation. Therefore a detailed determination of how this kind of contamination source affects the natural environment is urgently needed. The work presented in this article is focused on such a contamination source. It describes the impact of a mature landfill on soils with special focus on the binding. and mobility of heavy metals (Cu, Cd, Zn, Cr, Co, Ni and Pb) in soil profiles.

2 MATERIALS AND METHODS

2.1 *Site characteristics*

The research was carried out at the unsealed municipal landfill site "Grundman" in Opole (Figure 1).

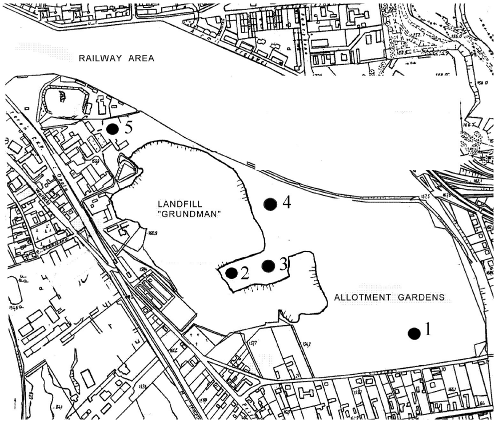

Figure 1. Study area showing locations of sampling points (1–5).

Table 1. Description of soil profiles and sampling site characteristics

Site number	1	2	3	4	5
Distance from landfill [m] and direction	220 SE	2 –	10 –	8 E	50 NW
Site character	Flat with poor runoff and dominant wind direction	Flat, location of the soil excavation – flat with poor runoff			
Land use	Sodden area	Garden plots			Sodden area
Soil type	Humic rendzina (partially deformed due to leveling process), moderately deep, formed of cretaceous limestone (Rc - gs:sk)				Transformed soil due to leveling process
Ap [cm]	0–20	0–20	0–20	0–20	0–25
A1 [cm]	20–55	20–45	20–50	20–50	25–45
A/C [cm]	55–60	45–55	50–65	50–60	45–50
C [cm]	>60	>55	>65	>60	>50

"–" between landfill areas.

The landfill is located at an abandoned opencast mine exploiting limy marl. The landfill site was investigated between the years 1994 and 1998 in order to determine the impact of the landfill on surface, groundwater, soils and plants.

Besides the built-up area, the landfill site is surrounded by arable land (garden plots), green areas and "fallow land".

The soils are humic rendzinas formed of Upper Cretaceous marls, characterized by a thick topsoil (up to 50 cm) with a 3% humus content and slightly alkaline pH.

A very thin transitional horizon of the described rendzinas is gray with numerous dark gray (humic) streaks. Lime rocks containing various degrees of erosion are found in deeper horizons. These are extremely dusty clays of a 50% floatable fraction content and approx. 22% colloids content. They are mainly categorized class II and IIIa of good and very good wheat complex. Location of excavations for soil sampling was set up taking into account the predominant wind direction. Soil excavations were made in garden plots situated in the predominant wind direction within the distance of 2–200 m from the landfill site. Soil was sampled from all genetic horizons. Several samples from each horizon of the excavation were collected for further analysis (Table 1).

2.2 *Methods*

The reaction (pH) of soil samples in water and in 1 N KCl, electrical conductivity (EC) and total (quantitative) content of heavy metals (in nitric and perchloric acids) were determined. The samples were extracted from soil excavations from particular soil horizons and dried at ambient temperature. Dry samples were ground in a ball grinder and sieved to 2 mm. Qualitative determination of heavy metals – fractional composition was performed using Tessier's (1979) sequential chemical extraction. The following five fractions were selected: fraction I – exchangeable, i.e. which could be the most easily mobilized in soil, fraction II – carbonate fraction, comprised of metals bound to carbonates which may mobilize at decreased pH e.g. in acidic soils or after acid precipitation, fraction III – iron and manganese oxide fraction, contained metals adsorbed on the surface of hydrated iron and manganese oxides which occurred in the form of a cement or coating covering mineral particles, sensitive to redox potential changes, fraction IV – organic fraction, contained metals bound with organic substance which may mobilize in significant amounts only under oxidizing conditions (in natural conditions the mineralization process progresses very slowly), fraction V – residue fraction,contained metals persistently bound to Silicate minerals and other persistent compounds. Metals in this fraction were chemically stable and biologically inactive. Samples for total (quantitative) heavy metals investigations were wet mineralized in nitric and perchloric acid (2 : 1) for 2 hours.

Analysis of heavy metal content in water extracts was carried out using the AAS method (atomic absorption spectrophotometry). Quantitative analysis was performed on a PU 9100X Unicam-Philips using calibration curves with certified standard solutions (Central Office Of Measures). Analyses were carried out with detection limits: 0.02, 0.01, 0.04, 0.04, 0.02, 0.06, 0.03 mg/kg for Cu, Cd, Zn, Cr, Co, Ni and Pb, respectively.

3 RESULTS AND DISCUSSION

Soil samples were classified according to their pH in 1 N KCl (exchangeable acidity) and pH in water (active acidity). In general, soils from excavation nos. 1–5 were predominantly basic (pH in 1 N KCl from 7.07 to 7.85 – Table 2). This fact was justified by the origin of the soils (rendzinas). The pH value increased with the decreasing depth i.e. toward the C-horizon (carbonate bedrock). The electrical conductivity of the soils fluctuated between 115 µS/cm (at depth: 10–25 cm – in soil profile no. 2) up to 305 µS/cm (at depth: 20–30 cm – in soil profile no. 4). The highest conductivity was noted in the 0–10 cm horizon in soil profiles no. 1, 2 and 5. Then for 0–25 cm horizon in soil, profile no. 5 and at 0–30 cm horizon in soil profiles no. 4 and no. 5. The effect of the landfill site and anthropopressure was observed to a maximum depth of 30 cm (soil profiles no. 4 and no. 5).

Figure 2 presents the total zinc content in soil profiles samples. Analysis of the obtained data show that the total content of zinc increased with the depth in profiles 1, 2, 4, decreased in profile 3 and in profile 5 zinc gradually increased to the depth of 20 cm and then started decreasing. The maximum level of zinc was observed in profile 1 (from 577 mg/kg d.w. at the depth between 0–10 cm – II° level of contamination by Institute of Soil Science and Plant Cultivation – (ISSPC), to 1783-mg/kg d.w. at a depth of 20–55 cm - III° level of contamination by ISSPC. These results are 2–5 times higher than the maximal level (300–350 mg/kg d.w.) according to regulation. Fourfold lower amounts were determined in profiles 4, 5 and 3; the lowest value was observed in profile 2, however on account of its content it was assigned the I° level of contamination by ISSPC. Our values confirm data published by other authors (Remon 2005, Moller 2005, Cicek 2004, Critto 2003). Sequential extraction of zinc in soil from profiles (Figures 5, 7, 9, 11, 13) shows that Zn in profiles 1–5 was mainly bound with ferrous and manganese oxides (fraction III) and next with aluminosilicates (fraction V) which confirms data published by Lu (2003). In soil profiles 1, 4, 5 zinc concentrations bound with fraction V increased with depth.

Figure 2 presents the total content of lead in samples from soil profiles. Analysis of the obtained data shows that the total content of lead increased with the depth (form 186 mg/kg d.w. depth 0–10 cm – I° level of contamination by ISSPC and to 281.8-mg/kg d.w. at a depth of 20–55 cm – II° level of contamination by ISSPC) only in profile no.1. These results are 2–3 times higher than the maximal level (100 mg/kg d.w.)

Table 2. Basic properties of soil profiles 1–5 (n = 5).

Profile		Nr 1					Nr 2				Nr 3				
Depth [cm]		0–5	5 – 10	10–20	20–55	55–60	0–10	10–25	25–45	45–50	0–10	10–20	20–40	40–55	55–60
Reaction in	H_2O	7,48	7,71	7,71	7,82	7,92	7,68	7,62	7,93	7,86	7,54	7,43	7,82	7,88	7,96
	1 M KCl	7,12	7,16	7,15	7,20	7,28	7,10	7,08	7,45	7,13	7,13	7,08	7,32	7,49	7,85
Conductivity [$\mu S * cm^{-1}$]		253	214	116	209	187	209	115	123	189	247	248	228	177	143

Profile		Nr 4					Nr 5			
Depth [cm]		0–10	10–20	20–30	30–50	50–55	0–15	15–25	25–45	45–50
Reaction in	H_2O	7,67	7,65	7,53	7,96	8,02	7,45	7,56	7,92	7,85
	1 M KCl	7,12	7,10	7,08	7,28	7,29	7,07	7,15	7,28	7,37
Conductivity [$\mu S * cm^{-1}$]		242	229	305	224	199	295	223	166	173

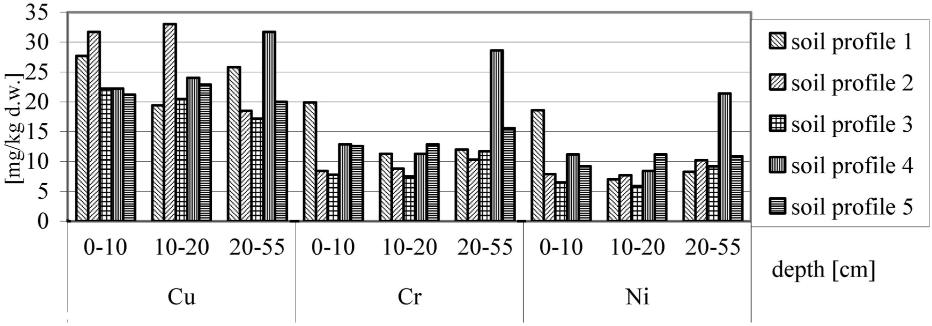

Figure 2. Total content of Zn and Pb in the successive horizons of soil profiles 1–5 [mg/kg d.w.].

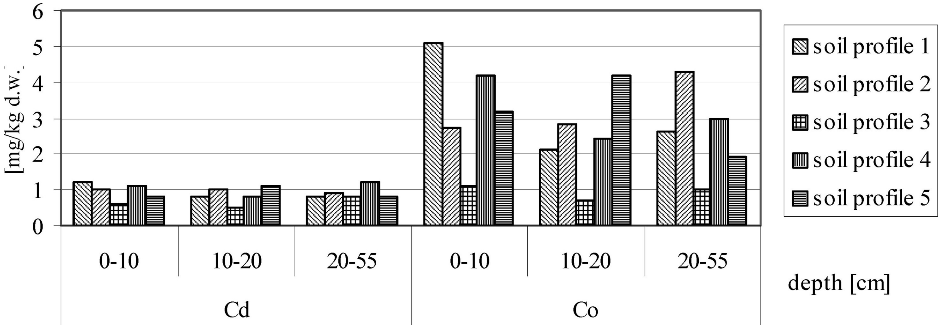

Figure 3. Total content of Cu, Cr and Ni in the successive horizons of soil profiles 1–5 [mg/kg d.w.].

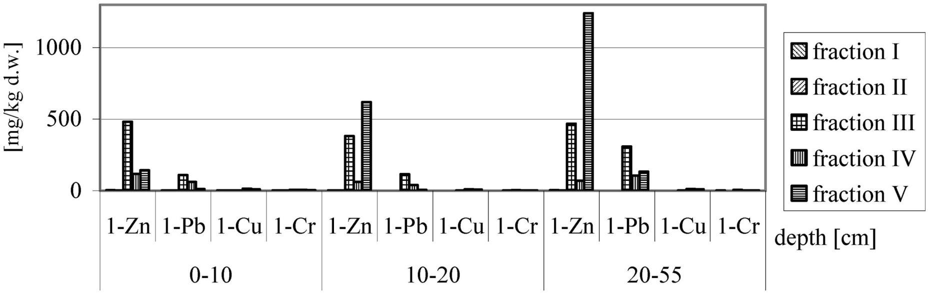

Figure 4. Total content of Cd and Co in the successive horizons of soil profiles 1–5 [mg/kg d.w.].

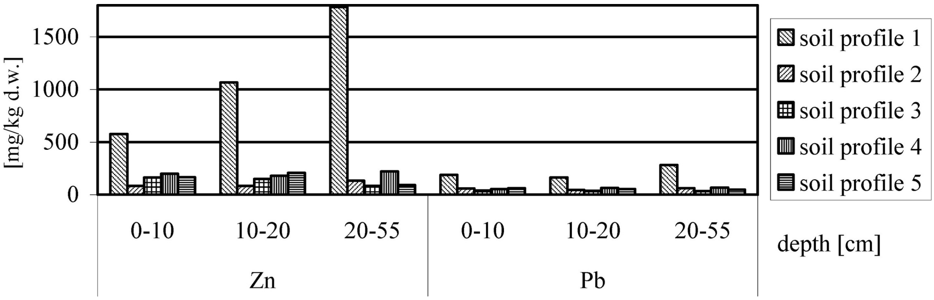

Figure 5. Metal contents in fractions I–V of the horizons studied. Soil profile 1 [mg/kg d.w.].

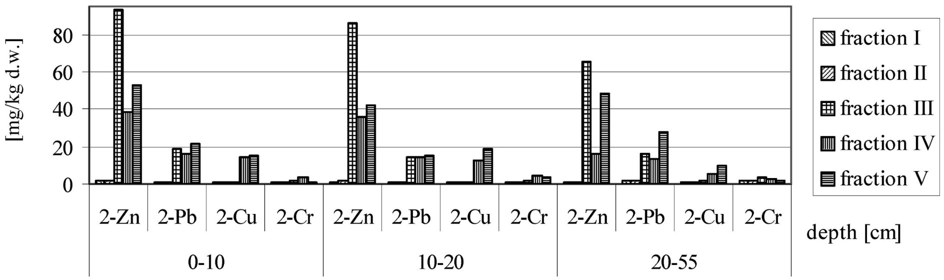

Figure 6. Metal contents in fractions I–V of the horizons studied. Soil profile 1 [mg/kg d.w.].

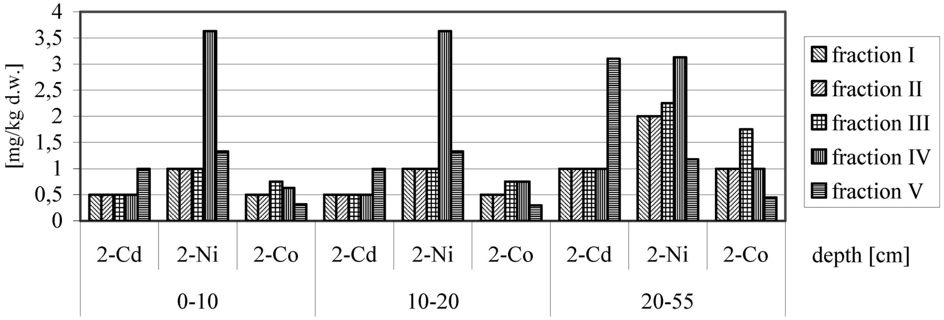

Figure 7. Metal contents in fractions I–V of the horizons studied. Soil profile 2 [mg/kg d.w.].

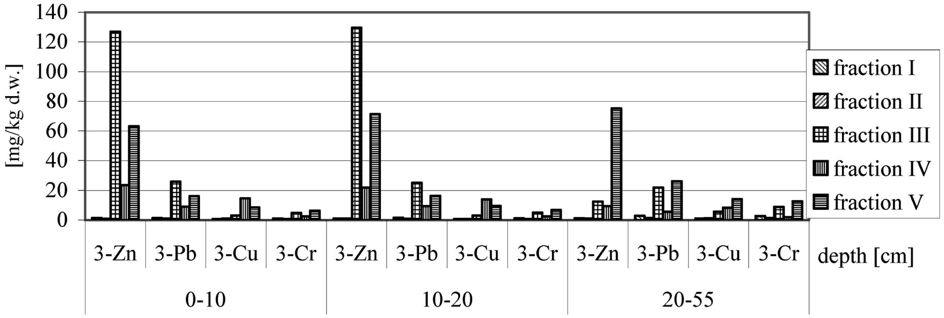

Figure 8. Metal contents in fractions I–V of the horizons studied. Soil profile 2 [mg/kg d.w.].

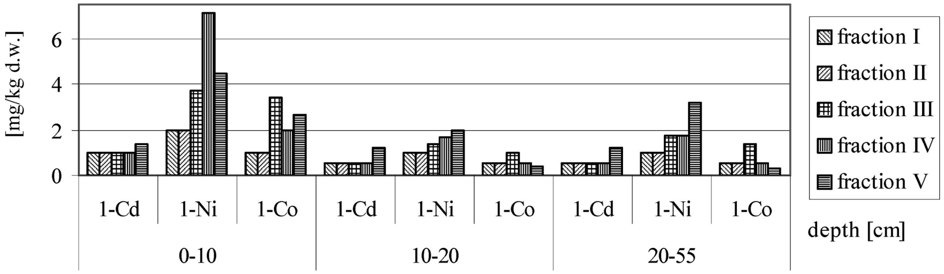

Figure 9. Metal contents in fractions I–V of the horizons studied. Soil profile 3 [mg/kg d.w.].

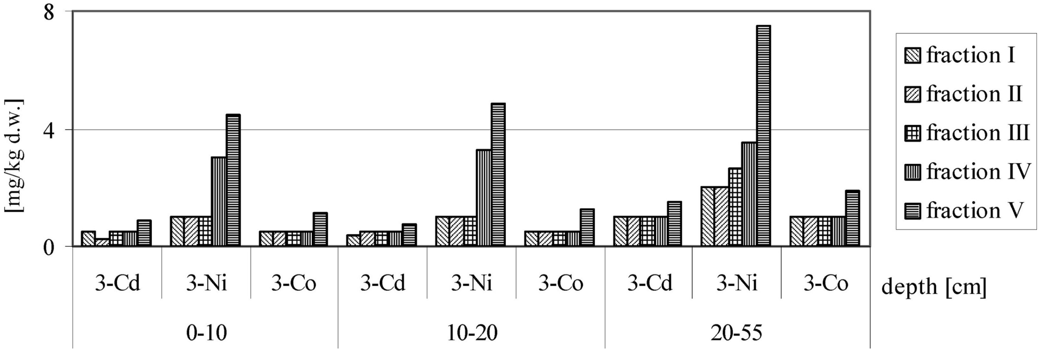

Figure 10. Metal contents in fractions I–V of the horizons studied. Soil profile 3 [mg/kg d.w.].

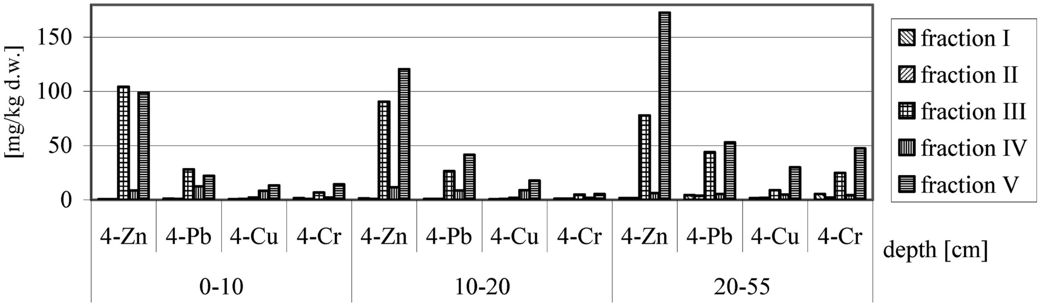

Figure 11. Metal contents in fractions I–V of the horizons studied. Soil profile 4 [mg/kg d.w.].

according to regulation of Minister of Environment. Comparable data was determined by Cicek (2004) and Critto (2003). In the other profiles it was low (defined by ISSPC as natural) and on similar level in all profiles confirmed by Moller (2005). Sequential extraction of lead in soil from profiles extracted for the purposes of this paper (Figures 5, 7, 9, 11, 13) shows that Pb in profiles 1–5 was mainly bound with fraction III and then with IV, in comparable amounts. Pb occurred in decreasing sequence in fractions IV and V and equally small Pb amounts were detected in fractions II and I. This proves the low probability of Pb being washed out from soil i.e. very limited availability for plants.

The maximum level of cadmium (Figure 4) was observed in profiles 1 and 4 (both 1.2 mg/kg d.w. I° level of contamination by ISSPC and lower than in Regulation – 4–5 mg/kg d.w.). The total cadmium content decreased with the depth in soil profiles no. 1 and no. 2. In soil profiles no. 3 and no. 4 Cd content degreased up to the depth of 20 cm, then an increase was noted. In soil profile no. 5 an opposite tendency was observed i.e. the total Cd content increased to the depth of 20 cm, then it suddenly decreased. The background concentration cited by Kabata-Pendias (1985) was ten times lower than the data obtained in this work. Soil polluted by industrial dust reaches much higher concentrations – up to 21.7 mg/kg d.w. (Cicek 2004). Speciation analysis (Figures 6, 8, 10, 12, 14) shows, the highest amounts of cadmium bound in the residue fraction (V) for all soil samples taken from profiles. Much smaller amounts of cadmium (in all soil profiles) occurred bound in decreasing sequence in fractions III, IV, II and I. Additionally, it was observed that cadmium content bound in fraction V increased with the depth in soil profiles no. 2, no. 3 and 5 while, in soil profile no. 1, it decreased. In the case of soil profile no. 4, a decrease of Cd content bound in fraction V to the depth of 20 cm was recorded, subsequently the content of cadmium increased.

The total content of copper (Figure 3) was low (defined by ISSPC as natural). Analysis of the obtained data allows us to state that the maximum total content of copper was noted in profile 2 and 4 (from 33 to 32 mg/kg d.w.). These results are lower than the maximal level (100–150 mg/kg d.w.) stated in the regulations. Higher values (up to 470 mg/kg d.w.) are cited by Cicek (2004), Critto (2003), Madrid (2002) and Moller (2005). Much lower values (max. 6.8 mg/kg d.w.), were cited by Mwiganga (2005). Sequential extraction of copper (Figures 5, 7, 9, 11, 13) in soil from profiles showed that Cu in profiles 1–5 was mainly bound with fraction V and IV, which confirms

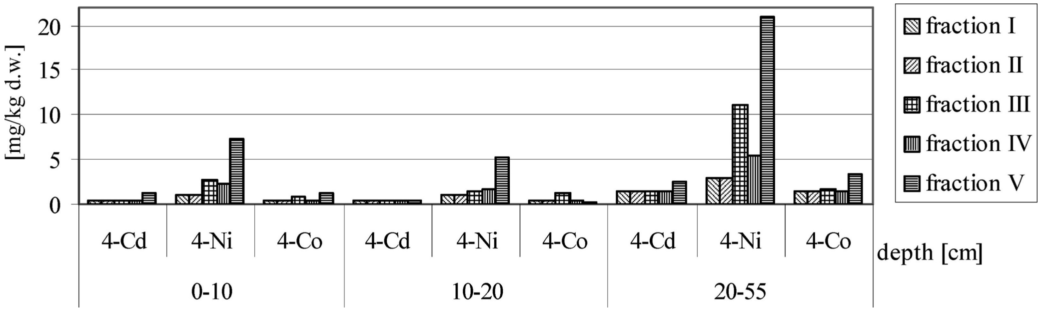

Figure 12. Metal contents in fractions I–V of the horizons studied. Soil profile 4 [mg/kg d.w.].

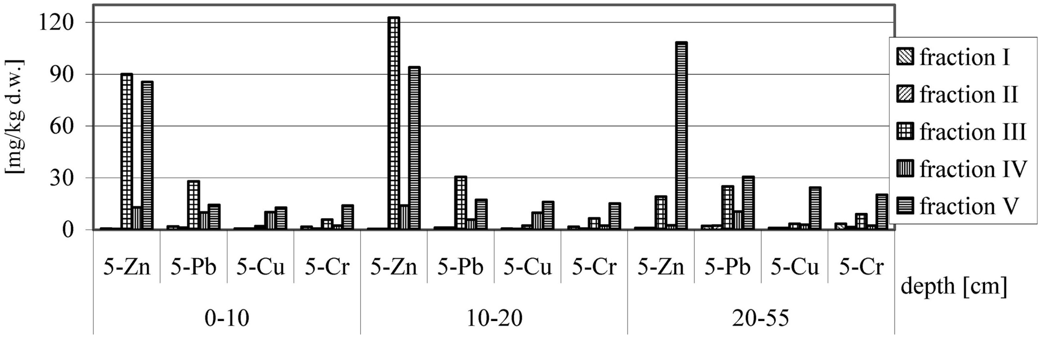

Figure 13. Metal contents in fractions I–V of the horizons studied. Soil profile 5 [mg/kg d.w.].

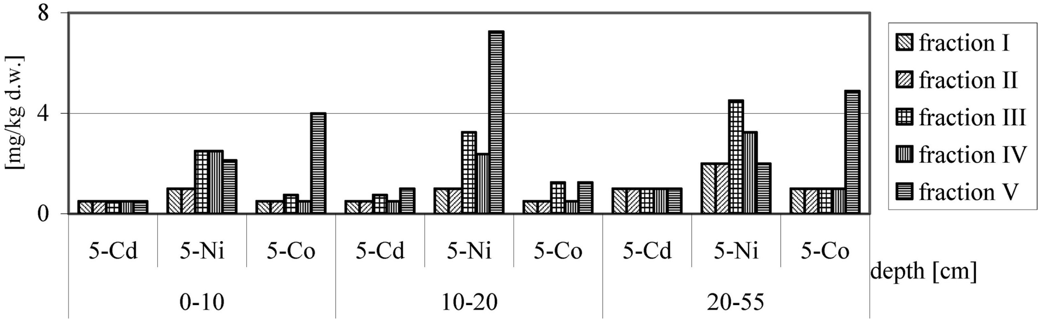

Figure 14. Metal contents in fractions I–V of the horizons studied. Soil profile 5 [mg/kg d.w.].

data cited by Lu (2003), and in much lower amounts with fractions III, II and I. Analysis of the obtained data indicates that the content of copper bound with fraction V increased along with the depth in profile 3, 4 and 5.

The total content of chromium (Figure 3) was low (defined by ISSPC as natural). Analysis of the obtained data shows that the maximum total content of chromium was present in soils of profiles 4 (29 mg/kg d.w. – 20–55 cm) and profile 1 (20 mg/kg d.w. – 0–10 cm). These results are lower than with the maximal level (100 mg/kg d.w.) stated in the regulations. Comparable data by Dudka (1992), Madrid (2002) and Critto (2003) were noted. Analysis of the obtained data illustrates that the content total content of chromium increased with the depth in profile 2, 3, and 5 and decreased in profile 1. In profile 4 with the chromium content decreases to depth 20 cm, and below that – increases strongly. Sequential extraction of chromium (Figures 5, 7, 9, 11, 13) in soil from profiles shows that Cr is bound with fraction V, III and IV in decreasing sequence, confirming data cited by Lu (2003).

Total forms of remaining metals (Co, Ni – Figures 4 and 3) were low (Co- 5.1 mg/kg d.w. – 0–10 cm in profile 1, Ni – 21 mg/kg d.w. – 20–55 cm, in profile 4) and concentrations are defined as background contents for these types of soils. These results are lower than the maximal level (30 and 100 mg/kg d.w. for cobalt and nickel respectively) stated in the regulations. Comparable data have been published by Dudka (1992), Moller 2004 and Madrid (2002). Sequential extraction of these metals (Figures 6, 8, 10, 12, 14) shows that they are bound mainly with fraction V (residues). In much lower quantities Co and Ni in soils of all profiles were bound with fraction II (carbonate) and I (exchangeable).

4 CONCLUSIONS

The work presented above allows us to draw the following conclusions: the maximum level of heavy metals (total forms) was observed down to soil levels are of 30 cm depth. In the extracted profiles higher values of Cd, Pb and Zn (> natural concentrations) were noted thus these profiles were classified as I–III level of contamination by ISSPC. The concentrations of Cr, Cu, Ni and Co were low (compared to natural). The maximum level of zinc and lead increased along with the depth in profile 1 located far from with the landfill (about 220 meters) in the predominant wind direction. The speciation extraction of all analyzed heavy metals for the soil from the discussed profiles showed that the main fraction occurs (about 41% of sum content of fractions I–V) in chemically stable and biologically inactive forms determined as fraction V – residue. A significant amount (about 26% and 18% of sum content of fractions I–V) of heavy metals, mainly Zn and Pb were bound with ferrous and manganese oxides and organic matter (fraction III and IV). The smallest amount of the discussed trace elements was bound to carbonates (fraction II) and in the exchangeable fraction (fraction I), which proves their limited utility for plants, soil and water. The highest concentrations of Zn, Pb and Cd in soil profiles to a depth of 30 cm (quantity) showed an influence of the long-term exploitation of landfill. However the reaction of soils and leaching of metals (in particular fractions) showed only little risk to the ecosystem.

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The influence of the wastes disposal on heavy metals in soil and plants

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ABSTRACT: The aim of the study was to evaluate the influence of the furnace wastes landfill on the heavy metals accumulation in soil and plants. The landfill covers 45 ha and has been used since 1962. The amount of wastes stored in the dump is estimated at 4 million tons. Evaluated correlation indexes usually indicate that the amount of heavy metals (Pb, Cd, Co, Cr, Ni, Mn, Zn, Cu) in the roots of vegetables is well correlated with their amount in soil. Whereas the amount of such metals as manganese and zinc in the soil was highly correlated to their contents in tree and vegetable leaves, the correlation in the case of lead was low. The content in tree and vegetable leaves was due rather more to dust deposition than to the uptake from soil. Metal concentrations in soil, however, strongly influenced their content in roots.

Keywords: Heavy metals, pollution, fly ash, landfill, soil, plants.

1 INTRODUCTION

Fly ash, resulting from combustion of coal at high temperatures, is regarded as a problematic solid waste all over the world. Many possible beneficial applications of fly ash are being examined to minimize waste, decrease disposal costs and to provide value-added products (Jala & Goyal 2006). Whenever the disposal of fly ashes and slags from coal-fired power stations and thermal power plants is carried out the influence of this activity on the environment should be taken into account. This influence may reveal itself in various forms. On the one hand, the furnace wastes may constitute the source of the air pollution by dusts, and on the other, it can be a mineral fertilizer rich in macro- and micronutrients.

It is possible to properly evaluate the threat posed by the disposed wastes to the environment provided that the chemical composition of the stored wastes as well as that of the soils adjacent to the landfill is known. The best indicator of the environmental risk is a determination of the pollution in plants – this reflects the amount of the elements present in soil that may enter the biosphere.

The aim of the present study was to evaluate the influence of furnace wastes landfill on heavy metals accumulation in soil and plants.

2 MATERIALS AND METHODS

2.1 *Description of research object*

The examined furnace waste landfill is situated on the left bank of Vistula river (5 m above the river level). The substructure of the landfill and of the adjacent area consists of Quaternary fluvial deposits, sands of variable granulation, and with silt interbeddings. Their total thickness is about 70 m. The contemporary deposits consist of alluvial deposits and, in swampy land depressions, of peats.

The landfill covers 45 ha. It is bordered on one side by a dyke and on the other by a railway siding. During its use from 1962 to 1985 it was filled to the top of the dyke (90 m above sea level). During the succeeding years its level was raised to 114 m above sea level. The amount of wastes stored in the dump is estimated at 4 million tons. The landfill consists of the reclaimed part (20 ha), covered by a 40 cm – layer of soil on which grass grows, and a part which is still used, where the wastes are disposed.

Furnace wastes were being brought to the landfill during the heating season, and then in spring they were removed and used for various purposes. A 500 m safety zone was established around the landfill. It covers 285 ha, 130 ha of which are agriculturally used lands, and the rest are ecological wasteland, water bodies, roads and built-up residential areas.

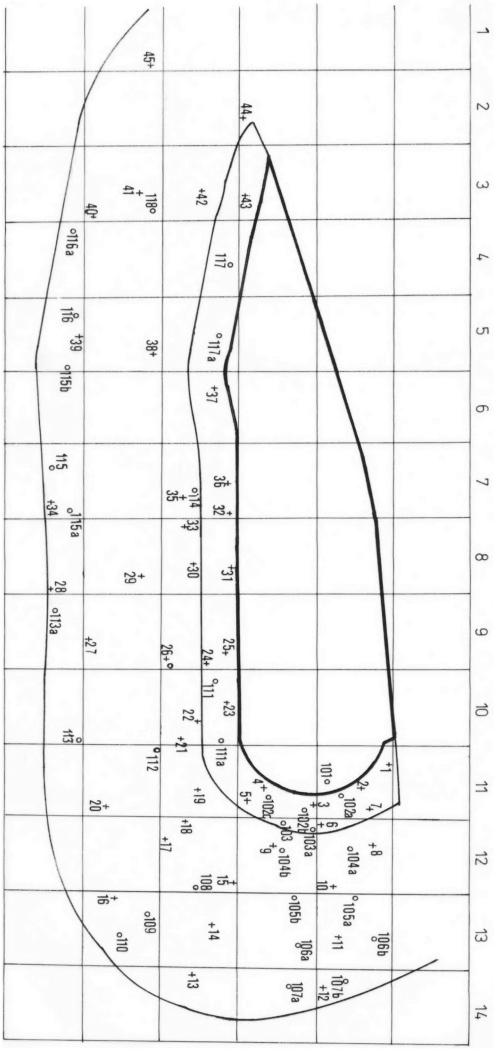

Figure 1. Localization of examination samples:
+1–45 samples of soil
• 101–118 samples of plants.

The soils in the vicinity of the ash landfill are typical floodplain soils. They are neutral alluvial soils containing in the upper layer 35–50% of particles <0.22 mm.

Because of the very good soils the lands around the landfill are used for vegetable growing, orchards and trees' nurseries (Przegląd Ekologiczny 2005).

The location of the landfill and the sampling scheme are presented in fig. 1. The samples of furnace wastes were collected from twelve points in the still-in-use part of the landfill, from the depth of 0–20 cm. A mean mixed sample was prepared for the analysis. In order to evaluate the level of the topsoil pollution soil samples were also taken from the 500 m-safety zone, from the layers 0–20 and 20–40 cm.

2.2 *Chemical analysis*

The soil and waste samples were dried and sieved through a 1 mm sieve. Afterwards, the soil samples were pyrolysed at 480°C, and then both soil ashes and waste samples were dissolved in 20% HCl (Allen et al. 1974). The resulting solutions were analysed for the content of heavy metals using the AAS technique (Morton & Roberts 1991). The pH of the analysed samples was measured in H_2O using the potentiometric method. The analysed plant material was ripe vegetables collected on the fields in the vicinity of the dump site and tree leaves collected from the research area. The plant material, after drying and grinding, was treated in the same way as the soil samples.

3 RESULTS AND DISCUSSION

The stored ash, when dry, is loose friable and very dustable. It is very uniform in terms of its granulometric composition and corresponds to a light silty loam. It is alkaline (pH 8.9) (Tab. 1). The average content of the majority of heavy metals in this material is close to the upper limit set for the unpolluted soils (Kabata-Pendias & Pendias 1992).

In order to determine the influence of the distance from the landfill's edge on the accumulation of heavy

Table 1. Main physical and chemical properties of fly ash.

Percent of fraction				pH in H_2O	Fe	Mn	Zn	Cu	Pb	Cd	Co	Cr	Ni
>1.0	1.0–0.1	0.1–0.02	<0.02		%	$mg \cdot kg^{-1}$ d.w.							
–	37	40	23	8.9	0.32	184	63	64	38	1.8	12	56	31

metals in soils and plants on areas adjacent to the landfill, three research zones were established. The first zone – A, next to the landfill was 0.1 km wide. From this zone the soil samples No. 1–7, 23–25, 31, 32, 36, 37, 43 and plant samples No. 102, 103, 111, 117 were taken. The second zone – B was located on the north-eastern side of the landfill (the direction of the prevailing winds in Poland). From this zone soil samples No. 1–12 and plan samples No. 102–107 were taken. The third zone – C, was located on the southern side of the landfill. From there the soil samples No. 13–45 and plant samples No. 108–110 were taken.

3.1 *Soils*

The results of study indicate that the content of the determined elements in soil was higher in the layer 0–20 cm than in the layer 20–40 cm (Tab. 2, Fig. 2). This is probably due to the strong binding of the trace elements by the soil components, particularly by the organic matter. (Kuo et al. 1983).

The analysis of the average content of heavy metals in the upper layer of soils from the given zones showed that, except for Pb, this parameter was the highest in zone B. The concentrations of Mn, Zn, Cu, Pb, Cd, Ni in soils were higher in zone A than in zone C. This distribution of heavy metals indicates that the main factor responsible for the enrichment of soils within each zone with heavy metals was the direction of winds blowing off the ashes stored on the landfill, and only then the distance from the landfill's edge (0,1 km).

The significant influence of the winds' direction on heavy metal concentrations in soils adjacent to this landfill was supported by the data on dust deposition (Przegląd Ekologiczny 2005). In the zone B it was $161\,\mathrm{g} \cdot \mathrm{m}^{-2} \cdot \mathrm{y}^{-1}$, while in zones A and C $137\,\mathrm{g} \cdot \mathrm{m}^{-2} \cdot \mathrm{y}^{-1}$. These values were below the permissible value, which is $200\,\mathrm{g} \cdot \mathrm{m}^{-2} \cdot \mathrm{y}^{-1}$ (The Decree of the Minister of the Environment, Natural Resources and Forestry 1990). The dust falls recorded on the research area, originate from both the landfill and the

Table 2. Average content of heavy metals in investigated soils depending on the distance from landfill and the wind direction.

Location	Depth cm		Fe %	Mn	Zn	Cu	Pb	Cd	Co	Cr	Ni
				$\mathrm{mg} \cdot \mathrm{kg}^{-1}$ d.w.							
A (15 No)	0–20	mean	1,26	395	58,3	11,2	29,5	1,11	5,9	19,9	25,3
		SD	0,46	175	16,7	3,0	26,2	0,62	3,0	2,7	8,4
		min.	0,68	208	33,0	6,1	8,0	0,60	2,0	16,0	11,0
		max.	2,48	760	85,0	16,8	94,0	2,90	16,0	24,0	43,0
	20–40	mean	1,17	329	47,0	8,4	24,7	0,74	4,4	18,1	22,3
		SD	0,35	147	14,3	2,2	23,3	0,38	2,9	2,5	7,6
		min.	0,79	201	30,0	5,7	10,0	0,40	2,0	11,0	15,0
		max.	2,25	780	79,0	13,8	76,0	1,50	14,0	21,0	44,0
B (15 No)	0–20	mean	1,45	508	62,3	11,8	18,5	1,34	6,1	20,3	29,8
		SD	0,51	178	17,0	3,6	6,7	0,66	3,4	2,7	9,5
		min.	0,90	290	36,0	7,2	12,0	0,40	2,0	16,0	19,0
		max.	2,48	850	90,0	16,8	31,0	2,90	16,0	24,0	49,0
	20–40	mean	1,36	435	53,3	8,9	13,3	0,93	4,3	17,8	25,7
		SD	0,44	185	16,0	2,9	3,2	0,57	3,2	2,6	9,7
		min.	1,01	270	32,0	6,5	9,0	0,30	2,0	11,0	15,0
		max.	2,25	820	84,0	14,4	18,0	2,20	14,0	21,0	44,0
C (15 No)	0–20	mean	0,94	264	45,9	8,1	27,9	0,76	5,5	20,5	20,9
		SD	0,21	58	12,2	2,5	31,9	0,25	1,3	2,9	6,1
		min.	0,45	144	28,0	4,5	8,0	0,30	2,0	12,0	11,0
		max.	1,35	420	77,0	15,0	145,0	1,50	8,0	29,0	37,0
	20–40	mean	0,91	258	40,8	7,5	25,7	0,48	3,7	19,4	19,5
		SD	0,18	58	8,9	1,9	28,0	0,15	1,2	3,0	5,8
		min.	0,56	100	29,0	4,2	6,0	0,30	2,0	12,0	6,0
		max.	1,24	400	69,0	12,4	124,0	0,90	7,0	30,0	32,0
acceptable contents in the arable soils*			–	1500–3000	150–400	50–140	100–500	1–8	20–50	75–600	30–100

* values given by the various authors and recommended by EU (Kabata-Pendias & Pendias 1999)

A – for samples collected in the zone adjacent to the landfill 0,1 km (no: 1–7, 23–25, 31, 32, 36, 37, 43)

B – for samples collected north-eastwards from the landfill (no: 1–12)

C – for samples collected southwards from the landfill (no: 13–45)

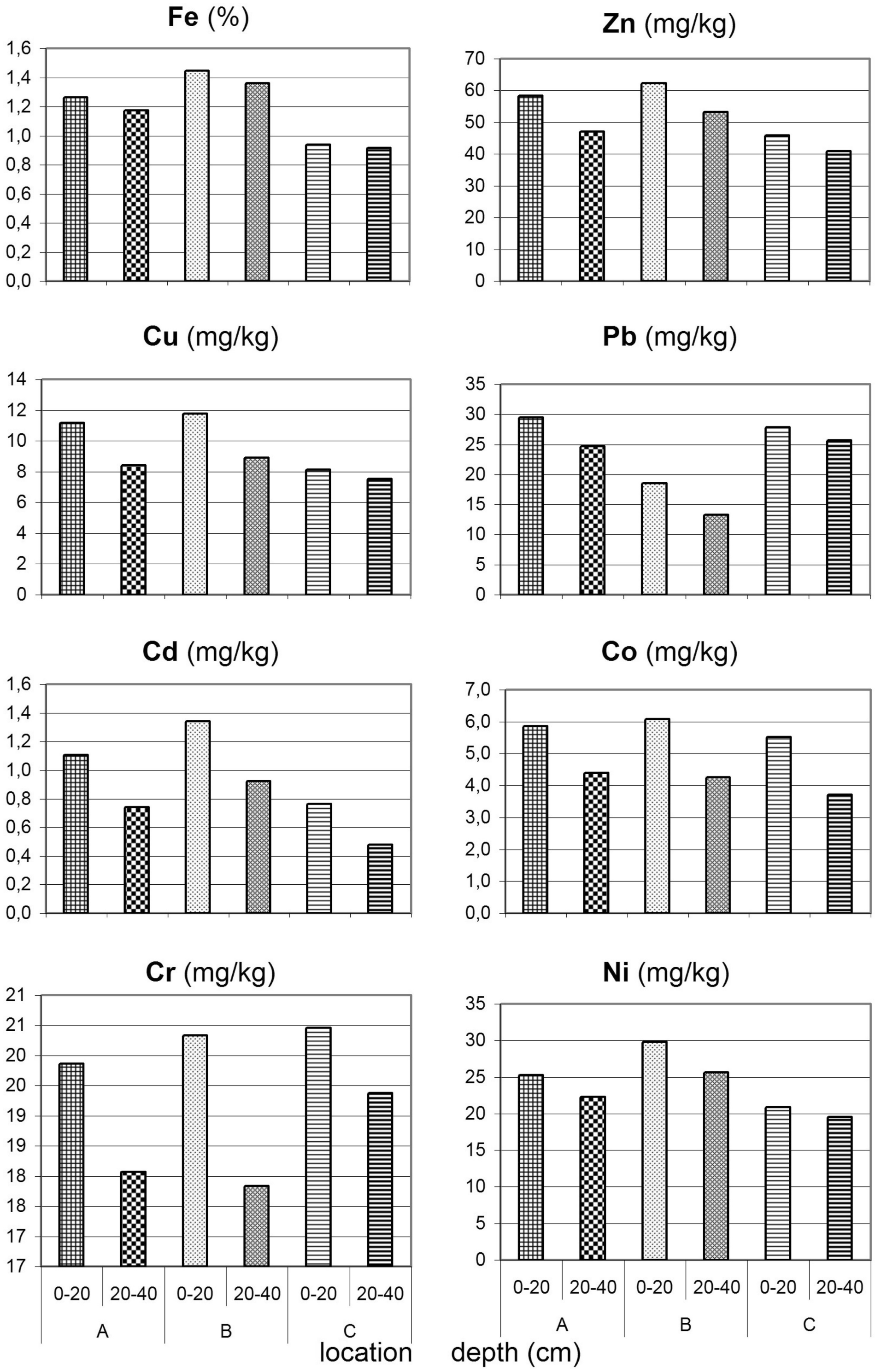

Figure 2. Dependence of heavy metals in investigated soils on the distance from landfill and wind direction.

thermal power plant located 5 km from the landfill. Intensive agricultural activity in this zone and transport are other sources of the dust emissions. Therefore, the transport of the ashes to the landfill is the most probable cause of the elevated concentrations of lead in the upper layer of soils situated in the zone A.

Despite the observed tendency for the accumulation of heavy metals in the upper layer of soils located on the research area it has to be stated that the concentration of these elements is within the limits set for the unpolluted Polish soils originating from sedimentary rocks (Czarnowska & Gworek 1990). The slightly elevated content of Cd in these soils may be attributed to agricultural activities, mainly to the application of the phosphorus fertilizers (Kabata-Pendias & Pendias 1992).

3.2 *Plants*

The concentration of heavy metals was determined in the leaves of the trees (*Sambucus nigra, Prumus cerasus, Populus alba*), the aboveground parts of the vegetables (*Daucus carota, Beta vulgaris, Petroselium sativum, Brassica oleracea, Lactuca sativa*) and other plants (*Medicago sativa*), and in the roots of the vegetables (*Daucus carota, Petroselium sativum, Beta vulgaris*). All these values are presented in Table 3.

Another table – Table 4 presents the results of the correlation between the concentrations of heavy metals in soils and parts of plants in all three examined soils. These results show that, in most cases, there is a positive correlation between the content of the quantified elements in soils and plants growing on them, in relation to the designated zones. Also, for most of the examined sampling points, this correlation is significant.

In the examined tree leaves the highest content of metals was observed for plants growing in the zone B. This, in turn, means that the factor most likely influencing this parameter was the dustfall. The statement can be further supported by experiments in which the content of heavy metals was determined in unwashed and washed leaves of lettuce (*Lactuca sativa*) and alfalfa (*Medicago sativa*) collected on the research area. These studies indicated that the significant amounts of the elements such as Fe, Pb and Cr, Cd were removed with dust washed-off from the aboveground parts of these plants.

In case of the analysed vegetables' roots the opposite relationship was noted. In the plant samples collected in the zone B, the content of the examined heavy metals was lower than in the samples collected in zones A and C. This may be caused in the latter zones by the higher fall of dust having a greater sorption capacity towards heavy metals. Moreover, the greater dustfall increased the pH of the soil, thus decreasing the mobility of the discussed elements. Similar results on the influence of the ashes application on the bioavailability of Zn, Cd, Ni and Cu to plants and on the pH of soils were obtained by Scotti et al. (1998).

The Cd content in lettuce, regardless of the zone from which the material was collected and the method of analysis, is worth special attention. It is much higher than in any other analysed plants. This can be attributed rather to the fertilization than to dust deposition. This is even more probable because this plant has a very short vegetation period. It is well known that the phosphorous fertilizers contain significant amounts of cadmium – 0.4–40 mg kg^{-1}. This makes them the significant source of pollution of soils, and consequently plants, with this element (Górecki 1990). According to Polish law the upper limit of cadmium in leafy vegetables is 0.05 mg kg^{-1} fresh weight, which corresponds to 0.4–0.5 mg kg^{-1} dry weight (Dziennik Ustaw 2001). The lettuce grown in the vicinity of the landfill contained 1.2–1.7 mg kg^{-1}, which confirmed the high level of pollution of soils. Lettuce of this quality can not be consumed by humans. However, the analytical methodology used in the study did not allow us to determine what percentage of cadmium resulted from the use of phosphorous fertilizers, and what from emission from the landfill. Cadmium is regarded as the metal of most concern due to bioaccumulation through the soil-plant-animal food chain (Peijnenburg et al. 2000).

3.3 *Statistical analysis of the results*

Evaluated correlation indexes usually indicate that the amount of heavy metals in analyzed vegetable roots is strongly associated with their soil concentration, independent of the location of sampling. (Tab. 4).

For most of the samples the level of dependency was highly significant. When trees' and vegetables' leaves are considered these dependencies occurred in a substantially smaller number of samples. Significant statistical dependencies were mostly related to the content of manganese and zinc, for other metals they occurred occasionally and, in case of chromium, lead and nickel, they did not occur at all. A similar relation with regard to lead was discovered by Finster et al. (2004); a significant correlation between contamination in root and soil, and highly insignificant correlations between contamination in roots and leaves and virtually no correlation between soil contamination and its contents in fruits.

Generally, we can say that the amount of such metals as manganese and zinc in the soil was highly correlated to their contents in plants. This relation is lowest in the case of lead. The levels of other analyzed heavy metals lie between those two results. Similar results where noted by Intawongse et al. (2006) – their result showed that the uptake of Cd, Cu Mn and Zn by plants corresponded to the increasing level of soil contamination, while the uptake of Pb was low.

Table 3. Average content of heavy metals in investigated plants ($mg \cdot kg^{-1}$ d.w.).

Plant 1	Location/ Zone 2	Fe 3	Mn 4	Zn 5	Cu 6	Pb 7	Cd 8	Co 9	Cr 10	Ni 11
Leaves of trees										
Sambucus nigra	A	294 ± 68	42 ± 9	34 ± 9	19.6 ± 4.9	5 ± 1	0,3 ± 0.06	1.5 ± 0.4	20.1 ± 5.2	6.5 ± 1.6
	B	446 ± 104	62 ± 16	38 ± 10	15.2 ± 3.2	9 ± 2	0.2 ± 0.06	1.5 ± 0.3	20.1 ± 4.6	8.6 ± 1.9
	C	305 ± 72	74 ± 19	33 ± 7	16.9 ± 4.4	7 ± 2	0.2 ± 0.06	1.8 ± 0.5	19.2 ± 4.5	7.0 ± 1.9
Prunus cerasus	A	252 ± 58	33 ± 8	18 ± 7	18.4 ± 4.2	9 ± 2	0.2 ± 0.04	1.8 ± 0.5	20.1 ± 4.3	6.9 ± 1.8
	B	270 ± 70	34 ± 7	23 ± 5	15 ± 4.4	6 ± 1	0.5 ± 0.15	1.7 ± 0.5	34.1 ± 8.0	7.1 ± 1.8
	C	240 ± 55	28 ± 6	20 ± 4	14.0 ± 2.9	4 ± 1	0.3 ± 0.07	1.7 ± 0.5	28.3 ± 6.4	6.4 ± 1.5
Populus alba	A	121 ± 38	41 ± 9	46 ± 12	4.7 ± 1.3	7 ± 2	0.3 ± 0.07	1.4 ± 0.4	19.2 ± 5.7	7.6 ± 1.7
	B	137 ± 36	47 ± 10	51 ± 13	9.4 ± 2.4	6 ± 1	0.4 ± 0.09	1.4 ± 0.4	28.1 ± 5.9	11.0 ± 2.5
	C	120 ± 25	44 ± 12	47 ± 12	5.6 ± 1.3	7 ± 2	0.4 ± 0.08	1.2 ± 0.3	17.2 ± 5.1	7.0 ± 1.4
Leaves of vegetables										
Daucus carota	A	179 ± 46	18 ± 5	37 ± 9	8.2 ± 2.5	6 ± 1	0.5 ± 0.14	0.6 ± 0.1	3.7 ± 0.9	3.4 ± 1.0
	B	138 ± 33	17 ± 4	29 ± 7	10.6 ± 3.1	7 ± 2	0.7 ± 0.17	0.7 ± 0.1	4.2 ± 0.8	3.2 ± 0.7
	C	126 ± 38	18 ± 4	13 ± 3	12.9 ± 2.7	24 ± 5	0.2 ± 0.06	0.7 ± 0.1	4.6 ± 0.9	3.9 ± 0.8
Beta vulgaris	A	480 ± 120	60 ± 14	67 ± 13	14.2 ± 3.6	9 ± 2	0.6 ± 0.12	0.9 ± 0.1	9.8 ± 2.4	6.1 ± 1.9
	B	670 ± 160	76 ± 19	82 ± 19	18.3 ± 5.7	19 ± 6	1.2 ± 0.31	1.8 ± 0.5	14.6 ± 3.8	7.2 ± 2.0
	C	550 ± 165	54 ± 14	66 ± 17	16.1 ± 4.2	28 ± 5	0.6 ± 0.14	1.2 ± 0.4	12.0 ± 3.7	7.2 ± 1.9
Petroselium sativum	A	396 ± 103	31 ± 7	67 ± 14	23.0 ± 6.1	26 ± 6	0.9 ± 0.18	1.9 ± 0.5	18.3 ± 4.7	6.9 ± 1.7
	B	331 ± 86	30 ± 9	54 ± 11	8.0 ± 2.1	6 ± 1	1.0 ± 0.32	1.7 ± 0.5	26.1 ± 6.8	12.4 ± 3.1
	C	308 ± 65	33 ± 8	53 ± 12	15.2 ± 4.2	42 ± 8	0.6 ± 0.15	1.4 ± 0.4	26.4 ± 6.6	10.2 ± 2.4
Brassica oleracea	A	60 ± 14	20 ± 5	23 ± 6	4.1 ± 0.8	3 ± 1	0.2 ± 0.04	1.2 ± 0.3	20.6 ± 5.4	12.1 ± 3.4
	B	88 ± 19	24 ± 5	27 ± 6	9.0 ± 2.8	7 ± 2	0.4 ± 0.10	1.4 ± 0.4	21.4 ± 6.2	11.2 ± 2.8
	C	150 ± 39	26 ± 6	25 ± 5	15.1 ± 3.6	9 ± 2	0.3 ± 0.07	1.6 ± 0.4	16.0 ± 3.8	7.0 ± 2.1
Lactuca sativa	B*	1060 ± 254	94 ± 24	39 ± 9	16.5 ± 3.4	11 ± 2	1.7 ± 0.5	1.9 ± 0.4	22.0 ± 5.1	9.3 ± 2.3
	B**	540 ± 140	108 ± 23	34 ± 7	15.9 ± 4.1	4 ± 1	1.4 ± 0.3	1.8 ± 0.4	6.0 ± 1.6	9.0 ± 2.2
	C*	620 ± 161	89 ± 21	41 ± 8	14.2 ± 3.7	9 ± 2	1.3 ± 0.3	1.8 ± 0.5	16 ± 4.1	9.1 ± 2.4
	C**	580 ± 133	72 ± 19	36 ± 7	13.6 ± 3.4	3 ± 1	1.2 ± 0.3	1.9 ± 0.5	8.4 ± 2.3	8.6 ± 2.2
Medicago sativa	B*	600 ± 138	50 ± 14	34 ± 7	12.2 ± 3.4	6 ± 1	2.2 ± 0.7	1.9 ± 0.5	26.0 ± 6.7	9.3 ± 2.4
	B**	222 ± 55	34 ± 8	30 ± 7	12.0 ± 3.5	4 ± 1	0.6 ± 0.1	1.6 ± 0.5	18.0 ± 4.8	6.0 ± 1.7
	C*	248 ± 57	52 ± 12	36 ± 10	11.6 ± 3.6	6 ± 2	1.8 ± 0.5	1.8 ± 0.2	18.0 ± 5.2	8.1 ± 4.9
	C**	202 ± 53	48 ± 11	30 ± 8	10.4 ± 2.1	6 ± 2	0.6 ± 0.1	1.6 ± 0.3	14.6 ± 4.0	6.4 ± 1.6
Roots of vegetables										
Daucus carota	A	170 ± 39	18 ± 5	39 ± 8	12.3 ± 2.5	12 ± 3	0.5 ± 0.1	0.7 ± 0.2	3.7 ± 0.9	3.4 ± 0.8
	B	158 ± 38	17 ± 4	29 ± 7	13.4 ± 3.3	7 ± 2	0.7 ± 0.2	0.7 ± 0.2	3.2 ± 0.6	3.3 ± 0.8
	C	232 ± 81	18 ± 4	31 ± 7	12.9 ± 3.3	23 ± 6	0.8 ± 0.2	0.8 ± 02	3.7 ± 0.9	3.9 ± 1.0
Beta vulgaris	A	188 ± 49	40 ± 9	48 ± 12	17.8 ± 5.2	5 ± 1	0.5 ± 0.1	0.7 ± 0.2	3.7 ± 1.3	3.3 ± 0.8
	B	147 ± 38	31 ± 7	28 ± 7	13.5 ± 3.2	7 ± 2	0.5 ± 0.1	0.7 ± 0.2	3.2 ± 1.1	3.3 ± 0.8
	C	207 ± 48	31 ± 9	57 ± 15	21.2 ± 5.3	22 ± 5	0.7 ± 0.2	0.6 ± 0.1	3.9 ± 1.0	3.6 ± 0.9
Petroselium sativum	A	311 ± 71	24 ± 5	46 ± 11	15.8 ± 4.1	18 ± 4	0.6 ± 0.1	0.9 ± 0.2	4.7 ± 1.1	4.7 ± 1.4
	B	228 ± 69	21 ± 5	43 ± 9	15.1 ± 3.5	4 ± 1	0.4 ± 0.1	0.7 ± 0.2	3.8 ± 0.8	3.1 ± 0.7
	C	238 ± 71	28 ± 6	47 ± 10	17.0 ± 4.2	18 ± 4	0.8 ± 0.2	0.8 ± 0.2	4.8 ± 1.3	3.8 ± 0.9

* unwashed
** washed

Soil-to-plant transfer factor (TF) values decreased from Mn > > Zn > Cd > Cu > Pb. Similarly, with respect to zinc, a strong correlation between soil-root-shoots was observed by Wang et al. (2003) and Notten et al. (2005). The dominant source of Pb contamination might be atmospheric deposition, as was indicated by the Pb concentration on the surface films of leaves (Nabulo et al. 2006).

Table 4. The correlation between the contents of heavy metals in plants and soils.

Location/ zone	Part of the plant	1.1 ***Fe***	Mn	Zn	Cu	Pb	Cd	Co	Cr	Ni
A	Leaves of trees	0.374	0.671**	0.721**	0.341	0.320	0.241	0.421	0.240	0.319
	Leaves of vegetables	0.666**	0.433	0.420	0.581**	0.246	0.566**	0.646**	0.383	0.274
	Roots of vegetables	0.532**	0.743**	0.567**	0.724**	0.368	0.540**	0.724**	0.670**	0.563**
B	Leaves of trees	0.268	0.526**	0.542**	0.283	0.280	0.268	0.384	0.310	0.293
	Leaves of vegetables	0.423	0.273	0.421	0.383	0.344	0.672**	0.470*	0.260	0.324
	Roots of vegetables	0.498*	0.591**	0.621**	0.721**	0.576**	0.720**	0.691**	0.740**	0.688**
C	Leaves of trees	0.328	0.472*	0.634**	0.246	0.382	0.320	0.328	0.324	0.346
	Leaves of vegetables	0.596**	0.621**	0.721**	0.465*	0.440	0.430	0.510*	0.392	0.430
	Roots of vegetables	0.471*	0.706**	0.830**	0.671**	0.647**	0.399	0.720**	0.548**	0.728**

4 CONCLUSIONS

The results of the study demonstrate that the landfill, actively used for forty three consecutive years, had not caused heavy metal pollution of the soils situated within 0.5 km distance. Accumulation of Fe, Mn, Zn, Cu, Cd, Ni, Cr in the top (0–20 cm) layer of these soils was, however, observed. Being in accordance with the prevailing winds observed in the area this was attributed to the wind-blown dispersal of ashes. The content of elements listed above in plants was not always correlated to their concentrations in the soil. For the majority of them their content in tree leaves and above-ground parts of vegetables was rather more due to the deposition of dust than to direct uptake from soil. On the other hand, the concentration of heavy metals in soil strongly influenced their content in roots.

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Evaluation of the effectiveness of elimination of heavy metals from petrochemical wastewaters by zeolites

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ABSTRACT: Industrial development results in the increased production of wastewaters entering the environment and carrying toxic substances, for instance heavy metals. One method of eliminating heavy metals from wastewaters is by using natural and synthetic zeolites. The aim of the present study was to check the effectiveness of aluminosilica zeolites in eliminating heavy metals (Pb, Cu, Mn) from petrochemical wastewaters. The research system consisted of columns, each filled with a specific type of zeolite, through which the wastewaters were filtered. In this experiment the wastewaters from the Płock Petrochemical plant and three types of zeolite: synthetic K-Na zeolite (3A), synthetic Ca-Na (5A) and natural zeolite rock containing about 90% of clinoptilolite (ZN), were used. The study confirms the effectiveness of the chosen zeolites in eliminating heavy metals from such specific wastewaters as petrochemical wastewaters. The nature of wastewaters influenced the observed decrease of concentration of heavy metals in petrochemical wastewaters.

Keywords: Petrochemical sewage, heavy metals, zeolite.

1 INTRODUCTION

The unique physicochemical properties of zeolites have made them among the most interesting class of minerals examined by scientists. These materials have received great attention since the 1950s because of their high specific surface area, superior cation exchange capacity and catalytic properties. Zeolites are three-dimensional aluminosilicates with specific crystal structures (so-called *molecular sieves*), due to which they owe their strong and selective sorption capacity. The main component of their structure is the tetrahedral $[SiO_4]^{-4}$ ion. The Si^{4+} cation can be replaced by the Al^{3+} cation, which does not, however, change its tetrahedral framework. Zeolites are considered to be, next to clays, iron oxide-coated sands, low-cost sorbents. They are either natural or synthetic silicate minerals. Clinoptilolite is probably the most abundant natural zeolite, which renders it readily available and inexpensive (Ghobarkar et al 1999, Chojnacki et al 2004, Erdem et al 2004). Natural and synthetic zeolites are used, for example, in the construction industry, drying and purification of gases and liquids, separation of gases, adsorption, wastewater treatment (in ammonia and metal ion removal), soil conditioning and fertilization, also nuclear waste treatment (Mondale et al 1995, Ghobarkar et al 1999). The results of many studies on zeolites demonstrate that they possess a strong affinity towards heavy metal ions.

The increasing concentration of heavy metals in the environment poses a serious threat to human health, living resources and ecological systems. Heavy metals are toxic to living organisms and can be accumulated in their tissues. The toxicity of heavy metals depends on their nature as well as on the chemical form in which the given element is present in the environment (Sultan et al 1998, Alvarez – Ayuso et al 2003). They can cause the decrease of biomass synthesis, influence the efficiency of photosynthesis and even cause disturbances within the food chain. They can also act as mutagenic and carcinogenic factors. The presence of heavy metals in wastewaters signifies that, at the end of many industrial processes, it is necessary to reduce their concentrations to below the prescribed legal limits. The adsorbent most commonly used, because of its high effectiveness and despite the high costs of its use, is active carbon. This sorbent is also used in treatment of wastewaters. The high cost could be reduced if the sorbent could be regenerated and reused. Zeolites, although not so efficient turn out to be cheaper

(Catalfamo et al 2006). Purified wastewaters, which contain many biogenic elements, can be used as soil fertilizers in agriculture or forestry, but the potential use of wastewaters in agriculture is limited by the high concentrations of the toxic substances, such as heavy metals. This is why the possibility of purification of wastewaters using zeolites is so interesting from an economic point of view (Zorpas et al 2000, Zorpas et al 2002).

The effectiveness of zeolites in elimination of heavy metals from various matrices is well known. In many research projects zeolites were used to either remove heavy metals from soils, wastewaters and sewage sludge or to immobilise them in polluted soils (Shanableh et al 1996, Ouki et al 1997, Cheng-Fang Lin et al, 1998, Zorpa et al 2000, Zorpas et al 2002, Alvarez – Ayuso E et al 2003, Chojnacki et al 2004, Erdem et al 2004, Pitcher et al 2004, Hui et al 2005, Wingeltender et al 2005, Cataltamo et al 2006). The types of zeolites used in these studies were chosen especially for their particular sorption capacity towards heavy metals.

Generally, the content of heavy metals in petrochemical wastewaters is not very high. Specific treatment of wastewaters during the refinery industrial processes makes petrochemical wastewaters a daunting problem because of their physical and chemical composition. They are particularly dangerous and hard to treat, mainly due to the high content of hydrocarbons, which disturb the treatment process.

The main aim of the present study was to evaluate the effectiveness of selected natural and synthetic zeolite to purify petrochemical wastewaters from heavy metals. The most important aspect of this study was to check whether the chosen zeolites would remain effective in elimination of heavy metals despite their low concentration and the specific physico-chemical properties of petrochemical wastewaters.

2 MATERIALS AND METHODS

The petrochemical wastewaters used in this study were collected from the Płock Petrochemical Plant, which is part of the refinery at Płock. The samples were taken in two time periods: in July (period I) and January (period II), from two systems:

- system I – wastewaters collected from the refinery part of the plant
- system II – wastewaters collected from the petrochemical part of the plant.

Each sample was analysed for its main physicochemical properties: pH, density, dry weight and organic substances content. The concentrations of some alkaline metals (Na, K, Ca) and heavy metals were determined using AAS technique (obtained results were encoded as "control").

In the purification process the following zeolites were used:

- 3A – synthetic Na – K zeolite activated at 200°C
- 5A – synthetic Ca – Na zeolite activated at 200°C
- ZN – natural Ca – K zeolite – ground natural zeolite – bearing rock containing about 90% of clinoptilolite; grain size about 3 mm.

After using the zeolites the content of organic substances in wastewaters' eluates was examined. In order to determine the selectivity of the zeolites towards the chosen heavy metals a dynamic experiment was carried out. The petrochemical wastewaters were filtered through a column (internal diameter 5 cm packed with a given zeolite 100 g). The thickness of the sorbent layer was 7 cm. The flow rate of the wastewaters was 100 ml per 5 minutes.

Samples of wastewaters (1 litre) taken from systems I and II during period I were filtered through each zeolite. The amount of wastewater samples taken in period II was 1.5 litre. Each 100 ml of eluate from each column was analysed for the content of metals. In total, for the wastewaters sampled in period I, 10 consecutive eluates were examined, while for those sampled in period II 15 consecutive eluates were examined. Samples were evaporated to dryness and calcined at 480°C. The remaining ash was dissolved in 20% HCl. These solutions were analysed for the content of some alkaline metals (Na, K, Ca) and heavy metals (Cu, Mn, Pb) using AAS.

3 RESULTS AND DISCUSSION

The basic physico-chemical properties of the examined wastewaters are summarised in table 1. They were similar for both sampling periods, therefore this factor is not taken into account in the table.

The concentrations of the examined metals in untreated wastewaters were low (see table 2). The highest concentrations of metals were noted in wastewaters from system II collected in period I. Also in system II collected during period II the concentrations of metals were either similar or higher than those from the system I sampled during period II.

Additionally, the content of organic substances was the highest in system II. Clearly, wastewaters from system II were more polluted than those from system I,

Table 1. Basic physicochemical properties of the examined wastewaters.

Sampling point	pH	Density [g/cm^3]	Dry weight [%]	Organic substances [%]
System I	7.65	0.9764	0.0828	34.42
System II	7.71	0.9698	0.1425	37.89

especially when sampled in summer. The content of lead in wastewater samples from system I collected during both periods I and II was below the detection limit and therefore analyses for this element were discontinued.

The content of organic substances was similar in both sampling periods; the time of sampling was therefore not taken into account during the further examination of this substance type. Analysis of the behaviour of organic substances in treated wastewaters demonstrated that they were sorbed by the zeolites and that this sorption was almost as strong as in the case of heavy metals. For the wastewaters sampled from the system I, the most effective sorption of organic substances was after using 5A zeolite. The content of organic substances in consecutive eluates decreased from 34.42% to 8.73%–13.44%.

For zeolite 3A the content of organic substances in the eluates decreases from 8.49% to 14.06%, while when the zeolite rock ZN was used, it decreased from 1.70% to 26.12% in consecutive eluates.

The effectiveness of elimination of organic substances from the wastewaters from system II using zeolites was much lower. The lowest effectiveness of this process was observed for the natural zeolite ZN, where the content of organic substances in treated wastewaters decreased from 37.89% to 16.95%–33.31%. The use of the synthetic zeolite 3A resulted in the decrease in content of the organic substances in treated wastewaters to the level of 13.42%–31.94%. The most efficient sorbent was again zeolite 5A. The use of this sorbent resulted in the decrease in content of organic substances in treated wastewaters from 37.89% to 14.76%–30.76% in consecutive eluates.

The mean concentrations of metals in eluates from each variant of the experiment are presented in table 3. Analyses of these data lead to the conclusion that, despite the use of zeolites in the treatment of specific wastewaters such as petrochemical wastewaters, these sorbents also proved to be efficient in the removal of heavy metals.

Use of zeolite ZN for the treatment of the wastewaters from system I sampled at period I resulted in an 800%-rise in the mean content of potassium and a 150%-rise in the mean content of calcium ions in treated wastewaters, while the content of the other metal ions sorbed on the zeolite bed decrease and followed the order: Mn (∼57%) > Na (about 40%) > Cu (∼18%). In wastewaters from system II sampled at the same period and treated with the same zeolite the mean content of K ions in the eluates increased by 300%, while that of Ca by 26%. The concentrations of the remaining metal ions decreased as follows: Mn (∼56%) > Cu (∼49%) > Pb (∼37%) > Na (∼23%). In wastewaters from the system I sampled in the period II, the mean content of K and Ca increased after treatment respectively by 1240% and 20%. The observed decrease of the other examined metal ions followed the order: Mn (∼70%) > Na (∼30%) > Cu (∼19%). In treated wastewaters from system II sampled at the same period the mean contents of K and Ca ions in eluates increased by 720% and ∼100% respectively, while the mean contents of the other metal ions decreased in the following order: Pb (∼75%), > Cu (∼59%) > Mn (∼44%) > Na (∼9%).

For system I wastewaters sampled in period I and treated with the zeolite 3A the mean content of Na increased by about 190%, and that of potassium by about 3944%. At the same time, the decrease in the concentration of the other examined metals followed the order: Ca (∼86%) > Mn (∼77%) > Cu (∼12%). In the wastewaters from system II sampled in the same period and treated the same zeolite the mean contents of sodium and potassium increased respectively by ∼20% and ∼996%, while the mean contents of other metal ions in the eluates decreased in order: Ca (∼81%) > Mn (∼62%) > Cu (∼49%) > Pb (∼47%). When this zeolite was used for treatment of wastewaters sampled at period II from system I the mean contents of all alkaline metal ions in the eluates increased as follows: K (∼2350%) > Ca (∼2292%) > Na (∼75%), while the mean contents of the other metal ions in the same treated wastewaters sample decreased in order: Mn (∼74%) > Cu (∼40%). In the treated wastewaters from the system II mean contents of sodium and potassium increased by ∼12% and ∼1284% respectively, while the concentrations of the other examined metals decreased in order: Ca (∼87%) > Pb (∼75%) > Cu (∼58%) > Mn (∼51%).

Table 2. Mean concentration (n = 6) of metals [$mg \cdot l^{-1}$] in untreated wastewater (control).

Sampling period	Sampling point	Type of metal					
		Na	K	Ca	Cu	Mn	Pb
Period I	System I	61.9 ± 15.4	4.1 ± 0.9	86.7 ± 18.2	0.11 ± 0.01	0.20 ± 0.05	n.d.*
	System II	265.5 ± 58.4	31.0 ± 6.8	132.3 ± 27.7	0.18 ± 0.05	1.89 ± 0.49	0.35 ± 0.07
Period II	System I	76.6 ± 16.0	5.1 ± 1.2	102.3 ± 21.4	0.10 ± 0.02	0.29 ± 0.07	n.d.*
	System II	200.6 ± 42.6	14.8 ± 3.1	26.0 ± 5.2	0.11 ± 0.03	0.18 ± 0.05	0.04 ± 0.007

* not determined

Table 3. Mean concentration of metals [$\mathrm{mg \cdot l^{-1}}$] remaining in wastewater eluates after completion of the experiment as a function of zeolite type.

Sampling period	Sampling point	Type of used zeolite	Type of metal					
			Na	K	Ca	Cu	Mn	Pb
period I **	system I	ZN	36.6 ± 1.9	37.2 ± 5.9	150.2 ± 57.7	0.09 ± 0.01	0.09 ± 0.02	n.d.*
		3A	179.7 ± 15.6	165.8 ± 25.0	12.0 ± 8.6	0.10 ± 0.01	0.05 ± 0.03	n.d.*
		5A	159.8 ± 51.4	76.1 ± 62.2	13.3 ± 25.1	0.09 ± 0.02	0.06 ± 0.02	n.d.*
	system II	ZN	205.5 ± 32.2	128.3 ± 21.6	167.1 ± 40.2	0.09 ± 0.06	0.83 ± 0.58	0.22 ± 0.12
		3A	317.2 ± 71.2	339.6 ± 52.2	25.0 ± 10.3	0.09 ± 0.06	0.72 ± 0.53	0.19 ± 0.10
		5A	345.9 ± 23.7	319.9 ± 49.0	28.8 ± 10.0	0.10 ± 0.05	0.56 ± 0.39	0.19 ± 0.08
period II ***	system I	ZN	53.6 ± 5.4	68.3 ± 32.9	123.4 ± 17.3	0.08 ± 0.01	0.09 ± 0.04	n.d.*
		3A	133.9 ± 16.8	124.8 ± 22.4	2447.2 ± 439.1	0.06 ± 0.04	0.08 ± 0.01	n.d.*
		5A	158.3 ± 22.5	6.3 ± 0.9	122.8 ± 17.2	0.08 ± 0.01	0.07 ± 0.03	n.d.*
	system II	ZN	184.4 ± 14.3	121.4 ± 32.5	51.9 ± 25.1	0.04 ± 0.01	0.10 ± 0.02	< 0.01
		3A	223.1 ± 17.2	204.8 ± 41.6	3.5 ± 1.2	0.05 ± 0.01	0.09 ± 0.01	< 0.01
		5A	249.5 ± 30.6	12.6 ± 1.2	8.0 ± 4.5	0.08 ± 0.02	0.08 ± 0.02	< 0.01

* not determined

** mean concentration of metals in 10 eluates

*** mean concentration of metals in 15 eluates

Finally, for the wastewaters samples filtered through the zeolite 5A, in wastewaters from system I sampled in the period I, the mean concentrations of sodium and potassium after treatment increased by $\sim$158% and $\sim$1756% respectively, while those of the other examined metals decreased in the following order: Ca ($\sim$85%) > Mn ($\sim$70%) > Cu ($\sim$23%). In wastewaters from the system I sampled at the same period the mean contents of sodium in eluates increased by $\sim$30%, while that of potassium by $\sim$932%; at the same time the mean contents of the other examined metals in the eluates decreased as follows: Ca ($\sim$78%) > Mn ($\sim$71%) > Pb ($\sim$47%) > Cu ($\sim$45%). However, in wastewaters from system I sampled in period II the mean concentrations of all alkaline metals in eluates increased as follows: Na ($\sim$106%) > K ($\sim$23%) > Ca ($\sim$20%), while the mean concentrations of heavy metals in eluates decreased by $\sim$74% for Mn and $\sim$17% for Cu. Finally, in wastewaters from system II sampled in the same period only the mean content of sodium increased by $\sim$24%after treatment, while in case of the other examined metals it decreased in the following order: Pb ($\sim$75%) > Ca ($\sim$69%) > Mn ($\sim$54%) > Cu ($\sim$25%).

Figures 1–6 present the change (%), in the contents of the examined alkaline metals (Na, K, Ca) and heavy metals (Mn, Cu, Pb) in the treated wastewater samples. The analysis of the graphs presented in Figures 1–6 show that there is no well established tendency.

The wastewater samples were taken from two systems having similar physico-chemical properties (see Table 1). Nevertheless, the amounts of metal ions removed from each of these samples via adsorption on zeolites differed significantly, even when the treated

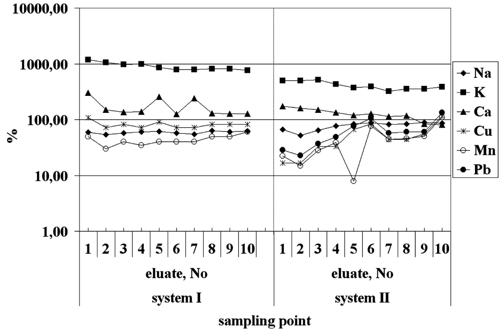

Figure 1. The percent changes (increase and decrease) of metals after using zeolite ZN in wastewaters sampled in period I.

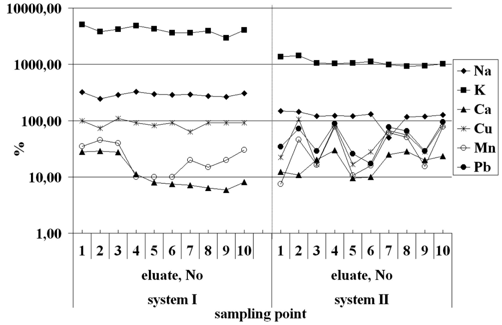

Figure 2. The percent changes (increase and decrease) of metals after using zeolite 3A in wastewaters sampled in period I.

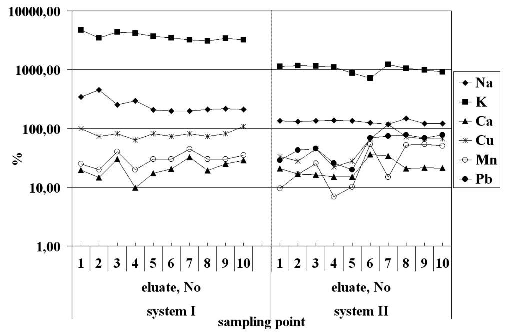

Figure 3. The percent changes (increase and decrease) of metals after using zeolite 5A in wastewaters sampled in period II.

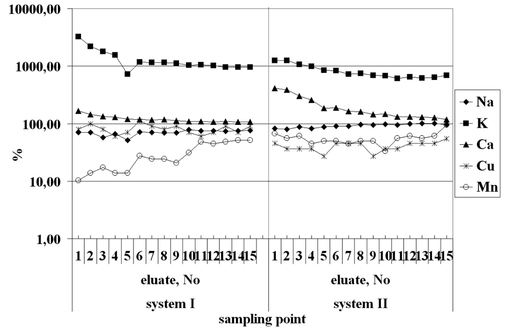

Figure 4. The percent changes (increase and decrease) of metals after using zeolite ZN in wastewaters sampled in period II.

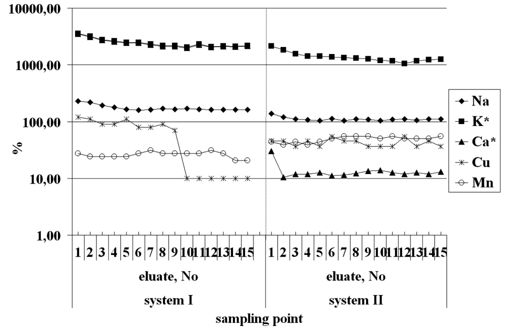

Figure 5. The percent changes (increase and decrease) of metals after using zeolite 3A in wastewaters sampled in period II (* the experimental points for K and Ca for the system I overlap one another giving on the graph one set of points and one line).

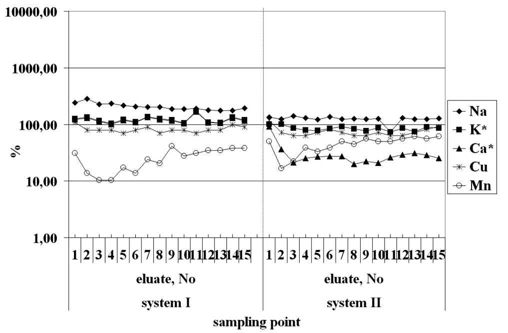

Figure 6. The percent changes (increase and decrease) of metals after using zeolite 5A in wastewaters sampled in period II (* the experimental points for K and Ca for the system I overlap one another giving on the graph one set of points and one line).

samples originated from the same system. This can be explained by the fact that the zeolites had become overloaded during the process. This interpretation is supported by the increase in content of metal ions in the latter eluates, noted for the treated wastewater samples from the system II taken at period I (see figures 1–3), in which the concentration of heavy metals was the highest (see table 2). On the other hand, it is difficult to explain the lower rate of sorption in some of the first eluates, where the content of heavy metals increased. This was the case for copper in samples from system I taken during both periods (I and II), where it increased about 16% (see Figures 1 and 6).

A possible explanation for this is that the sorption equilibrium between sorbent and solution was still not established at that time. It is generally assumed that the sorption equilibrium establishes itself very quickly, usually within a few minutes. However, some studies show that the sorption equilibrium for the process of the sorption of heavy metals reaches 90% only after one hour. (Alvarez – Ayuso et al 2003). The results obtained may also be caused by the specific nature of petrochemical wastewaters. The high concentration of organic compounds in wastewaters and the fact that the latter all contained oil products could have affected metal sorption by zeolites. Especially since the sorption of organic substances by zeolites is known to be efficient, it seems probable that organic substances were sorbed before metals. Furthermore, metal ions present in the solution formed many complexes of unknown structure, but sufficiently strong and large enough to prevent their entrance into the miniscule pores of zeolites. This might be especially true for petrochemical wastewaters where many inorganic and organic anions are present (Zorpas et al 2002). It could also possibly explain the lack of any dependencies of metal sorption in consecutive eluates.

The fundamental process on which the sorption of heavy metals by zeolites is based is sorption and desorption. A metal ion, which is absorbed, substitutes an exchangeable cation in the zeolite (Erdem et al 2004). In this study, in the case of the natural zeolite (ZN), the dominating cations were potassium and calcium (see table 4), hence the increase in the content of these two metals in wastewaters treated with this zeolite. Sodium, which was not a dominating cation in this zeolite, was also sorbed together with heavy metals (see table 3, figures 1 and 4). When the zeolite 3A was used, sodium and potassium, which are the dominant cations (see Table 4), were desorbed while the calcium, together with the heavy metal ions, were sorbed. The only exception was observed for a sample from system I collected in period II (see figure 5). In this sample all three alkaline metals were desorbed. Very similar results were observed in the same sample when the zeolite 5A was used (see figure 6). Also all three alkaline cations were desorbed, while mostly calcium was sorbed in other samples. Additionally, in samples collected from system I in period II, after using 3A and 5A zeolites, the desorption of calcium and sodium overlap one another (see figures 5 and 6). Furthermore, when the zeolite 5A was used, potassium, mostly instead of calcium, was desorbed while it should be sorbed as the cation which was not the dominating one. However, potassium, which is also contained in 5A zeolite, as a very light element is much more easily desorbed than calcium, which is considered as one of the best sorbed by zeolite element (Shanableh & Kharabsheh 1996, Cheng – Fang Lin et al 1998, Pitcher et al 2004). Also, probably the process of sorption and desorption is based rather on the chemical reaction than on the diffusion. Thus, the presence of the dominating cations does not necessarily mean that they all will be exchanged, this depends rather on the conditions of the chemical reaction and the sorbed cation (Biskup & Subotic 2004). Probably the chemical composition of the petrochemical wastewaters has a significant influence on the processes of the metal sorption and desorption. Additionally, the neutral pH of the treated wastewaters (see table 1) also influences the sorption process. In acidic solution, the sorption rate of zeolites is higher (Alvarez – Ayuso et al 2003, Ouki & Kavannagh 1997, Shanableh & Kharabsheh 1996). The analysis of the results leads to the conclusion that, in the present experiment, the desorption was at least three times higher than the sorption of the metal ions. It can also be stated that, in the case of the natural zeolite ZN, the sorption profile was similar for all four samples (see figures 1 and 4). Consequently, it can be stated that the sorption of the metals on this zeolite is much more predictable than by the synthetic zeolites. Probably this is influenced by processes occurring during the synthesis of the zeolites (Ghobarkar et al 1999, Querol et al 2002) and the specificity of the treated wastewaters. Furthermore, the external surface area of natural zeolite is the highest (see table 4) and the sorption of organic substances was still high even in the final eluates, what means that clinoptilolite has a high selectivity towards the large organic cations. All this leads to the conclusion that, despite the sorption of organic substances by the natural zeolites, the sorption of heavy metals is not perturbed.

Table 4. Basic physico-chemical properties of the examined zeolites (from Gworek & Kozera-Sucharda, 1999).

		CEC $[\mathrm{cmol}(+)\cdot\mathrm{kg}^{-1}]$			Surface of zeolite $[\mathrm{m}^2/\mathrm{g}]$	
Type of zeolite	Dominating cation	Na	K	Ca	specific surface	outer surface
ZN	K and Ca	1.7	46.1	44.6	116.3	37.1
3A	Na and K	146.5	200.3	6.8	182.4	17.6
5A	Na and Ca	134.0	6.0	23.1	169.9	21.0

It is difficult to explain the higher selectivity of zeolites towards manganese than towards copper or lead in some samples of wastewaters (see table 3, figure 1–6). It is assumed that copper is mainly sorbed through the precipitation of hydroxides, especially in acidic conditions (Panayotova 2001, Alvarez – Ayuso et al 2003). Since the pH of the treated wastewaters is 7, sorption of copper may be reduced.

Additionally, according to one of the theories, the cation selectivity of the zeolites, mainly those having the weaker ionic fields (like clinoptilolite), depends on the hydration energy (the cations having the higher hydration energy are much more easily sorbed) and the hydration radius of a given cation (Ouki & Kavannagh 1997, Woinarski et al 2003).

The sorption strength as the function of hydration energy and the radius of the hydrated ion should thus follow the order: Pb > Mn > Cu (see table 3). The values of hydration energy and the radius of the hydrated ion of manganese are unavailable in table 3, but according to Erdem et al, 2004 they should be between the values for lead and copper. On one hand, the metal having the highest hydration energy should remain in the solution from which it is much easier sorbed, while on the other hand, when the radius of hydrated ion is higher than the zeolite's pores the sorption rate should automatically decrease. The theories presented above explain the predominance of the sorption of manganese over copper, since the hydrated radius of manganese is smaller than that of copper (Erdem et al 2004). It does not however explain the reason for the decrease in the sorption of lead (see figures 1 and 3). It is assumed that lead is one of the metals best sorbed by zeolites (Shanableh & Kharabsheh 1996) The removal of lead from wastewaters by zeolites, especially by natural zeolite clinoptilolite (ZN), depends on the pH – the sorption is better in acidic condition. The high content of organic compounds may result in the creation of their complexes with metals and thus reduce the sorption of the latter from the treated wastewaters. Also

Table 5. Radii of hydrated ion and hydration energies for metals (from Ouki S.K. & Kavanagh M. (1997) after Semmens (1981).

Metal	Hydrated radius [Å]	Free energy of hydration [kcal g-ion^{-1}]
Cu	4.19	−498.7
Pb	4.01	−357.8

the competition of heavy metals with calcium, which is preferentially sorbed by zeolites after lead, may also influence the sorption of metals from wastewaters by these sorbents (Shanableh & Kharabsheh 1996, Cheng – Fang Lin et al 1998, Pitcher et al 2004). It was especially notable that in all samples in which calcium and heavy metals were sorbed together by the zeolites, its percentage decrease was mostly the highest. In the literature there are many publications on the sorption order of heavy metals by zeolites. The observed differences often result from the specificity of the used sorbents and the differences in the experimental methodology (Hui et al 2005).

4 CONCLUSIONS

The results of the study confirm the efficiency of the chosen natural and synthetic zeolites in eliminating heavy metals (Mn, Cu, Pb) from petrochemical wastewaters.

The selectivity of zeolites towards the heavy metals may be caused by the differences in the free energy of hydration of the three cations, and their hydration radius as well as by the specific nature of the petrochemical wastewaters, especially the content of organic substances and their sorption by zeolites concurrently to sorption of heavy metals.

During the elimination of the heavy metals from the treated wastewaters by the zeolites the desorption of alkaline metals dominates the sorption of heavy metals by at least three times. Furthermore, during the process of cation exchange, not only the dominating cations are desorbed, but rather all the alkaline metals contained by zeolites can be desorbed.

Of the zeolites used in this experiment, the most efficient elimination of heavy metals from petrochemical wastewaters was effected by the natural zeolite clinoptilolite (ZN). Its sorption selectivity for heavy metals was much more easily predicted than for the synthetic zeolites. This can be attributed to the specific processes taking place during the synthesis of the zeolites as well as to the specificity of the petrochemical wastewaters and the surface area of this zeolite – the highest of those investigated.

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Influence of sludge treatment processes on heavy metal speciation

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ABSTRACT: Sludge composition is depending on sewage quality and also affected by processing methods such as thickening, stabilization and dewatering. During those processes some of sludge's undesirable properties might be reduced or enhanced. The objective of the study is the assessment of the influence of sludge processing on selected heavy metals partitioning between phases (aqueous and particle) and sludge. Sludge from the WWTP in Gdansk was investigated. During mechanical and biological treatment with MUCT technology the effectiveness of metals removal was >80% (except for Cd). The predominant form of heavy metals present in sewage is as a suspension. The distribution of analysed heavy metals " differed depending on the type of metal. Only small amounts of cadmium and lead were accumulated in the sludge, in contrast to zinc and copper. The loads of zinc and copper retained in the sludge were 780.4 mg/kg d.m. and 144.6 mg/kg d.m., respectively.

Keywords: Wastewater treatment, sewage, sludge, heavy metals partition.

1 INTRODUCTION

A significant portion of the anthropogenic emission of heavy metals ends up in wastewater. According to Wang et al. (2005) the source of heavy metals in wastewater, whether domestic or industrial, also has a profound effect on the total content as well as the chemical speciation of metals in sludge. Industrial effluents are the predominant source of Cd, Hg, Cr and Ni while Cu and Zn are mainly of domestic origin. Since Pb has been banned from fuels this source makes only a very strongly reduced contribution. Thus, currently, its main sources are from both domestic and industrial wastewater.

However, biological wastewater treatment systems with activated sludge are mainly designed for removal of organic matter and nutrient compound and the removal of heavy metals in these system may be regarded as a side-benefit. Thus, because of physical and chemical processes involved in activated sludge wastewater treatment, excessive sludge tends to accumulate heavy metals present in the wastewater. Due to these, heavy metal levels are generally higher in the sludge than in the treated wastewater or in soil (Obarska-Pempkowiak et al., 2003a, Alvarez et al., 2002).

Sewage sludge can have a different composition, depending on the sewage quality as well as the treatment method applied. Consequently, sludge composition is also affected by processing methods such as thickening, stabilization and dewatering. During these processes some of the undesirable properties sludge might be reduced or enhanced. For example, Chipasa (2003) found Cd, Cu, Pb and Zn concentrations in digested sludge were higher by 50÷99% than corresponding values in undigested sludge.

According to Alvarez et al. (2002), who investigated sludge composition after each stage of sludge processing in five municipal activated sludge plants in the Andalusian region of south Spain, higher concentrations of metals were present in the primary sludge than in secondary sludge. Sequential extraction of Al, Cr, Fe and Pb concentrations, according to the authors, indicated a distinct increase in the residual fraction after anaerobic digestion. The oxidizable Cd and Zn fraction increased after digestion. The conversion of metals during the anaerobic digestion results from decay of the organic matter associated with the metal, either due to formation of insoluble metal sulfides (Fe, Pb) or by transformation (reduction) in the case of Cd and Ni.

Karvalas et al. (2003) investigated the occurrence and partition of heavy metals (Cd, Pb, Mn, Cu, Zn, Fe and Ni) in the activated sludge WWTP at Thessalonica, northern Greece. Ni and Mn were found mainly in the soluble phase (80–93% and 65–85% respectively), while Cu, Cr, Pb, Cd and Zn were mostly associated with the particulate phase (65–95%). Fe also exhibited association with particles (58–75%).

According to Patrick and Verloo (1998) Fe forms complexes with a wide size distribution of soluble organic matter particles while Hg and Pb were associated with only the largest size soluble complexes.

In Poland investigation of heavy metal concentrations and speciation were carried out, among others by Dulewska-Rosik (1998) and Jakubus and Czekała (2000) and Obarska-Pempkowiak et al. (2003 a and b). Dulewska-Rosik (1998) investigated total concentration and speciation of Cd, Cr Cu, Ni, Pb and Zn in primary sewage sludge from the lagoon in the WWTP at Opole. The analyzed sludge was collected over several years in order to ensure stabilization. This author reported that the content of analyzed metals in the most labile fraction (exchangeable and carbonate fraction) was very small and did not exceed 3%. Some metals, e.g. Zn, Cd and Ni were associated with the reducible fraction (31–54%), while Cd, Cu, Pb and Cr were mostly associated with the most stable organic and residual fraction (which are not available to microorganisms).

According to Jakubus and Czekała (2000), who investigated heavy metals in sewage sludge from eight WWTPs, the concentration of analyzed heavy metals in each particular fraction is different in each of WWTPs. In general, the total content of Cd, Cu, Zn, Cr and Ni in the two most labile fractions did not exceed 2.9%. Copper was associated with the most stable combinations, the organic and residual fraction.Thus the partition of heavy metals during wastewater treatment and in the course of sludge processing into dewatered and digested sludge and reject water is not well documented in the literature. Also the distribution of heavy metals among different fraction is still not well recognised. For these reasons the assessment of heavy metal concentrations and their speciation seems to be an important and urgent task. The recognition of processes responsible for allocation of heavy metals during wastewater and sludge processing will give us information about which processes are responsible for retention or release of metals. Up till now there is a lack of information about the influence of the applied wastewater treatment method on the distribution of metals.

The objective of the study is the assessment of the influence of sludge processing on the partitioning of selected heavy metals between phases (aqueous and solid) and sludge after each sequential step of the treatment. Sludge from the WWTP in Gdansk was investigated. To achieve the aims of the study it was necessary to evaluate the efficiency of heavy metal removal in subsequent stages of the sewage treatment and their partitioning into sewage sludge and reject waters during the course of sludge processing.

2 MATERIAL AND METHODS

2.1 *Study area*

The object of the investigation was the municipal wastewater treatment plant "Wschód" in Gdańsk. The WWTP is supplied with 88 000 m^3/day of wastewater from the city of Gdańsk and the region. The fraction of industrial sewage in the total sewage inflow is 10%. The wastewater treatment at WWTP Wschód consists of a mechanical and an enhanced biological treatment section. Mechanical treatment consists of screens, an aerated sand trap and radial primary sedimentation tanks.

The biological treatment takes place in six biological reactors of Modified University of Cape Town system (MUCT), followed by twelve radial secondary sedimentation tanks. Each of the reactors consists of five separate chambers. In the first three chambers the following processes take place successively: dephosphatation, denitrification and nitrification. Dephosphatation is periodically supported with PIX coagulant. The MUCT process units are additionally equipped with an intermediate chamber (predenitrification) located before the denitrification chamber, where either nitrification or denitrification can take place and with the final-fifth chamber, where deoxidation of the recirculate from the nitrification chamber to the denitrification chamber is performed (Fig. 1). Up till now there has been no disintegration of bacteria apply. The reject waters generated during mechanical thickening and dewatering of sewage sludge are directed to the technological line of sewage treatment (after the screens). The volume of reject waters from thickening belt presses is approximately 2100 $m^3 day^{-1}$ and in the dewatering process another 500 $m^3 day^{-1}$ is generated.

During the sewage treatment process two types of sludge are generated: raw sludge from primary sedimentation tanks (PS – primary sludge) (average dry mass content −3.5%) and excess secondary sludge (ES – excess sludge) from secondary sedimentation tanks (average dry mass content 5.8% after mechanical thickening). Primary and secondary sludge is mixed in a separate chamber of 50 m^3 volume, thickened and pumped (TS – thickened sludge) into two digestion chambers of volume of 7 000 m^3 each. After digestion, the sludge is dewatered (DwS- dewatered sludge) by centrifuge after addition of some polymers to improve its efficiency. The final concentration of mass is equal to 24.0%. The daily inflow of sewage and daily amount of generated sludge are given in Table 1.

2.2 *Methods*

The objective of the investigation was to evaluate the amount of selected heavy metals (Cu, Pb, Cd, Zn, Cr, Ag, Ni) after subsequent stages of treatment in a WWTP with activated sludge. Additionally, the concentrations of four metals (Cu, Pb, Cd and Zn) were measured in the aqueous and solid phases in sewage (1–3 – sampling points) and reject waters (4–5 – sampling points). The technology scheme and sampling points are given in Figure 1. The sewage samples were

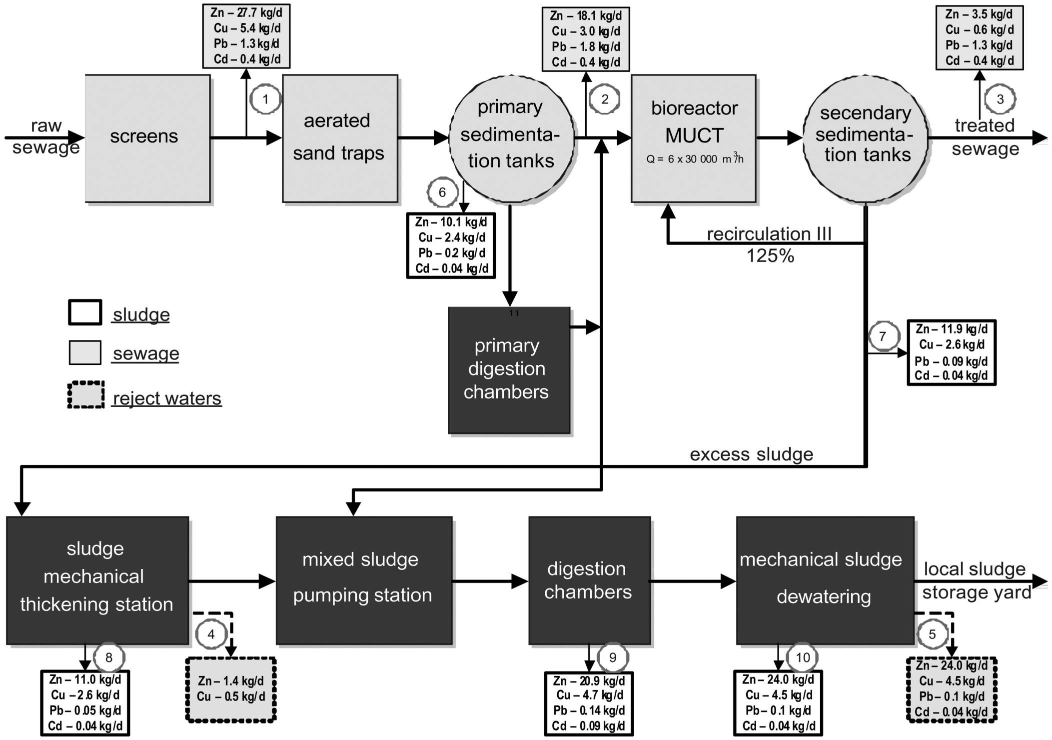

Figure 1. Technological scheme of WWTP Gdansk "Wschod".

Table 1. The average daily sewage inflow to the WWTP, the amount of generated sludge and reject waters from sludge thickening and dewatering, m^3/day.

Type of sewage* or sludge	Average daily quantity of sewage/sludge	Standard deviation
Raw sewage	88 000	4.8
Reject waters from presses	2 100	190.7
Reject waters from centrifuges	500	196.1
Primary sludge	500	95.2
Excess sludge	2 500	1 203.4
Thickened excess sludge	270	101.4
Digested sludge	770	139.5
Dewatered sludge	140	31.7

collected at the following locations in the plant: at the inflow, after mechanical treatment (after primary sedimentation tanks), after biological treatment (after bioreactors), reject waters after mechanical thickening of excess activated sludge (after Klein presses) and reject waters after mechanical dewatering of digested sludge (after Noxon centrifuges).

The following samples of sludge were collected: primary sludge, excess activated sludge (collected at the operation chamber of excess sludge), thickened excess activated sludge (after Klein presses), sludge discharged from digestion chambers and centrifuged sludge (transported to the local storage place at the WWTP area).

The averaged samples of sewage, rejected waters and sludge were collected once a month over six years.

In wastewater the following parameters were measured: organic matter expressed as BOD_5, COD, TSS and total nitrogen. In sludge samples determinations of suspended solids and dry mass concentration were carried out. All measurements followed Polish Standards Methods (1998).

Determination of heavy metals concentrations in wastewater were carried out both in solution (aqueous phase) and in the separated suspension (solid phase). A volume of 1.0 dm^3 of sewage was filtered on membrane filters (pore diameter 0.45 µm). The obtained solution was evaporated to dryness and then dissolved in 0.1 mol/l solution of HNO_3 (0.1 mol/l). The filters were dried and digested in a mixture of acids $HCl:HNO_3$ (3:1). The acid was evaporated and the residue was dissolved in HNO_3 (0.1 mol/l).

The determination of heavy metals determination in sewage sludge was as follows: a sample of homogenised sludge (1.000 g) was digested with $HCl:HNO_3$ (3:1; 5 ml) mixture for 2 hours at 80°C. The

Table 2. Average flow, concentrations of selected contamination in influent and effluent and their removal efficiency.

Year	Q m^3/month	Sampling point	BOD mg/l	COD mg/l	Ntot mg/l	TSS mg/l	ΣHM mg/l
2000	2 681 180	Inflow	393.0 ± 38.9	811.0 ± 48,7	66.7 ± 3.2	376.0 ± 40.4	0.769 ± 0.1
	±	Outflow	5.1 ± 1.7	37.5 ± 6.2	12.1 ± 1.8	21.0 ± 4.7	0.373 ± 0.08
	155916.3	RE %	98.7	95.4	81.9	94.4	51.5
2001	2 691 856	Inflow	333.0 ± 38.8	746.0 ± 86.4	63.2 ± 6.9	341.0 ± 54.1	0.927 ± 0.3
	±	Outflow	7.6 ± 3.5	40.8 ± 8.1	12.7 ± 2.1	16.0 ± 8.7	0.370 ± 0.03
	257 481.4	RE %	97.7	94.5	79.9	95.3	60.1
2002	2 671 524	Inflow	345.0 ± 347	877.0 ± 83.4	68.1 ± 3.3	439.0 ± 63.9	0.429 ± 0.16
	±	Outflow	15.8 ± 11.7	54.7 ± 24.4	14.7 ± 3.4	22.0 ± 7.1	0.086 ± 0.04
	190 459.1	RE %	95.4	93.8	78.4	94.9	79.9
2003	2 534 549	Inflow	369.0 ± 42.1	862 ± 61.9	70.9 ± 3.5	433.0 ± 63.8	0.425 ± 0.09
	±	Outflow	5.4 ± 1.8	46.2 ± 8.7	11.9 ± 1.8	11.9 ± 5.7	0.052 ± 0.07
	137 765.3	RE %	98.5	94.6	83.2	97.3	87.8
2004	2 636 060	Inflow	361.0 ± 46.6	857.0 ± 110.7	72.1 ± 4.7	442.0 ± 91.9	0.433 ± 0.07
	±	Outflow	5.8 ± 1.9	47.5 ± 8.9	11.6 ± 1.2	14.0 ± 5.5	0.068 ± 0.03
	104 614.3	RE %	98.4	94.5	83.9	96.8	84.3
2005	2 596 673	Inflow	419.0 ± 71.2	952.0 ± 124.0	77.3 ± 5.8	445.0 ± 14	0.486 ± 0.13
	±	Outflow	5.1 ± 1.5	43.7 ± 7.4	10.8 ± 1.3	15.0 ± 4.9	0.064 ± 0.01
	220 442.6	RE %	98.8	95.4	86.0	96.6	86.8

final mixture was centrifuged and evaporated to dryness. The residue was dissolved in a solution of HNO$_3$ (0.1 mol/l) and the concentration of heavy metals were measured in the 11E ASA.

3 RESULTS

3.1 *The quality of wastewater*

The raw wastewater discharged to the analysed WWTP is a mixture of domestic and industrial sewage (9:1) with a composition typical of Polish municipal sewage.

In Table 2 average yearly concentrations and removal efficiencies (RE) of selected contaminations as well as the sum of Cd, Pb, Zn, Ni, Cu, Cr, Ag (Σ HM) are shown.

During the study period the quantity and quality of the influent was stable with time. Changes in the contaminants concentrations in the inflow did not exceed more than 25.0% in the six year period with the exception of Σ HM in years 2001 (27.8%) and 2002 (37.3%) (Table 2). The COD/BOD$_5$ratio in the influent ranged from 2.0 to 2.5 and in the effluent from 5.2 to 8.1. Such a high ratio of COD/BOD$_5$ in effluent confirmed that the treated wastewater was biologically stable. The removal efficiency of the contaminants was very high. As a consequence, the contaminants concentration in the effluent did not exceed the permissible values (Dz. U. Nr 168, item. 1763). Since 2002 the load of heavy metals discharged to the WWTP significantly decreased due to implementation of an improved monitoring system. The effectiveness of the total heavy metals removal varied significantly from 51.5 to 87.8%. During the last three years the average total heavy metals concentration in effluent did not exceed 0.1 mg/l. The average concentrations of the analysed heavy metals are presented in Table 3.

The average efficiency removals of analysed metals followed the general order:

$$\mathrm{Cd} < \mathrm{Ni} < \mathrm{Ag} \approx \mathrm{Zn} < \mathrm{Cr} < \mathrm{Pb} < \mathrm{Cu}$$

$$48.8 < 65.6 < 83.3 \approx 83.3 < 87.7 < 90.3 < 94.7\%$$

The lowest efficiency was observed for cadmium and the highest for cupper. Silver and Zinc were removed with a comparable efficiencies.

The distributions of heavy metals (Zn, Cu, Pb and Cd) between the aqueous and solid phase of wastewater and rejected waters are presented in Table 4.

The reject waters from the sludge dewatering process were characterised by the highest concentration of TSS (2800 mg/l), while the lowest TSS concentration was observed in biologically treated sewage (14 mg/l). The heavy metals content in TSS was variable – for instance for Cd it ranged from 1.9 μg/g d.m. in raw sewage to 12.5 μg/g d.m. in biologically treated sewage, and for Zn from 491.4 μg/g d.m. in reject waters (from belt presses) to 894.2 μg/g d.m. (in mechanically treated sewage).

The linear regression between the efficiency of total suspended solids removal and total heavy metals removal is very strong for wastewater (see Table 2). The correlation coefficient for the relation is equal to 0.8, which means that better suspended solid removal (primary and secondary sedimentation) also caused a decrease in the heavy metals concentration.

Table 3. The average heavy metals concentrations in influent and effluent with their removal efficiency (RE), mg/dm^3.

		Mean with standard deviation*						
Year	Sampling point	Cr	Zn	Ag	Ni	Pb	Cd	Cu
2003	Inflow	0.0155	0.335	0.012	0.008	0.015	0.008	0.074
	Outflow	0.0014	0.06	0.002	0.003	0.0003	0.005	0.0014
	RE %	90.67	76.4	83.33	62.5	98.0	37.5	98.1
2004	Inflow	0.019	0.28	0.011	0.006	0.012	0.009	0.07
	Outflow	0.001	0.0325	0.0015	0.0017	0.0013	0.0002	0.0033
	RE %	90.67	76.4	83.33	71.67	98.0	37.5	98.1
2005	Inflow	0.022	0.28	0.012	0.008	0.016	0.0014	0.083
	Outflow	0.004	0.008	0.002	0.0036	0.004	0.0004	0.01
	RE %	81.8	97.1	83.3	62.5	75.0	71.4	87.9

Table 4. The average concentrations of TSS and heavy metals in wastewater after subsequent stages of treatment and reject water.

		Aqueous, µg/dm^3 solid, µg/g d.m.			
Type of sewage	TSS mg/dm^3	Zn	Cu	Pb	Cd
Raw sewage	412,67	314.9	61.2	<15.0	<5.0
		662.0	158.2	20.2	1.9
Mechanically treated sewage	312	206.0	34.7	<15.0	<5.0
		894.0	148.9	11.5	2.7
Biologically treated sewage	14	40.4	6.8	<15.0	<5.0
		621.0	98.3	11.2	12.5
Reject waters from presses	450	677.7	259.0	16.0	<5.0
		491.4	127.3	3.5	2.3
Reject waters from centrifuges	2 800	6572.0	1110	38.0	20.6
		651.0	123.6	3.0	2.3

Table 5. The average concentration of heavy metals in primary sludge and sludge after digestion, mg/kg dm.

	2001		2002		2003	
	Primary sludge	Digested sludge	Primary sludge	Digested sludge	Primary sludge	Digested sludge
Cd	7.0 ± 4.28	9.94 ± 5.2	4.55 ± 0.96	5.66 ± 0.71	5.45 ± 1.44	7.04 ± 1.69
Pb	60.0 ± 11.47	76.41 ± 9.95	61.18 ± 23.89	70.86 ± 19.61	51.47 ± 10.15	60.93 ± 10.63
Zn	1124.89 ± 235.68	1584.36 ± 700.34	971.8 ± 145.8	1286.95 ± 273.32	928.27 ± 230.54	1209.47 ± 317.63
Ni	26.31 ± 10.39	37.08 ± 7.4	17.80 ± 3.67	26.43 ± 5.07	17.73 ± 4.01	25.81 ± 7.37
Cu	204.59 ± 53.09	296.63 ± 24.05	263.26 ± 73.82	340.81 ± 44.68	277.77 ± 40.99	367.39 ± 43.80
Cr	59.57 ± 21.21	93.62 ± 21.71	37.88 ± 13.6	61.57 ± 17.14	57.65 ± 20.21	93.18 ± 42.3
Ag	25.84 ± 11.55	29.46 ± 8.74	34.96 ± 22.37	34.67 ± 23.73	35.33 ± 10.15	37.76 ± 20.56

3.2 *The concentration of heavy metals in sludge*

Table 5 shows the average concentrations of heavy metals in primary sludge and sludge after digestion.

Zinc and Cadmium exhibited the highest and lowest abundances, respectively All metals were detected at comparable concentrations in primary sludge and excess sludge, while the concentrations of metals in digested sludge are double those in primary sludge. This appears to result from the reduction of organic matter and dry matter content.

The loads of heavy metals in the inflowing sewage were as follows: Zn – 27.7 kg day^{-1}, Cu – 5.4 kg day^{-1}, Pb – 1.3 kg day^{-1} and Cd – 0.4 kg day^{-1} (Fig. 1). The very small loads of Zn and Cu (3.5 and 0.6 kg day^{-1}, respectively) in treated wastewater discharged from the plant suggest that a huge quantity of these elements

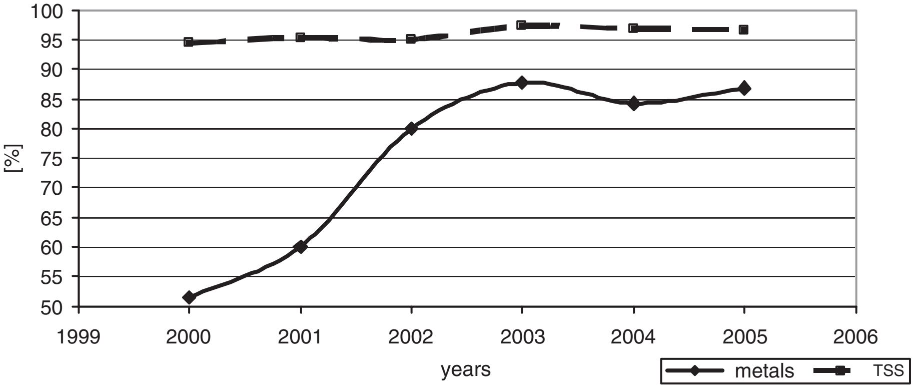

Figure 2. The relationship between metals and TSS efficiency removal.

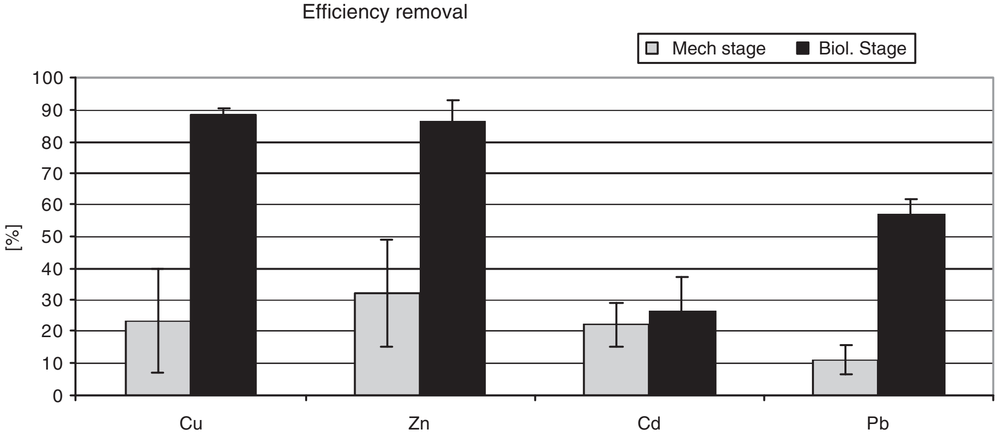

Figure 3. The removal efficiency of selected heavy metals after subsequent stages of treatment.

is retained in sludge (an average 87.0% Zn and 83.0% Cu). On the other hand, Pb and Cd were discharged to the Bay of Gdansk with treated sewage. The concentrations of these elements in the effluent ($Pb < 15$ μg/l, $Cd < 5$ μg/l) are lower than the admissible concentrations defined in Polish regulations (1st August 2002. Dz.U.02/134/1140). Comparing the loads of heavy metals in reject waters generated during mechanical dewatering of digested sludge and the loads discharged with the reject waters, showed that huge amounts of heavy metals were released from the sludge. On the contrary, mechanical thickening of excess sludge did not lead to such effects.

4 DISCUSSION

The relative abundance of metals in the wastewater and sludge samples at all stages followed the general order: Cd < Ni < Cr < Ag < Pb < Cu < Zn (Table 3 and 5). Similar relative abundances and metal concentration levels for influent and effluent wastewater have been reported by other authors (Chipsa, 2003, Karvelas et al. 2003) Generally in three types of the analysed wastewater (raw, mechanically- and biologically treated) the concentrations of metals in solids were higher (from 2 to 15 times) than their concentrations in the aqueous phase (Table 4). While in both types of reject waters the concentrations of metals were from 2 to 10 times higher in aqueous in comparison to solid phase.

Also, the correlation between the efficiency of total suspended solids removal and heavy metals removal is statistically significant (0.8). Moreover, when the efficiency of suspended solids was higher than 95.0%, over 85% of heavy metals was removed (Fig 2). These observations could indicate that metals were accumulated in sludge and that some fraction of them was released to reject waters during the thickening and dewatering processes.

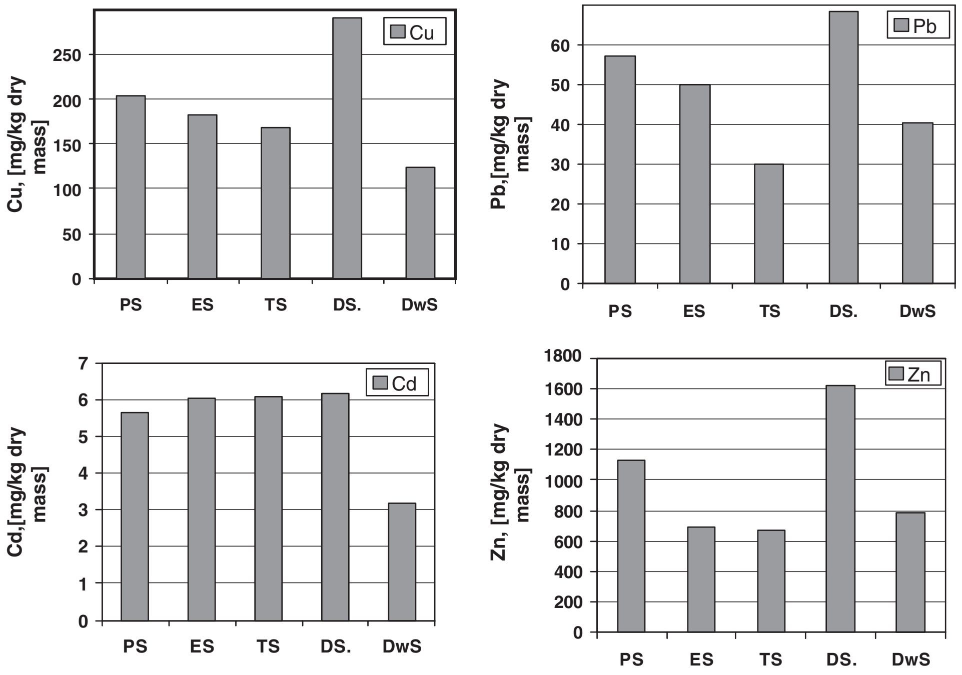

Figure 4. The average concentration of metals in the analysed types of sludge, mg/kg dry mass.

The average effectiveness of total heavy metal removal from sewage in WWTP – Wschód in the study period changed from 51.5 to 87.8% (Table 2). According to Bernacka and Pawłowska, (2000) the mechanical and biological treatment processes are able to remove from 50.0 to 80.0% of discharged loads of heavy metals. In the mechanical stage of treatment the removal efficiency of analysed metals was much lower in comparison to the biological stage (Figure 3). The lowest efficiency removal in the first stage was observed for Pb (10.9%) and the highest for Zn (32.2%). In the second stage the removal efficiencies were much higher and varied from 56.7% for Cd to 88.6% for Cu.

The average values of metal removal efficiencies were: Cu – 94.7%, Zn – 84.3%, Cd – 48.8%, Pb – 90.3%. Consequently removals of zinc and copper in WWTP Wschód were higher than given in the literature but for cadmium the effectiveness is much lower than previously reported (Dulewska-Rosik, 1998; Alvarez et al., 2002; Karvelas et al. 2003).

In general, the partition of heavy metals between the aqueous and particular phases of wastewater (Table 4) exhibited only little change during the treatment process. According to Stantarsiero et al (1998) mechanical treatment (mainly primary sedimentation) strongly affected the distribution of Zn, Pb and Cr, while biological processes and secondary sedimentation influenced mostly the Cu, Cd and Ni distribution. In our study, wastewater treatment processes appeared to affect only slightly the phase distribution of the analysed metals. According to Karvelas et al. (2003), treatment processes do not affect the distribution of heavy metals between the aqueous and particulate phases. On the contrary, phase distribution appears to be metal-specific suggesting that metals are present in sewage in a variety of chemical forms differing in water solubility and bioavailability.

In Figure 4 the average concentrations of four metals in sludge after subsequent stages of treatment are presented (PS- primary sludge, ES- excess sludge, TS- thickened excess sludge, DS- digested sludge, DwS – dewatered sludge).

Higher concentrations of heavy metals in the digested sludge (Table 4 and 5, Fig. 4) could be attributed to the weight loss of fresh sludge during anaerobic digestion, caused by the loss of degradable organic and inorganic matter (Karvelas et al. 2003). The concentration of Cd, Cu Pb and Zn in digested sludge is 11.0 – 68.5% higher than the corresponding concentration in undigested sludge. Similar large differences in heavy metal concentrations before and after digestion were described by Chipasa (2003). However, due to the mechanical dewatering, the load of heavy metals in the final product (dewatered sludge) was lower compared to the loads in primary or excessive sludge (Fig. 4). Additionally, high concentrations of heavy metals in rejected water from the centrifuges (especially in the aqueous phase) confirmed that, during mechanical dewatering, a significant amount of heavy metals was released to the aqueous phase.

Measurements of the heavy metal concentrations at subsequent stages of sludge processing indicated that the portion of cadmium and lead retained in the sludge was very small and these elements were almost totally discharged to the receiver with the effluent from the WWTP. However, these results need to be confirmed by further investigations. High concentration of zinc and copper were measured in sludge. It was calculated that the amount of heavy metals released in effluent from the WWTP in "Wschód" via the treated wastewater stream varies from 52.2 for Cd to only 5.3% for Cu. Thus, it was found that Cu, Pb, Cr, Zn and Ag were primarily removed through the sludge stream. According to Karvales et al. (2003) in the case of Cr, Pb, Ni, Cd and Zn almost 50% of their daily input to the WWTP ends up in the sludge and the other 50% is released with the final effluent stream.

Our results confirm that highly effective biological methods of sewage treatment lead to an increase of heavy metals accumulation in sewage sludge, especially in digested sludge. Biological treatment process caused a change in the lead speciation. In sewage after mechanical treatment the concentration of lead was equal to 33.5% of discharged loads while after biological treatment the concentration increased to 66.4%.

5 CONCLUSIONS

1. Allocation of analysed heavy metals passing through the multistage bioreactors (MUCT-system) of the WWTP "Wschód" differed depending on the type of metal. Only small amounts of cadmium and lead were accumulated in the sludge, in contrast to zinc and copper. The loads of zinc and copper retained in the sludge were 780.4 mg/kg d.m. and 144.6 mg/kg d.m., respectively.
2. During mechanical and biological treatment with MUCT technology the efficiency of metals removal was over 80% (except for Cd). A strong linear regression between total suspended solids and heavy metals removal was observed. The greater than 95% removal of suspended solids was accompanied, in its turn, by >85% removal of heavy metals.
3. The predominant form of heavy metals present in wastewater in WWTP "Wschód" is in suspension.
4. During wastewater treatment processes in WWTP "Wschód" there were indications that heavy metals are accumulated in sewage sludge. Despite this, during sludge processing (mechanical thickening and dewatering) some metals are released to reject waters.
5. The rejected waters recirculated to the biological section of the MUCT system did not cause changes during wastewater treatment processes and the effluent is safe for disposal in the Gdansk Bay.
6. The concentration of Zn, Cu, Cd and Pb in mechanically dewatered sludge (after digestion) fulfilled Polish obligatory criteria regarding heavy metal concentrations in sludge applied to land.

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Minimization of the impact of waste and sewage sludge on the environment

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Geocomposite with superabsorbent in landfill recultivation and slope protection

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ABSTRACT: Embankments of slopes are usually protected against erosion with grass cover. In the upper part of slope there are difficult conditions for plants, because of lack of water. The same problem occurs during draught periods. As a solution to this problem a new kind of geocomposite with superabsorbent (SAP) was developed. In its basic form it is a flat tube made of geotextile filled with superabsorbent. It allows the depth and placement of the superabsorbent application to be controlled. The aim of the investigation was to determine the influence of SAP geocomposite on the grass roots system and strength parameters of soils, at the site at which it was installed. During the tests an increase in the root density in the vicinity of the applied SAP geocomposite was noted. The presence of SAP geocomposite positively influences the strength parameters of the grass roots system and increases forces linking soil or humus with geocomposite.

Keywords: Erosion, superabsorbent, geocomposite

1 INTRODUCTION

Embankments of municipal and industrial landfill sites and other earth structures are usually protected against erosion with a grass cover. Grass and its roots protect soil built in slopes against rainfall, wind erosion and mass wasting (or solifluction). During dry periods and droughts, plants, especially on slopes, do not have enough water to grow and to fulfill their functions. Groundwater is normally out of their reach. There are many technical solutions to assure stability of the grass cover. They have often a form of a space mesh made of synthetic fiber. These materials do not solve the problem of water availability.

To increase water retention in agriculture, superabsorbents (SAP) are often used. Superabsorbents are loosely crosslinked hydrophilic polymers. They are usually made of partially neutralised, lightly crosslinked poly(acrylic acid), which has been proven to give the best performance vs. cost ratio (Elliot, 2004) and to absorb a large amount of water (Junping et al., 2006). In recent decades they have also been used in hygienic products (Bucholz, Graham, 1998), horticulture (Abd El-Rehim et al., 2004) and medicine (Wichterle, Lim, 1960).

The easiest way to apply SAP is to mix it with soil. It is applied to 400 000 irrigated hectares annually in the USA to control irrigation-induced erosion (Lentz et al., 2002). However superabsorbents mixed with soil decrease its strength parameters (Sojka et al., 1998). SAP decreases soil porosity and in extreme cases it can even became impermeable. On a slope a soil layer mixed with SAP can be subject to solifluction.

To improve soil water retention a new kind of geocomposite containing superabsorbent was introduced (Orzeszyna et al., 2003). It is a flat tube made from two bands of non-woven geotextile, joined together on the edges and filled with superabsorbent. It can retain 100–1000 times more than its dry mass (Fig. 1). The new geocomposite can be easily installed on the slopes of landfills and the depth and position of its application can be easily selected. Superabsorbent can also

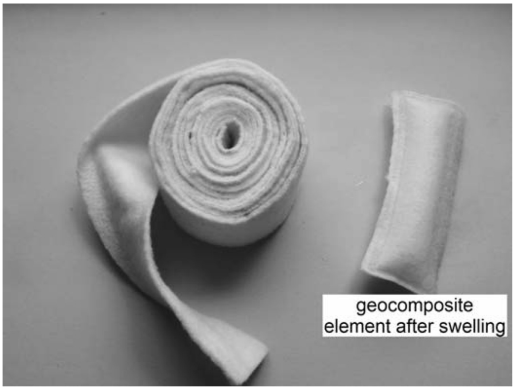

Figure 1. Geocomposite with SAP.

absorb some pollutants. The eventual removal of geocomposite from the soil, even after several years, is realizable.

Plants reduce soil erosion rates by intercepting rain, enhancing infiltration, transpiring soil water and by providing additional surface roughness by adding organic substances to the soil. Plant roots have a mechanical effect on soil strength. By penetrating the soil mass, roots reinforce the soil and increase the soil shear strength (Styczen, Morgan, 1995). Roots increase a soil's infiltration capacity (Bellot et al., 1999). They physically restrain or hold soil particles in place, for example when concentrated flow occurs (Gray, Sotir, 1996). Development of grass roots and its strength parameters can be influenced by use of a geocomposite absorbing water. This influence has to be investigated in different subsoil conditions.

Use of geocomposite with water absorbing SAP can, because of the increased soil water retention, be an easy and effective method to improve vegetation on the slopes of landfills, river embankments etc. Retaining water, it should also allow plants to be protected from the consequences of droughts. Use of the geocomposite can also be very useful in the case of industrial landfills where embankments are built of the same wastes as those deposited (e.g. wastes from flotation of copper ore or fly ash from hard coal combustion). The grass cover, if in good condition, not only stabilizes the embankment but also protects against pollutant dispersal to the environment.

The aim of the study was to determinate whether placement of geocomposite in the subsoil has an influence on the shear strength parameters of soil – geocomposite systems reinforced with roots and on the root – soil system itself. Initial tests, executed without quantitative evaluation of the results showed that placement of the SAP geocomposite in the subsoil positively influenced the growth of the root system. To determine more precisely the changes in root density distribution and strength of soil reinforced with roots, an investigation program was prepared. It was expected, in the presence of an SAP geocomposite retaining water that the total root mass would enlarge and the shear strength of the complete roots – soil system would increase.

2 MATERIALS AND METHODS

To investigate the influence of the new geocomposite on the grass roots system a slope with inclination 1 : 2 was prepared and placed outdoors in a suburb of city of Wroclaw (Poland). Containers (40 × 25 × 20 cm) with humus topsoil layer derived from alluvial soil and sand or different kinds of industrial wastes subsoil were installed in several combinations (Fig 2). The space between containers was filled with sand. In one set of containers geocomposite was installed at a depth from 6 to 20 cm. In the second set of containers the same order of soil layers without geocomposite was prepared. The system was installed in April 2005 and the experiment was completed in July 2006 during a very dry and hot summer. The same amount of grass seeds (about 25 g/m^2) was manually planted in April 2005. The installation was irrigated only during the first two weeks of the experiment. No fertilizers were used.

All of the containers were filled with medium sand or with wastes, covered with humus and a mixture of amenity grasses was seeded. The following industrial wastes were used:

- wastes from flotation of copper ore (CuW), granulation equivalent to silty sand,
- fly ash from hard coal combustion, granulation equivalent to sandy silt.

All the subsoil materials were placed without compaction.

Two types of SAP geocomposites were investigated, i) one dimensional in the form of wide strips (in practical application they are supposed to be placed in ca. 0.30 m spacing) and ii) two-dimensional geocomposite. They were placed on the bottom of the container or on the contact surface between humus and CuW subsoil.

Analysis of changes in root density as a function of depth was carried out only for sand and fly ash (test arrangements AB1 and AB9 in fig. 1). After measuring the volume of samples taken from different depths, roots and soil were separated. The roots were dried and their mass determined. To facilitate comparison, the results were calculated as the root dry mass per unit volume (g/m^3) and described as the root density.

One of the factors most important for the stability and performance of biotechnical slope protection against erosion is the strength of grass root systems. Because the depth of water available for plants influences the development of the root system, tests were carried out to show, if, after application of SAP geocomposite to a defined depth, such an influence could be observed and how it changes the shear strength of soil layers penetrated with roots. Special attention was also paid to root connections ("anchorage") between soil and geocomposite.

Tests were carried out on specimens cut from materials taken from different zones of the root system:

Zone 1 – from roots system in humus layer
Zone 2 – from contact zone between soil and the geocomposite.

For comparison some tests were carried out on soil material not containing roots or on material with roots, after roots, in the zone of shear plane, had been cut or broken. The details of layer arrangements, from where the specimens were taken, are presented in Table 1.

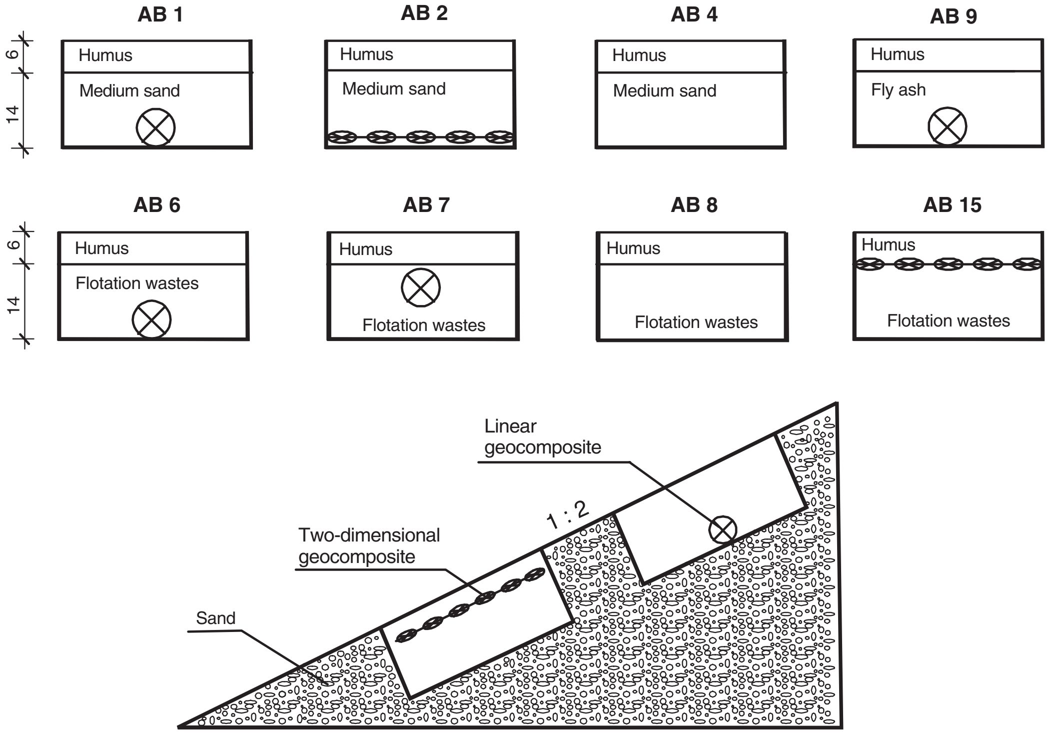

Figure 2. Above: arrangement of humus and different subsoil layers with location of SAP geocomposite in containers; below: scheme of experimental test slope.

Table 1. Description of specimens origin.

Description of layers arrangement	Unit	1	2	3	4	5
Thickness of humus layer	mm	50–60	50–60	50–60	50–60	50–60
Kind of subsoil		Medium sand	Fly ash	CuW	CuW	CuW
Subsoil thickness	mm	150	150	150	150	150
Type of geocomposite		L	L	S	L	–
Depth of geocomposite installation	mm	200	200	50	50	–
Symbol of subsoil composition		AB1	AB9	AB15	AB7	AB8
Zone, from where specimens were taken		2	2	2	1 and 2	1

CuW – wastes from flotation process of copper ore, L – linear geocomposite element, S – two-dimensional (surface element with superabsorbent placed between two layers of geotextile) geocomposite.

The test arrangement, in which the geocomposite was placed under a 150 mm thick layer of wastes from the copper ore flotation process, was not further investigated, as roots did not penetrate into the subsoil. It is therefore omitted from Table 1. In this case the SAP geocomposite had no influence on root development in the container.

Strength tests were made in a direct shear machine. The specimen, removed using a quadratic steel frame from zone 1 (root system in humus layer) or zone 2 (contact zone between soil and the geocomposite), was placed in sample chamber (60 × 60 mm) of the apparatus. The specimen height was 2-3 cm. The shear strength was determined by relatively low vertical pressures – 3.1 and 12.5 kPa, which corresponds to ca. 0,20 or 0,8 m soil cover thickness (depending on soil density). During measurements of the shear strength between roots zone and geocomposite the lower box of the shear machine was filled with a concrete block and dry sand underneath the geocomposite.

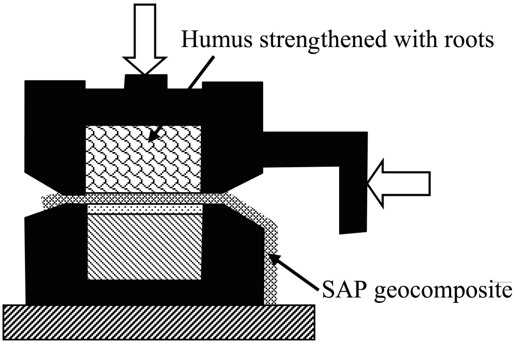

Figure 3. Test arrangement for investigation of shear strength between SAP geocomposite and humus overgrown with roots.

This forced the shearing plane to orientate precisely along the contact surface. Geocomposite was fixed at one end of the box, but along the rest of its length it was freely movable. The arrangement of this test is shown in Fig. 3. Afterwards, roots binding with geocomposite were mechanically destroyed (cut with a knife) and specimen was sheared again to determine the shear strength based only on soil/geocomposite friction without the influence of the roots.

During the test shear forces and displacements were measured under a constant vertical force. Most of the tests were carried out on systems with wastes from flotation of copper ores, because this material is very difficult for recultivation. Roots do not penetrate through the waste so a grass cover with fertile soil must be placed over the waste surface. The stability of the upper layer depends only on frictional forces between the layer of fertile soil and waste subsoil. Hence, on a slope it would need to be secured against sliding. There are two remaining problems to be solved, i) because the roots cannot use water suspended in the subsoil, the only water useful for plants is that retained in the uppermost layer, which, because of costs, should not be too thick and, ii) the stability of the whole system. Application of geocomposite containing superabsorbent could retain additional water and is easy to combine with other geosynthetic materials eventually necessary to improve grass blanket stability. Penetration of roots into geocomposite increases the forces resisting sliding of the cover along geotextile elements containing SAP.

3 RESULTS AND DISCUSSION

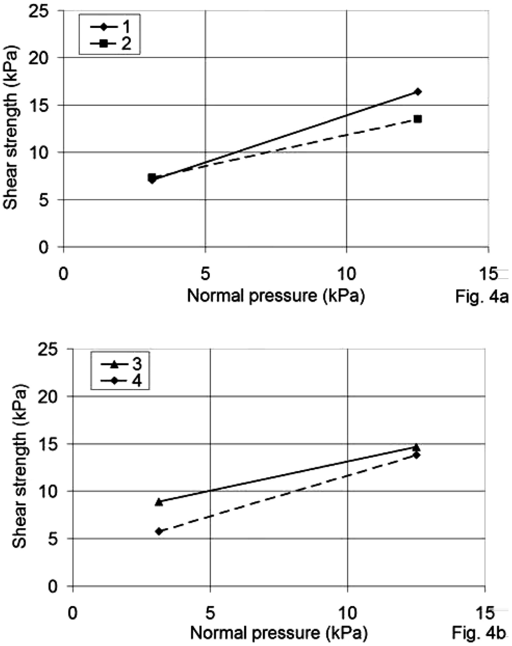

Figure 4. Results of shear strength investigation in direct shear apparatus, (1) sand with roots/SAP geocomposite, (2) loose medium sand, (3) fly ash/SAP geocomposite, (4) fly ash.

Tests results, made with medium sand and fly ash subsoil were presented in Fig. 4a and 4b. Root penetration inside these materials has been observed. They also grow into the inner space of geocomposite. Specimens for shear tests were also taken from this zone. The shear strength of the connection between granular material reinforced with roots and geocomposite was compared with the results of shear tests of the friction between sand or fly ash and geocomposite after the roots binding the soil in the upper and lower chambers had been damaged (by cutting them with a knife along a shear plane).

More comprehensive studies were performed for the subsoil consisting of wastes from the copper ore flotation process (CuW), which form a barrier stopping the development of roots into the CuW layer. Thus, the result of recultivation measures on the sloping part of the area depends on contact forces between geocomposite and humus layer laid over the embankment made of CuW (material not penetrated with roots). The same tests with and without roots reinforcement contribution in shearing forces on the contact surface between humus layer and geocomposite were made (Fig. 5a and 5b). The tests were completed by determination of the difference of shearing strength between humus penetrated with roots and humus itself (Fig. 6).

The main factor determining the magnitude of shear forces between tested medium sand or fly ash from hard coal combustion and SAP geocomposite was friction. Roots connecting the soil with linear type of SAP

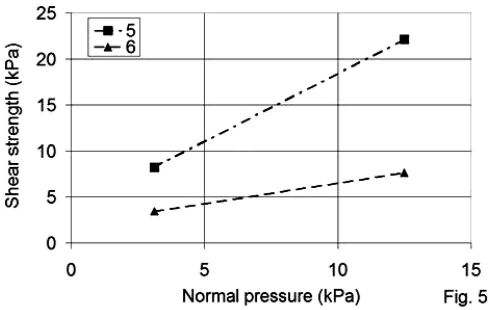

Fig. 5a

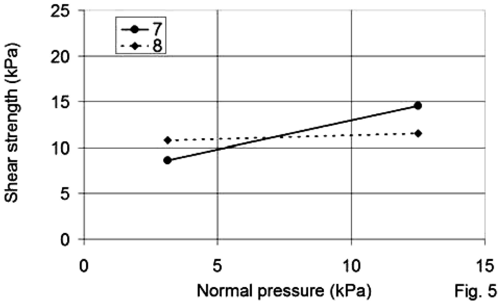

Fig. 5b

Figure 5. Results of shear strength investigation in direct shear apparatus, (5) humus with root system above CuW (two-dimensional SAP geocomposite), (6) Humus as in point 5 after deterioration of roots system/two-dimension. SAP geocomposite, (7) humus with roots system above CuW/linear SAP geocomposite, (8) humus as in point 7 after deterioration of roots system/two dimensional SAP geocomposite.

geocomposite could only slightly increase the shear strength.

For subsoil made of wastes from (CuW), a two-dimensional geocomposite (Fig. 5a) has also been used. It has shown the best performance – by normal stress 12.5 kPa shear strength increase due to the root penetration into the geocomposite compared with shear strength between humus and geocomposite due to friction only, reached 15 kPa (almost 200% shear strength increase due to roots reinforcement compared to shear strength between humus and geocomposite without roots contribution; by normal stress 3.125 kPa shear strength increase was much smaller, in order 5 kPa (over 130% increase). The same tendency, i.e. of a larger shear strength increase by larger values of normal stress has also been observed when linear elements of SAP geocomposite were applied (Fig. 5b). However, this increase was much smaller than for two-dimensional material.

Another problem analysed was the influence of SAP geocomposite on the development of the root system (Fig. 6). Humus reinforced with roots, placed over a CuW layer, was also investigated in the direct shear apparatus. It was noted that the presence of SAP geocomposite also slightly increased the shear strength of the humus/roots system. Due to the presence of geocomposite, the root system was better developed, so more roots with determined tensile strength are reinforcing the analysed layer. To compare these values with shear strength of humus, roots were cut along the whole shear plane before the tests, so in these case roots were not contributed in shear forces. The results have shown the strong influence of roots on shear strength of humus. Roots increased the strength by about 10 kPa, by normal pressure 3.125 kPa i.e. over 150% shear strength increase if compared to humus without roots reinforcement. It is difficult to compare these results with results of other researchers, because usually tests are made with different soils and in different conditions. The work presented here confirms the conclusion that plant species and their root density are factors strongly influencing the shear strength value (Wu, 1994).

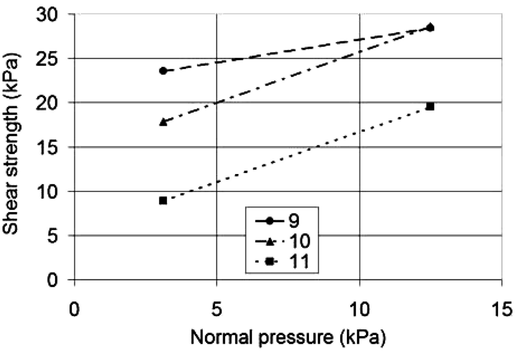

Figure 6. Results of shear strength investigation in direct shear apparatus, (9) humus with root system above CuW (linear SAP geocomposite) (10) humus with root system above CuW (without SAP geocomposite) (11) humus above CuW after the root system was damaged by cutting along shear surface.

When soil samples strengthened with roots were investigated, the shear stress development as a function of displacement during the tests in a direct shear machine, all had a similar shape to that presented on fig. 7.

Shear stresses increased in the first stage and then remained constant or only small drop of shear stresses could be observed in the end phase. Rest shear strength values were always higher than for soil without roots or with roots cut along shear surface before the test. This means that during the test roots were not sheared or torn off and that the mechanism of measured shear strength is based upon friction between roots and soil surrounding them. Such a damage pattern was confirmed during examination of the samples after the test. There was displacement between lower and upper part of the sample but nevertheless it remained as a

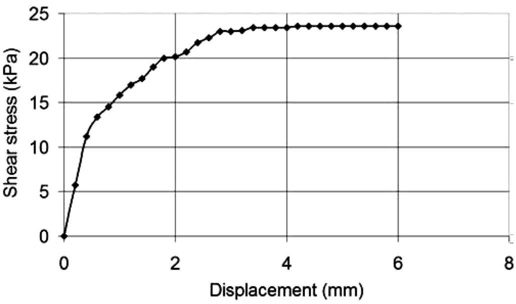

Figure 7. Shear stress – displacement relationship for humus with roots – samples taken from the layer over SAP geocomposite laid on post flotation copper ore waste subsoil.

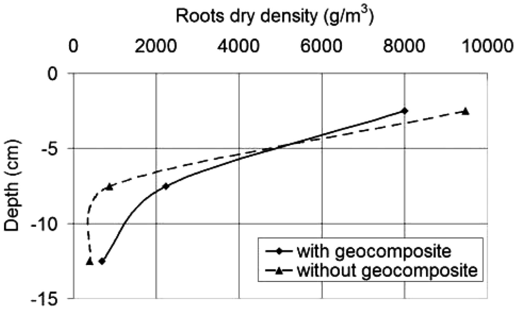

Figure 8. Influence of SAP geocomposite on roots dry density.

single block. In the lower box one could observe a gap between rear sample surface and box wall. So it should be assumed, that the ultimate shear strength of roots must be higher than that determined in small direct shear apparatus. To determine ultimate shear strength of the roots, the tests equipment would have to ensure sufficient length of roots anchoring, which was not possible because of box dimensions.

As was expected SAP geocomposite placed near the bottom of the container influences the root density distribution causing increase of root mass near the geocomposite, where additional water can be retained. This increase, which reached values 80–150% compared to the results for subsoil without linear SAP geocomposite placed near the bottom of the container, is shown on Fig. 8 and Fig. 9. We anticipate that these changes depend on time, but this factor was not monitored during our investigation.

4 CONCLUSIONS

The studies presented here show that SAP geocomposite encourages better development of the root system, even when applied over post-flotation copper ore wastes, which block root penetration inside this layer.

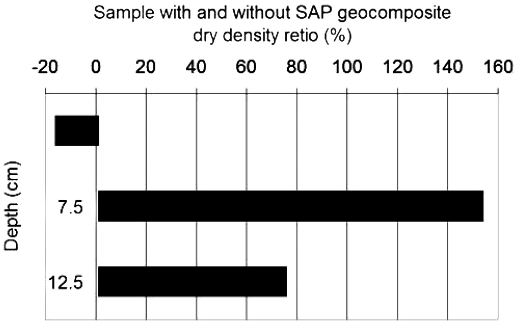

Figure 9. Changes of roots dry density as a result of SAP geocomposite application.

Based on the results of shear stress analysis, analysis of root density distributions and direct observation of dismantled container test application of SAP geotextiles the following conclusions can be drawn:

1. The root system increases the shear strength of the humus layer.
2. Usage of geocomposite containing SAP can change the density of root distribution, increasing its density in the vicinity of the geocomposite.
3. Roots penetrating into the SAP geocomposite improve the shear strength between soil and geocomposite. When two-dimensional geocomposite was used, a higher increase in the shear strength occurred than for the linear form of geocomposite.
4. During tests in a small direct shear machine (60 × 60 mm), roots were not torn off along the shearing plane, so that the determined shear strength is not the ultimate one but depends on the friction between roots and surrounding soil. Shear strength values determined using this method are conservative. To determine the ultimate shear strength value of the soil with the roots requires another test arrangement, securing large enough anchoring forces.

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Effect of mineralogical composition and compaction conditions on sealing properties of selected mineral materials likely to be used for landfill construction

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ABSTRACT: Municipal waste landfills have to be considered as biochemical reactors, in which leachates are the medium by which soluble materials inside the landfill may subsequently be transported into the environment. Thus, bottom and top liners play an important role in controlling migration of pollutants from waste deposits and prevent uncontrolled atmosphere, soil and groundwater pollution. The paper presents results of laboratory compaction studies and water permeability measurements at different bulk densities, carried out on three mineral materials: natural Cracovian clay, mineral waste rock from Bogdanka coal mine and their mixture (0.3 clay: 0.7 waste). The addition of Markowicze clay reduced the water permeability of the coal mine waste suggesting its potential applicability for the construction of liners of landfills for inert wastes. The effect of mineralogical composition of the materials, of their bulk density, and of water content during compaction on porosity and water permeability is discussed.

Keywords: Landfills, clay liner, compaction, water permeability, Proctor test, bulk density.

1 INTRODUCTION

Landfill bottom and top capping systems must prevent not only infiltration of rainwater into the waste body but there is a necessity to eliminate leachate penetration from the waste deposit to aquifers. The basic method of landfill sealing consists in constructing an isolation liner. Under European conditions different constructions such as clay liners, synthetic liners and more complex combinations of both are recommended.

In the literature many data concerning landfill sealing and numerous comparisons of the materials applied can be found (Bell, 1988a, 1988b; Pingpank et al., 1994; Prashanth et al., 2001; Tay et al., 2001; Horn & Stępniewski, 2004; Marques et al., 2005: Sivapullaiah & Lakshmikantha, 2005). Numerous authors draw our attention to the fact that landfill liners constructed according to the up-to-date techniques may, in a relatively short period of time, become permeable because changes of water content as well as resulting changes of the spatial arrangement of the particles lead to the formation of cracks causing an increase of the air and water permeability. If the changes of water content are regarded as inevitable, there is a need to modify the mineral liner to make it more resistant to changes of water content when, simultaneously, good hydro-isolation properties are to be maintained. One of the approaches is to look for materials or their mixtures, which already possess good isolation properties (Quigley et al., 1988; Wagner, 1994; Prashanth et al., 2001). For this purpose waste mineral materials (coal wastes, fly ashes) themselves are more often considered as possible alternatives. Another approach concentrates on modification of properties (filtration, shear strength) of already available materials (Bell, 1988a, 1988b; Pingpank et al., 1994; Horn & Stępniewski, 2004; Sivapullaiah & Lakshmikantha, 2005). In most publications water permeability is presented as the parameter which decides a material's usefulness for landfill construction.

Requirements concerning water permeability are more restrictive for landfill than for water engineering works. However, in more fine textured soils no other geotechnical parameter is so difficult to determine, and to relate the data to the real boundary conditions as the water permeability. More than forty years ago Mitchell et al. (1965), using loam samples, stated, that even a small change of water content and density may cause changes in water permeability even by as much as two orders of magnitude. This sensitivity was attributed to the structure of clays which depends, to a great extent, on the method and the degree of compaction.

Pollutant movement from landfill to the environment may occur due to leakage by filtration and/or diffusive flow. It should be added that leakages are usually uncontrolled and difficult to repair. Wagner & Böhler, (cited after Wagner, 1994) have shown that for very fine-porous media such as mineral bottom liners, the advective solute transport at a low hydraulic gradient and at hydraulic conductivity between 10^{-10} and 10^{-11} m/s, is almost the same as the diffusive solute transport (i.e. transport due to concentration difference). However, very often the bulk density and filtration coefficient are considered as the most important criteria for evaluation of the usefulness of a given isolating material (Holzlöhner et al., 1995; Met et al., 2005). Bulk density and void ratio are commonly used to characterise the state of soil compactness. The effect of varying energy, method and compaction conditions on the bulk density of a given material is described in more detail by Head (1980). The maximal bulk density as a function of water content is determined under laboratory conditions by the Proctor method. A Proctor compaction test should be carried out in connection with measurements of the filtration coefficient in order to establish its dependency on the compaction degree. The principles of control studies are the object of standards and specific recommendations included in technical approvals of the particular materials and should be verified at the site of the construction.

1.1 *Factors influencing the hydraulic properties of the sealing mineral materials*

Water permeability of clay liners is critically dependent on water content of the material during its compaction and the resulting bulk density. The compaction curve shows a maximum dry bulk density at optimum water content (w_{opt}). This curve is specific for a given material and equivalent data sets must be generated for each liner material under consideration (Allen, 2001). Legislative regulations define the permissible value of Proctor density. In legislative recommendations in Poland (ITB No. 337/1995) and in Germany (TASi 93), the values of water content during in situ compaction are required to be located on the moist i.e. the negative slope of the Proctor curve. However, a higher water content of the compacted material enhances the crack formation (Baumgartl & Horn, 1997). The after-effect of scratches and crack formation is a loss of the isolating function of the layer. More and more often the benefit of clay compaction at water content on the dry side of the Proctor curve is discussed. Although reaching a high level of compaction in this case more energy is required than at w_{opt}, because the soil material remains in the residual shrinkage range (Chertkov, 1995, 2003; Peng & Horn 2005, Hartge & Bachmann, 2000), which is characterized by a higher stability. In this state even a considerable loss of water will not cause undesired crack formation or loss of sealing properties.

The influence of organic and inorganic pollutants contained in leachates on sealing properties of the liner depends on its mineral composition. For a mineral base liner of bentonite-bearing mixtures, the water permeability slowly increases as a result of the sorption processes (Fernandez & Quigley, 1985; Wagner, 1994). Based on crystallo-chemical and thermodynamic considerations, May et al. (1986) and Wagner, (1994), came to the conclusion that illite and smectite represent completely unstable phases. The interaction between inorganic pollutants and smectitic clays can lead to cracking and thus influence the permeability of the clays. According to Wagner (1994), long-term stability of smectite, and thus of mineral bentonite liner, does not seem to be achieved because of the continuous interaction with the leachate components. This is why mineral sealing materials of more stable clay mineral mixtures (e.g. kaolinitic clays) are used increasingly.

Among other factors considerably influencing the hydraulic properties of sealing materials the temperature inside the waste body and load should be mentioned. Temperature increases result in higher water permeability because of a smaller viscosity and density of water (Holzlöhner, 1995). Bulk density change caused by external or internal stress has a considerable impact on the hydraulic properties which are generally variable in time (Fleige & Horn 2000; Baumgartl & Horn, 2001).

The aim of this paper is to present results of laboratory compaction studies and water permeability measurements at different bulk densities, carried out on three mineral materials, likely to be used for liner construction: natural Cracovian clay, mineral waste rock from the Bogdanka coal mine and their mixture. The effects of mineralogical composition of the materials, of their bulk density, and of water content during compaction on their porosity and water permeability are discussed.

2 MATERIALS AND METHODS

2.1 *Materials*

Three materials were used for the tests:

- natural Cracovian clay from the mineral resources mine of Markowicze (Lublin Region, Poland);
- carbonic waste rock accompanying hard coal mining in the Lublin Coal Basin (Poland);
- a mixture of waste rock (70% weight) with Markowicze clay (30% weight).

2.1.1 *Natural Cracovian clay formation*

The Cracovian clay used in the studies came from the Markowicze (Lublin Region, Poland). This material is used to produce brick with high durability parameters. It consists of 32.5% fraction <0.002 mm, 30% of 0.01–0.002 mm fraction, 36% of 0.06–0.01 mm fraction and 1.5% of the fraction >0.06 mm. This natural Cracovian clay in the region is also a waste produced during opencast mining of sulphur. The thickness of the clayey layer is even up to 70 m in the Machów mine. On average, Cracovian clays constitute 80% of the whole sulphur mine waste. Among mineral components, depending on the place of sampling, kaolinite and montmorillonite dominate.

During more than 30 years of sulphur exploration, the clays were deposited non-selectively on waste heaps. The waste heaps were subjected to reclamation. It is estimated that on the waste heaps in the Machów sulphur mine there are 280 mln tones of this waste. Moreover, despite the decision about closing the mine, there is a possibility of using the clays from the natural deposits.

Evaluating the Cracovian clays in the categories of a raw material for the construction of landfill liners it is important to stress some of their significant features, such as:

- ease of puddling and creating non-permeable isolating layers
- ease of dewatering and at the same time high sorption of organic and inorganic substances (cation exchange capacity 250–300 mmol/kg), neutral to a little alkaline reaction, a high plasticity index.

2.1.2 *Coal mine wastes*

The studies were performed on material subjected to weathering during 3 years of open air storage on a pile of Bogdanka coal mine. The waste rock was mechanically ground into granules less than 4 mm. The waste rock usually contains 60–80% of clay stones with 30–40% of kaolinite (Wiśniewska et al., 2002; Filipowicz & Borys, 2004).

Because of its low permeability, this material may be used in building flood embankments and settlements embankments, fishponds and waste disposal sites' dykes according to recommendation presented in "Guidelines for the application of mining wastes from the Bogdanka mine in flood embankments and other hydrotechnical buildings construction" (Borys et al., 2002).

From numerous studies (Borys et al., 2002; Wiśniewska et al.2002) it follows that in the whole period of coal deposits mining of the Lublin Coal Basin, there have been no significant changes in the chemical composition of the mining wastes. They are neither toxic nor radioactive. As shown by leaching tests, the heavy metal content in waste rock is low, and these metals are bound in forms mostly insoluble in water. Under the influence of intensive water action on rock, a small amount of iron is released, which is connected with the presence of siderite and pyrite. By limiting oxygen access to waste rock (proper compaction) significant inhibition of bacterial decomposition of sulphides is possible. As was shown in some recent studies (Borys et al., 2002) the heavy metals contained in mining wastes are not hazardous to the environment in the process of their economic use.

2.2 *Methods*

2.2.1 *XRD, SEM studies*

The mineral composition of the waste rock and Cracovian clay was analysed with the help of X-ray diffraction (XRD) with the powder method using a Philips X'pert APD X-ray diffractometer with a PW 3020 goniometer and a Cu lamp as well as a graphite monochromator. The analysis was carried out within the angular range 3–65°2Θ. For processing the diffraction data the Philips X'Pert software and the ClayLab ver. 1.0 programme were used. The identification of mineral phases was based on the PCPDFWIN ver. 1.30 database formalized by JCPDS-ICDD.

The form and morphology of the main components of both samples and examination of the chemical composition in the microregion was performed using a scanning electron microscope (SEM) with field emission (HITACHI company model S-4700) equipped with a system of chemical composition analysis based on X-ray energy dispersion (EDS) (VANTAGE; NORAN system, Thermo Fischer Scientific). The samples for SEM testing were stuck to a graphite holder with the help of graphite glue, and then the preparations were coated with a layer of graphite of about 50 nm thickness in a CRESSINGTON sprinkler. The presented methodology is essential to assure conductivity of the sample surface.

2.2.2 *Determination of compaction curves and optimal water content*

The Proctor test was carried out to determine the compaction curves and to derive the optimal water content and dry bulk density for each material. Each material was compacted in three small cylinders with a capacity of 1 dm^3 each. According to the previously selected method the following parameters of the device's functioning were applied: the type of the rammer -2.5 kg; the number of inserted layers – 3; the number of strokes – 25 per each layer; the height of the rammer's drop – 32 cm; the total compaction energy applied -0.6 kJ dm^{-3}.

2.2.3 *Determining the coefficient of water permeability "k"*

The coefficient of water permeability k was determined for particular Proctor density treatments with the falling-head method with rigid walls and constant

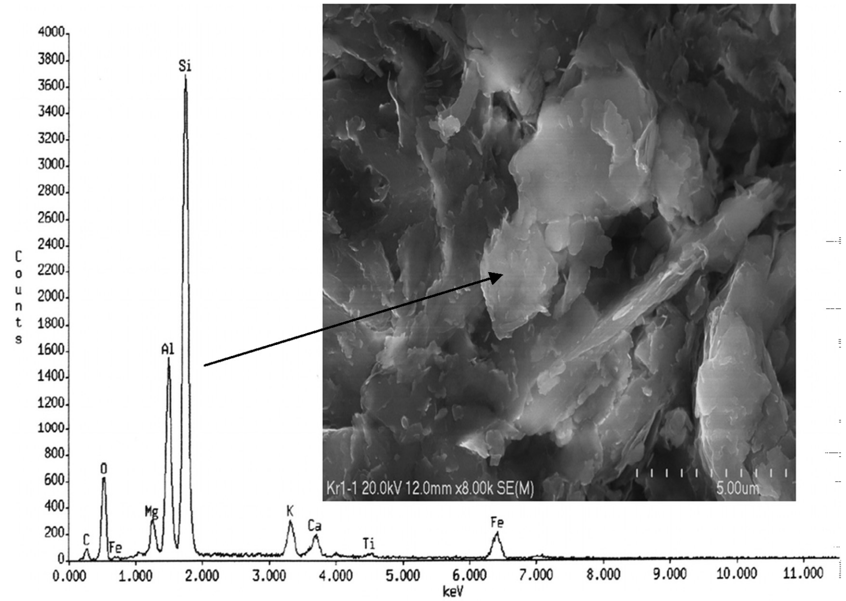

Figure 1. SEM image of smectite and an XRD analysis of the microregion.

cross-section area (Hartge & Horn, 1992; Niedźwiecki et al., 2003), with three repetitions for each cylinder. The measurement lasted up to several hours so that exchange processes can be ignored. The determination consisted in the measurement of the level of water head falling in time t. The values of the coefficient of water permeability *k* were calculated according to the formula:

$$k = \frac{H}{t_1 - t_0} \log_e \left(\frac{h_0}{h_1} \right) \tag{1}$$

where: k – coefficient of water permeability [m s^{-1}], t_0 – time of the beginning of measurement [s], t_1-time of the end of measurement [s], h_0 – water level at time t_0 [mm], h_1-water level at time t_1[mm], H – height of the soil sample [m].

3 RESULTS AND DISCUSSION

3.1 *XRD, SEM study results*

3.1.1 *Mineral composition of natural Cracovian clay*

The dominant components of Cracovian clay are the clay minerals. This has been confirmed by scanning microscope pictures complemented with chemical composition analysis (Figs. 1 and 2). The irregular and heavily torn thin blades visible in Fig. 1. are probably smectite. This assignment of confirmed by a chemical analysis spectrum, in which the main components are Si, Al, K, Ca, Mg, Fe. In the centre of Fig. 2 an idiomorphic feldspar crystal is visible, developed in the form of albite, deeply-embedded in the clay mass.

The ratios of the main mineral components of this clay are the following: kaolinite: 10–15%; illite: 25–30%; smectite – up to 15%. The remaining components are: quartz: 25%; feldspars: 15–20% and carbonates: 15% (including mainly calcite: 12% and dolomite: 3%).

3.1.2 *Mineral composition of the waste rock*

The main mineral component of waste rock is kaolinite. Chemical analysis in the microregion carried out on individual grains of this material supports the presence of kaolinite. In a characteristic spectrum of the chemical composition SiO_2 and Al_2O_3 dominate. The other elements present in the trace (K, Fe, Ti, Mg) are connected mainly with the mineral background of the waste rock.

Kaolinite is often present in the form of thin blades of about 1 μm thickness with a clearly marked hexagonal habit. In the scanning microscope images no vermicular morphological forms, characteristic for kaolinite were noted. An almost complete lack of a spatial ordering in the distribution of individual kaolinite grain is visible in Fig. 3. Sometimes kaolinite grains accumulate and assume cubic forms, in which kaolinite blades loose their hexagonal habit and take irregular heavily torn forms (Fig. 4.).

The contents of the main mineral components of the waste rock are the following: kaolinite: 30–40%; illite: 15–25%; smectite: up to 5%. The remaining

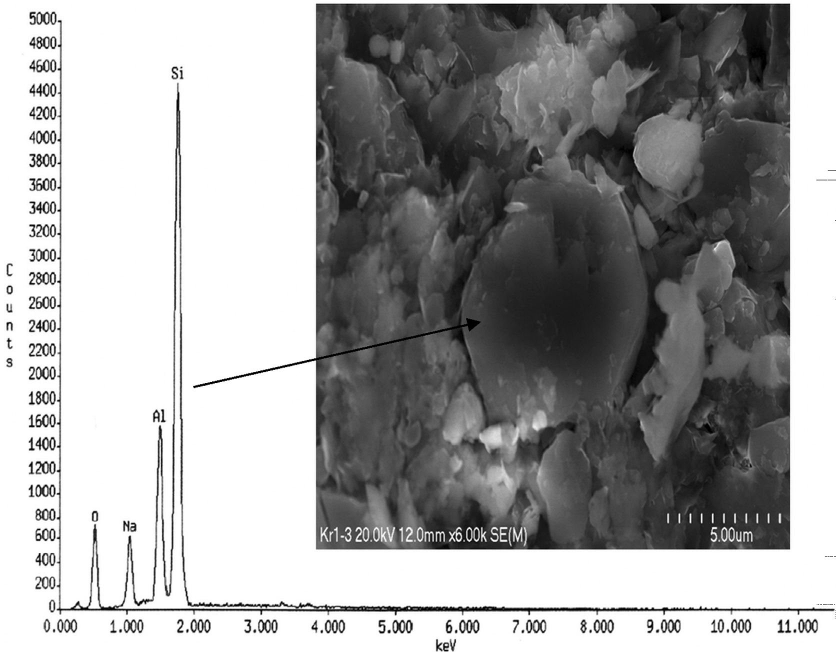

Figure 2. SEM image of a potassium feldspar grain (albite) with an XRD analysis of the microregion.

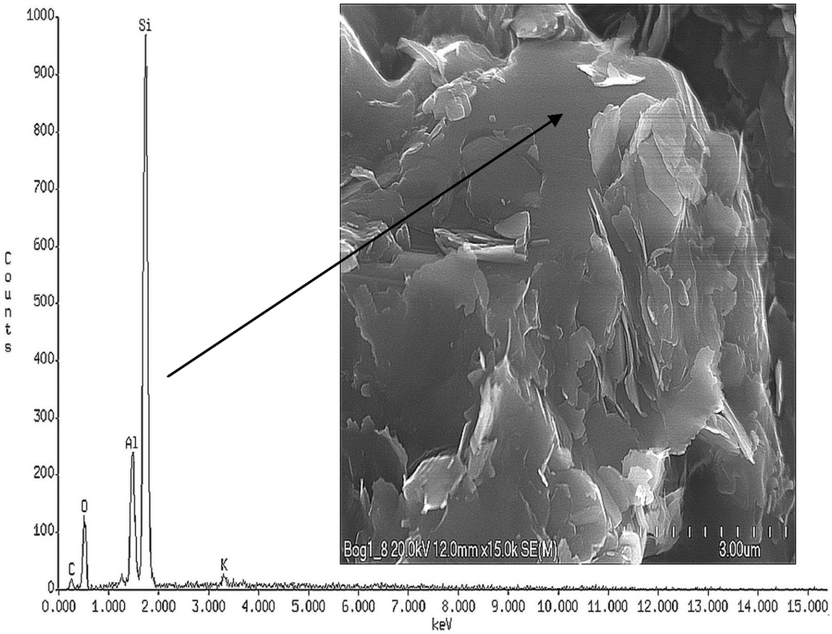

Figure 3. Accumulation of blade kaolinite grains (SEM image) with an XRD analysis of the microregion.

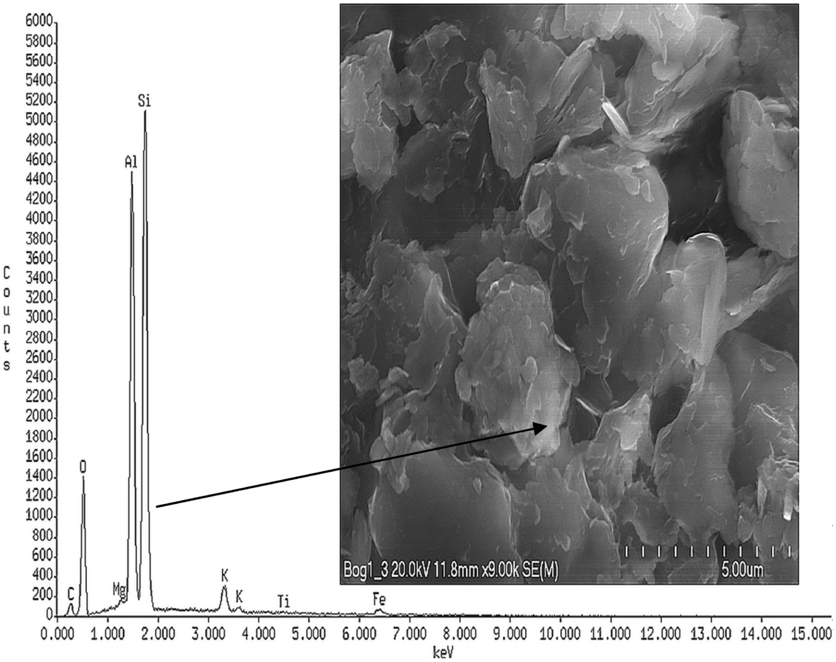

Figure 4. The form of kaolinite grains accumulation (SEM image) with an XRD analysis of the microregion.

components are mainly quartz: up to 30%, and other admixtures constituting up to 5%.

The main mineral components of both materials are illite and kaolinite, however, we can see characteristic inverted proportions of these components in individual materials. Kaolinite dominates in the mineral composition of waste rock, illite – in the composition of the Cracovian clay. The clay is characterized by a higher content of smectite and carbonate content of up to 15% compared to the waste rock.

3.2 *Determination of optimal water content*

Changes in compatibility which depend on the water content of the material during compaction are presented in Fig. 5. As can be seen the mine rock compaction curve substantially differed from that of the Cracovian clay in terms of Proctor densities and optimum water contents, while the mixture of both – as would be expected – showed intermediate properties. The values of optimum water contents and the corresponding void ratios at Proctor bulk densities of particular materials are presented in Table 1. The susceptibility of mineral materials to compacting is usually characterized by two parameters: optimal water content for compaction and the maximal bulk density obtained. Both parameters are determined from the compaction curve drawn on the basis of the standard Proctor test.

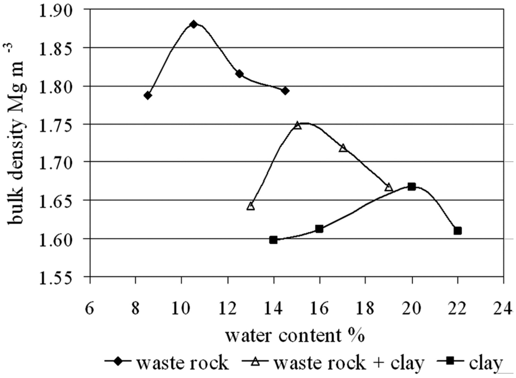

Figure 5. Dependence of the dry bulk density on the water content during compaction of the studied materials (according to the Proctor test).

The maximal bulk density of the waste rock $-1.88\,\mathrm{Mg\,m^{-3}}$ was obtained at 10.5% water content. The void ratio at the optimal water content was the lowest of the materials under study and equalled 0.27.

Borys (2002) carried out investigations on compaction of mine wastes from the Lublin Coal Basin with different degrees of weathering: fresh – taken from a conveyor belt and after 5 and 7 years of storage on a pile. The obtained results together with the compaction ability of mine wastes from the Upper Silesia Coal Basin are presented in Table 2 (Borys, 2002).

Table 1. Optimal water contents, maximal dry bulk densities and corresponding void ratios of the studied materials.

Type of material	Optimum water content [%]	Maximal bulk density [$Mg\,m^{-3}$]	Void ratio
Waste rock	10.5	1.88	0.27
Cracovian clay	20	1.67	0.64
Waste rock + clay	15	1.75	0.43

Table 2. Water content during storage, optimal water content for compaction and maximal bulk density for coal mine wastes from the Lublin Coal Basine (LCB) and Upper Silesia Coal Basin (USCB) (Borys et al., 2002, Filipowicz & Borys 2004).

Coal wastes	Natural water content* %	Optimal water content %	Maximal bulk density $Mg\,m^{-3}$
From LCB			
Fresh	$10 \div 13$	$11.6 \div 13.0$	$1.79 \div 1.92$
After 5 years	$10 \div 11$	$11.0 \div 11.5$	$1.69 \div 1.75$
After 7 years	$13 \div 15$	$15.0 \div 16.0$	$1.68 \div 1.71$
From USCB			
Fresh	$4 \div 10$	$7 \div 12$	$1.7 \div 1.9$
From multiannual piles	$5 \div 19$	$11 \div 19$	$1.2 \div 2.0$

*water content of coal wastes deposited at piles.

The maximal bulk density obtained for LCB coal wastes are, depending on the author, as follows:

- $1.85\,Mg\,m^{-3}$, at mean optimal water content $w_{opt} = 11.8\%$ (Borys et al., 2002),
- $1.88\,Mg\,m^{-3}$ at mean optimal water content $w_{opt} = 10.5\%$ (this paper).

It follows that the best effects of compacting during engineering and technical work may be obtained at minimum 10% water content in the waste rock. Wastes from the Lublin Coal Basin are characterised by a narrow range of natural water contents, at relatively wider ranges of optimal water contents (Table 2). This creates favourable conditions for compacting without taking special measures connected with pre-wetting or pre-drying the material.

Cracovian clay from Markowicze, is less susceptible to compacting than the mine waste rock. The obtained maximal bulk density at water content 20% (w_{opt},) is $1.67\,Mg\,m^{-3}$ (Fig. 5). The minimal void ratio obtained at these parameters (Table 1) is 0.64 and is more than two-fold higher than the minimal void ratio for the waste rock.

In comparison with the studied Cracovian clays, its mixture with the waste rock is characterised by a higher maximal bulk density ($1.75\,Mg\,m^{-3}$) at optimal water content 15%. At the point of maximal compaction the void ratio reached the value of 0.43.

Table 3. Coefficient of water permeability depending of water content during compaction.

Type of material	Coefficient of water permeability depending of water content during compaction $k[m\,s^{-1}]$		
	$W_{opt} - 2\%$	W_{opt}	$W_{opt} + 2\%$
Waste rock	4.87×10^{-7}	9.71×10^{-7}	1.93×10^{-6}
Cracovian clay	5.54×10^{-8}	8.83×10^{-8}	9.77×10^{-8}
Waste rock + clay	1.38×10^{-7}	3.32×10^{-7}	8.06×10^{-7}

W_{opt} – optimum water content [%].

Summing up the results of the compaction tests of the three materials, it was found that the highest bulk density of all the tested materials ($1.88\,Mg\,m^{-3}$) was obtained for the mine waste rock at the lowest optimal water content ($w_{opt} = 10.5\%$). However, introduction of clays to the waste rock, should be considered from the point of view of increasing the clay fraction content in the material, which should result in reducing water permeability of the layer formed of it.

3.3 *Comparison of hydraulic properties of the tested materials*

Changes in water permeability, depending on the water content during compaction are presented in Table 3. Compaction of the waste rock resulted in a water permeability of 10^{-6}–$10^{-7}\,m\,s^{-1}$, which corresponds to semi-permeable materials.

According to the directive 99/31/EC the materials of hydraulic permeability below 10^{-7} can be used to construct liners of landfills for inert wastes. The permeability of unmodified waste rock with kaolinite as a dominating clay mineral (1:1 type) was not low enough to allow its use as a sealing material for landfills for inert wastes. The permeability of mine waste depends on its composition, susceptibility to weathering processes and the storage period (weathering degree), water content during compaction and on the degree of compaction obtained. The processes of weathering of rocks proceed very rapidly in the initial period (the first year) of storage. As a result of weathering, the proportion of the clay fraction in the material increases (Sullivan & Sobek, 1982; Twardowska et al., 1988).

Thus, with the advancement of the weathering, the effective grain diameter d_{10} will decrease. This, in turn, according to the Hazenequation (Vrbka et al., 1999) will lead to a decrease in water permeability.

When compacting the waste rock on the left side of the Proctor curve (W_{opt} – 2%) the obtained bulk density was $1.79\,Mg\,m^{-3}$ (Fig. 5). However, despite a rather low value of compaction indicator (defined as the ratio of the bulk density to the maximum Proctor b. density), equal to 0.94, a considerably lower water conductivity of the material was obtained compared to the optimum water content (Table 3).

For all tested materials, a decrease of water content during compaction by about 2% from the optimum ($W_{opt} - 2\%$), resulted in a decrease of water permeability. Increase of water content during compaction by about 2% ($W_{opt} + 2\%$) resulted in an increase of water permeability of all tested materials. This is an experimental confirmation that, for the purpose of landfill liner construction, the compaction at water content slightly lower than the Proctor optimum is more favourable. The exact interval of water content during compaction as well as an explanation of this fact in terms of pore continuity, tortuosity and size distribution requires further studies. An important argument for compaction of the mineral materials likely to be used for landfill liner construction is that the shrinkage potential at lower water content during compaction decreases (Wysocka et al, 2006, Wiśniewska et al, 2006).

Assuming that water permeability is the most important parameter characterizing the usefulness of a material for waste deposit sealing (Holzlöhner et al., 1995; Met et al., 2005) with the legitimacy of the material's compaction on the "dry" side of the Proctor curve can be confirmed.

Addition of 30% of Cracovian clay with illite as the dominating clay mineral (2:1 type) to the mine waste rock increases the clay fraction content by 10% (enrichment with illite) of and, in consequence, decreases its water permeability, despite of the lower compaction parameters in comparison with original waste rock (Fig. 5). This decrease was not sufficient to meet the requirement of the permeability value below $10^{-7}\,\mathrm{m\,s^{-1}}$. It can be, however expected that the increase of the proportion of the Cracovian clay in the mixture would lead to further lowering of the permeability value. Significant changes of water permeability obtained in similar studies (Daniel & Benson, 1990; Benson et al., 1994; Met et al., 2005), are interpreted as a consequence of changes in the mineral composition of the material and the conditions of its compaction. Water permeability must therefore be considered as a function of the geotechnical and mineralogical properties of the material.

4 CONCLUSIONS

The choice of material for the construction of a landfill sealing should be made based, among other factors, on the relationship between compaction conditions, resulting bulk density and water permeability. The results obtained indicate that the water permeability of the materials under study is strongly related to the mineralogical composition and water content during compaction.

1. The mineral composition of the Lublin Coal Basin waste rock and of the clay from Markowicze, because of their large clay fraction with dominant kaolinite and illite indicates a potential application to the construction of mineral liners of landfills for inert wastes.
2. The mining wastes show good compactness, with optimal Proctor water content within the limits of natural water content of the material which enables their application without additional wetting or drying.
3. In comparison to the waste rock, Cracovian clay is less susceptible to compaction. The use of clay as an additive to the waste rock is beneficial. It causes an increase of the clay fraction content in the material and enables reduction of the water permeability coefficient.
4. The lowest values of water permeability coefficient were obtained for each of the tested materials during compacting on the left side of the Proctor curve with a water content slightly lower than the Proctor optimum water content ($W_{opt} - 2\%$). Under these conditions the shrinkage potential, and thus the liner cracking possibility, is also reduced.

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Sewage sludge disintegration – A promising way to minimize negative environmental impact

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ABSTRACT: A relatively new technology, sludge disintegration, presented in this paper, consists of pre-treatment of the sludge before its anaerobic digestion. This technology intensifies biogas production and improves the quality of digested sludge. Based on the literature, the methods used for sludge pre-treatment before its anaerobic digestion, are described. Additionally, the authors present results of their own experiments, performed on sludge samples taken from the Gdańsk WWTP. The sludge was disintegrated mechanically using homogenisation and sonification methods. The objective of the study was to examine methods of preliminary sludge preparation, before its anaerobic digestion, to enhance the dewatering and digestion processes. Besides, the methods of evaluation of the disintegration degree are discussed.

Keywords: Wastewater sludge treatment, sludge disintegration, anaerobic digestion, biogas

1 INTRODUCTION

Modern biological wastewater treatment plants (WWTP), due to their higher efficiency, generate ever increasing quantities of sludge. This causes a big problem with appropriate sludge management. Usually, it is thickened, stabilized, dewatered and finally, dumped or incinerated. A more sustainable way of processing is composting and use as fertilizer. However, each of these processes contains its own impact on the environment.

Recently, serious efforts to reduce the volume of sludge requiring treatment and final disposal have been undertaken. One of the most promising ideas is the mechanical disintegration of activated sludge. The advantages resulting from such an application are numerous and depend on the points in the sludge stream at which disintegration is applied (Wei et al. 2003, Wang et al. 2005, Yoon & Lee 2005, Gronroos et al. 2005). Currently the most popular is disintegration of excess sludge before its anaerobic digestion. This increases the anaerobic digestion efficiency and, as a consequence, increases the volume of biogas produced while at the same time reducing the volume of residual sludge.

If return sludge is disintegrated and supplied back to the wastewater treatment bioreactor, this provides an additional carbon source for the denitrification processes. The third application is disintegration of filamentous bacteria in the bulked sludge. This method can be a very useful way of sludge bulking or foaming minimization and control (Wünsch et al. 1993).

In many WWTP the process of digestion in anaerobic conditions is applied for excessive sludge stabilization. In this process, four phases can be identified. They are: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Evans 2001). It has been stated, that the preliminary hydrolysis phase is the limiting step in a digestion process. During this phase, particulate organics become solubilized and as such, they can serve as a substrate and an energy source for the anaerobic bacteria, responsible for the process. It may be assumed, that the increased surface of the sludge flocs particles (due to their decomposition) might also enhance the rate of hydrolysis. Therefore, any technology that can stimulate higher hydrolysis rates might also intensify both VFA production and methane digestion, since these processes are coupled. A simultaneous decrease of organic content in the digested sludge is also an important element of a sustained development principle.

Placing disintegration of the sludge ahead of the digestion process, results in a significant shortening of a digestion time and enhanced production of biogas.

When disintegrating sludge is already digested to some degree, both higher gas production and organic matter decomposition can be expected (Ried & Stapel 2002, Kim et al. 2003).

1.1 *Disintegration techniques*

Below we briefly review disintegration methods investigated at experimental and pilot scales and described in the literature. These methods are thermal, chemical and mechanical disintegration.

During thermal hydrolysis, a substantial fraction of particulates can be separated and decomposed to soluble and less complex forms. During so-called "subcritical wet oxidation" (Neyens & Baeyens 2003, Neyens et al. 2003) complete destruction of the organic fraction occurs at 374°C (22.1 MPa). The process is still under investigation and one of its main constraints is the recycling of soluble forms of nitrogen (mostly ammonium) with the produced VFA to biological reactors.

Another method of thermal disintegration is the heating of the excess sludge to temperatures above 150°C for over 30 minutes. In this process, the disruption of activated sludge cell membranes and conversion of organics to more readily digestible forms occurs.

Application of ozone presents a chemical method of sludge disintegration. As a result of ozone action, disruption of microbial cell membranes occurs, accompanied by a release of the intercellular material. Additionally, application of ozone brings about partial oxidation of slowly degradable material to simple, more readily biodegradable forms. Hence, at wastewater treatment plants where the C/N ratio is not favorable, disintegrated sludge may serve as an additional source of organic carbon for denitrification.

So far, the most popular is disintegration of excess sludge and a part of recycled sludge. The ozone doses varied from 30 g O_3/kg dry solids to 80 g O_3/kg dry solids; at these doses a floc structure of sludge is no longer noticeable (Ried & Stapel 2002, Liu 2003). Energy consumption in this process was 0.6 and 1.7 kWh/kg VSS, respectively. Apart from ozone, other chemicals can also be applied: sodium hydroxides and chlorine (Liu 2003).

The following mechanical disintegration techniques can be applied (Kopp et al. 1997):

- stirred ball mill (SBM) – disintegration by crushing;
- high pressure homogenizer (HPH) – disintegration by cavitation effect;
- ultrasonic homogenizer (UH) – acoustic generation of cavitation;
- mechanical smash technique (MJS) – pressurizes the sludge up to 50 bar and releases it through a nozzle;
- high performance pulse technique (HPP) – the sludge is treated by a pulsing high voltage of up to 10 kV.

At the Technical University of Braunschweig, Germany (Müller 2000, Lehne et al. 2001) different methods of sludge disintegration were examined. Best results were achieved using the stirred ball mill or the high-pressure homogenizer (500×10^5 Pa). The average energy consumption for these methods was: 0.224 kWh/kg of dry solids and 0.28 kWh/kg of dry solids, for the ball mill and homogenizer respectively.

German manufacturers already offer mechanical sludge disintegrators, which use the principle of cavitation to rupture microorganism cells. Energy consumption for the method ranges from 0.4 to 0.55 kW/m^3/h.

Ultrasonic disintegration is one of the most promising mechanical techniques. Ultrasonic technology is quite a new approach in sludge processing. Especially low frequencies, in the range from 20 to 100 KHz, exhibit a strong destructive power. In experiments on disintegration of primary sludge (Tiehm et al. 1997), 1:1 mixture of primary and excess sludge (Quarmby et al.1999) and excess sludge only, it was shown that the process generates smaller sludge particles and enhances production of VFA.

Use of disintegration in a full-scale application is still problematic, because such a treatment is very expensive. However, since 2003–2004 a number of attempts to introduce sludge disintegration (Fullinsdorf – Switzerland, Darmstadt-Eberstadt – Germany) have been carried out. An example of a full scale application is the WWTP in Leinetal (Germany), where 30% of the generated sludge is disintegrated by sonification. Since 2004 two modern disintegration devices (WWTP in Kecskemet and Zalaegerszeg have been installed in Hungary (Nickel 2005, Eder 2005).

Also, on a technical scale, Anglian Water has carried out a number of experiments. A disintegration unit was mounted on the pipe, which transports sludge to the anaerobic digesters. Energy consumption for sludge disintegration with ultrasound is approximately 0.3 kWh/kg dry solids (Müller 2000).

The calculation of energy-consumption and cost shows that disintegration processing of sludge could be realized economically. The surplus biogas could be used for electricity generation. The investment for the disintegration equipment has to be seen in relation to the reduced costs for the sludge disposal.

As it can be readily seen, many alternatives to anaerobic digestion are available, each having its own advantages and disadvantages.

Sludge disintegration is carried out mainly to intensify sludge treatment and enhance biogas production; other outcomes such as utilization of intermediate products (VFA and other easily biodegradable organics) are only partial goals of the process. This effect provides a valuable loading of easily biodegradable organics, necessary for biological nutrient removal by denitrification in the biological reactors.

1.2 *The analytical parameters of disintegration process control*

The sludge disintegration process can be described by the particle size analysis. An increase of the energy input leads to a decrease of the floc size (Lehne et al. 2001). However, in this method one can observe the disruption of sludge flocs, but not disintegration of bacteria cells. The disintegration degree (DD) of sewage sludge, including bacteria cell lysis, can be evaluated using two methods: analysis of oxygen consumption by bacteria and analysis of organic compounds concentration in supernatant (expressed as COD and protein content) (Lehne et al. 2001).

The disintegration degree DD can be determined by the measuring the specific oxygen consumption OC_d by disintegrated sludge in relation to the specific oxygen consumption OC_0 of the original sludge (eq.1). The oxygen consumption is directly dependent on the metabolism of aerobic microorganisms. If all bacteria in the sludge are disrupted the oxygen consumption of the sludge is zero and the degree of disintegration DD reaches 100% (Kopp et al. 1997).

$$DD = \left[1 - \left(\frac{OC_d}{OC_0}\right)\right] * 100\% \qquad (1)$$

Another method of measuring the degree of sludge disintegration uses COD analysis. Based on this method the organic material released from the cells by their mechanical disruption can be determined. The DD is described by the following equation (eq. 2):

$$DD = \frac{COD_d - COD_i}{COD_a - COD_i} \cdot 100\% \qquad (2)$$

where:

COD_d – COD of the centrate of the disintegrated sludge sample

COD_i – initial COD of the centrate of the original sludge sample

COD_a – the maximal value of COD, able to be obtained in the supernatant after alkaline hydrolysis of the sludge (chemical disintegration with NaOH).

According to literature data (Schmitz et al. 2000) the change in protein content can be applied as a simple and rapid method of determining the degree of disintegration of sewage sludge, however this method is not as popular as COD analysis.

1.3 *Comparison of various disintegration methods*

Comparison of different disintegration methods can be carried out based on e.g. COD analysis and specific energy consumption with regard to the initial concentration of solid phase (SS). The specific energy for the disintegration process provides information about the necessary energy input to achieve a certain degree of disintegration. Disintegration degree accomplished by these methods has been summarized in Fig. 1 with the use of literature data (Eder & Günthert 2003, Quarmby 1999, Zarzycki 2001).

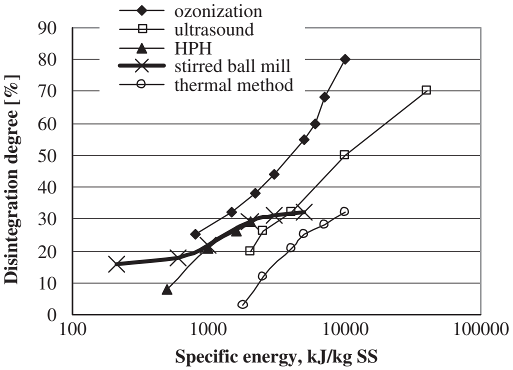

Figure 1. Comparison of selected sludge disintegration processes with regard to disintegration degree – ozonation SS = 8 g/dm^3; ultrasound SS = 26,2 g/dm^3; HPH SS = 38 g/dm^3; stirred ball mill SS = 43 g/dm^3; thermal method t = 10 min. (Eder & Günthert 2003, Quarmby 1999, Zarzycki 2001).

It is clearly visible that, for both mechanical and thermal disintegration, the maximal disintegration degree achieved varied from 29% to 32%. On the other hand, a disintegration degree as high as 80% could be achieved using of ozone and 70% using ultrasound. Also, the specific energy required by these methods tends to vary significantly. Use of a stirred ball mill required a specific energy of approx. 2500 kJ/kg SS to achieve a disintegration degree of 30%. The same disintegration degree using a HPH (high pressure homogenizer) required 2100 kJ/kg SS, while thermal disintegration required as much as 8000 kJ/kg SS to obtain the same effect. Use of ozone needed as low as 1500 kJ/kg SS and ultrasound necessitated approx. 3700 kJ/kg SS (all data are for 30% disintegration degree). These data are, however, of only limited comparability due to the varying nature of the sludge being tested and the different initial concentration of SS.

If one considers that sludge disintegration is carried out mostly to intensify sludge treatment and enhance biogas production during anaerobic digestion, it is very important to evaluate the disintegration degree. In the current research, two parameters were used for this purpose, the COD and ammonium nitrogen content. The selected analytical methods are simple and, based on their results, one can learn about the increase in content of easily available substrate for fermentation bacteria in the supernatant.

2 MATERIAL AND METHODS

In the current research, waste activated sludge (WAS) was collected from the municipal WWTP Gdańsk WSCHÓD operating for 900,000 population equivalents. In this wastewater treatment plant a huge amount of excess sludge is generated and considerable problems with dewatering are observed, even after its anaerobic digestion. Thus, improvement of the WAS treatment efficiency is necessary. One of the options is disintegration of the sludge before its fermentation.

In the experiments the WAS taken from the aerobic bioreactor was used. The suspended solids content amounted to 4–22 g/l. The sludge was disintegrated mechanically on a laboratory scale by using a homogenizer MPW-302 (homogenization time was varied from 1 to 10 minutes) and ultrasound generator Sanyo MSE Soniprep 150 (the frequency was 23 kHz and the sonification time was varied from 1 to 10 minutes).

After disintegration, the concentration of COD and ammonia nitrogen in supernatant were determined according to standard methods.

The degree of sludge disintegration was assessed by determining the chemical oxygen demand (COD) in the sludge supernatant (eq. 1). A reference (100% disintegration degree) was defined as the COD of supernatant obtained from sludge treated with 0.5 mol/l sodium hydroxide for 22 h at 20°C.

3 RESULTS AND DISCUSSION

In Figs. 2 and 3 COD and ammonia nitrogen ($N\text{-}NH_4$) concentration in supernatant obtained from sludge disintegrated by using of homogenizer are presented.

The COD increased significantly with the increase of disintegration time (Fig. 2) and depended also on the suspended matter content. The highest increase of COD (from 100 to 1900 mgO_2/dm^3) was observed for the sludge with the lowest suspended solids content ($SS = 3.95$ g/l), while in the case of the highest SS content (21.7 g/l) the COD increases from 100 to only 1020 mgO_2/dm^3.

The concentration of ammonia nitrogen rose rapidly after only 3 min of homogenization from about 1–2.5 to 7–17 mg $N\text{-}NH_4/dm^3$ (Fig. 3), depending on the content of suspended solids in the sludge. Such dependence is also visible after 5 minutes of disintegration. However, after 10 minutes of disintegration the effect of initial SS content is negligible and the content of ammonia nitrogen was about 22–25 $N\text{-}NH_4/dm^3$.

The degree of disintegration calculated from equation 2 are presented in Figs. 4 and 5.

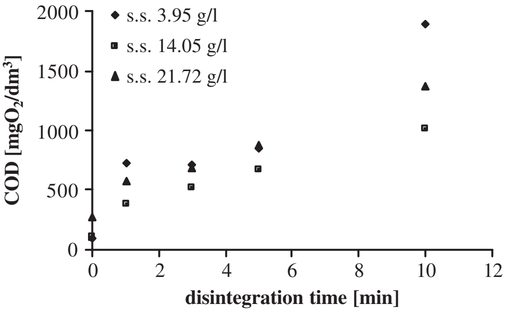

Figure 2. COD in supernatant, versus homogenization time for sludge of different initial content of suspended solids.

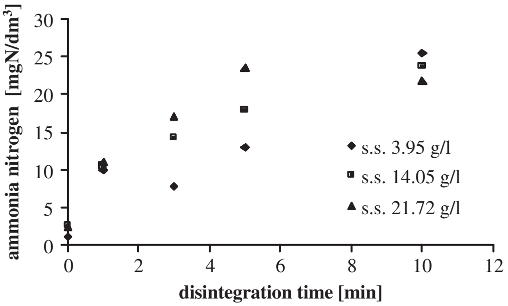

Figure 3. N–NH_4 concentration in supernatant, versus homogenization time for sludge of different initial content of suspended solids.

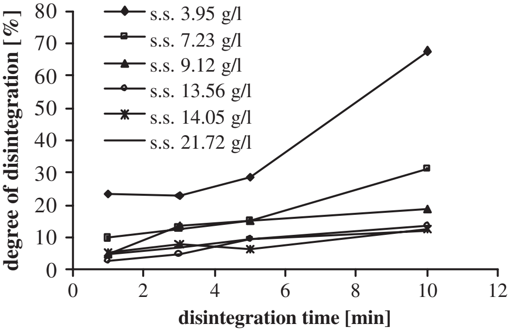

Figure 4. Degree of disintegration versus homogenization time, for different contents of suspended solids in the sludge.

It can be seen from Figs. 4 and 5, that, as the homogenization time was increased, the disintegration degree also increased. After 5 minutes of homogenization of sludge with the lowest suspended solids content the DD value was 28%. For sludges with suspended solids equal to 3.95 and 7.23 mg/l, the disintegration degree was about 70 and 30% respectively. For more concentrated sludge the effect of disintegration was

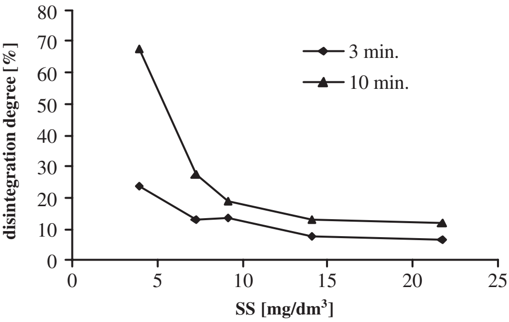

Figure 5. Degree of disintegration after 3 and 10 min of homogenization; dependence on content of suspended solids in the sludge.

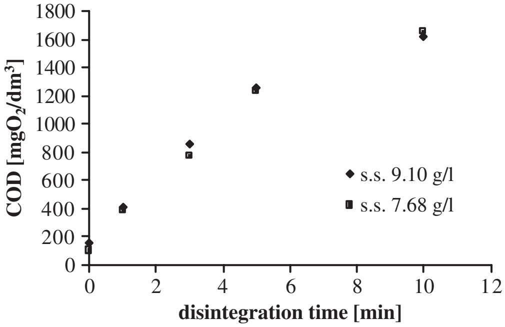

Figure 6. COD in supernatant, versus sonification time for sludge of different initial content of suspended solids.

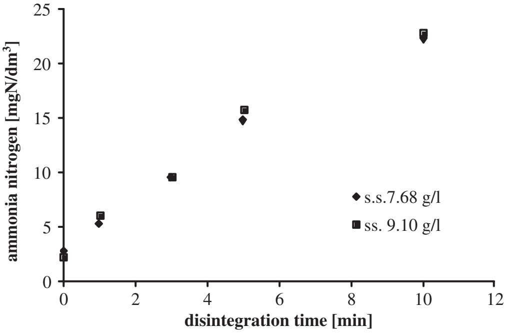

Figure 7. N–NH_4 concentration in supernatant versus sonification time for sludge of different initial content of suspended solids.

still not satisfactory (DD = 12–19%). In Figs. 6 and 7 results are presented of COD and ammonia nitrogen (N-NH_4) concentration in supernatant from sludge disintegrated by sonification. In Fig. 8 the comparison of effects of disintegration using two different methods – homogenization and sonification, is presented.

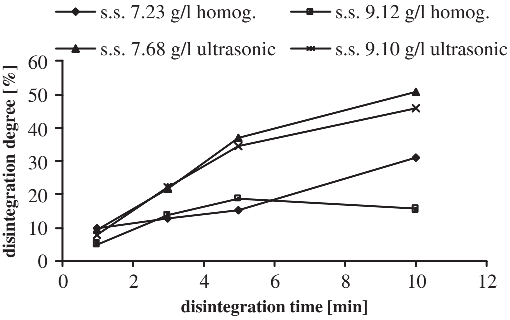

Figure 8. Comparison of disintegration degree for homogenization and sonification depending on the time.

As can be seen from Figs. 6 and 7 the trends in the increase of COD and ammonia nitrogen concentration, resulting from sonification were similar to those observed when the homogenization method was applied. However, if one compares the degree of disintegration obtained for sludge of similar SS content, the ultrasonic disintegration was more effective than the homogenization process. The DD after sonification reached 46 and 50%, while after homogenization it was only 15–30%.

4 CONCLUSION

Disintegration of sludge will be an area with major perspectives in the field of sewage sludge treatment. The mechanical disintegration of sewage sludge destroys the flocks structure of sludge and disrupts the cell walls of the micro-organisms. Consequently, an increase of COD and ammonia nitrogen in supernatant was observed. The advantages resulting from mechanical disintegration of the sludge can be listed as follows:

- increase of the sludge anaerobic digestion efficiency; this increases the volume of biogas produced and reduces the volume of residual sludge;
- provides an additional carbon source for the denitrification processes when disintegrated sludge is returned to activated sludge reactor (savings of external carbon costs); sludge bulking or foaming minimization and control.

In the current research it has been reported that the increases of COD and ammonia nitrogen concentration resulting from sonification were similar to those observed when the homogenization method was applied. However, the degree of disintegration obtained for sludges of similar SS content, the ultrasonic disintegration was higher than for the homogenization process. After 10 min. of treatment, the DD of sonification was about 50%, while that of homogenization was only 30%. Besides, it was clearly shown that disintegration efficiency was higher for sludges with a lower contents of dry matter.

The COD and ammonium nitrogen determination are relatively quick, inexpensive and effective methods of assessing the efficiency of sewage sludge disintegration procedures. However, to obtain the enhancement of anaerobic sludge digestion a more comprehensive assessment is needed. Probably more valuable will be determination of bacteria methanogenic activity, which is strongly connected with methane fermentation effectiveness. Such experiments are currently in the planning stage.

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Chemical composition and treatment of landfill leachate

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The chemical composition of leachate from municipal solid and mechanical biological treatment wastes

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ABSTRACT: The loads of impurities washed out from a municipal solid waste and mechanical biological treatment over a 2.5 year period of measurement are presented. The study was conducted in the area of the Municipal Waste Composting Plant in Zielona Góra, which belongs to Waste Processing and Disposal Plant. The two reinforced concrete bunkers of the composting plant equipped with a leachate intake system were filled with waste. The amount of pollutants washed out in leachate from initially biologically processed waste was considerably lower than in the load removed from the MSW by: organic substance approximately 57% – COD, 61% – TOC and 75% – BOD_5; general nitrogen: 76%. In the case of mineral components, the reduction of loads in washed out chloride was 14%. The sulphate reduction was similar.

Keywords: Leachate; Municipal solid waste (MSW); Mechanical biological treatment wastes (MBT).

1 INTRODUCTION

The basic task in the waste management field in the first decade of the 21st c. is to reduce the amount of waste, mainly biodegradable waste, which lands in the waste landfills. The European Council Directive on the Landfill of Wastes 1999/31/EEC (LFD), plays the significant role in this scope. The Directive obligates Poland to reduce the amount of storage of communal biodegradable waste, with reference to the mass produced in 1995, by the year 2010 by 25%, by the year 2013 by 50% and by the year 2020 by 65%.

It is anticipated that mechanical and biological treatment (MBT), incineration of municipal waste will increase considerably, in order to achieve these objectives. The directives of the state Policy of the Waste Management [Resolution 2002] and the law in force allow us to assume that the requirements of the LFD will be achieved in Poland mostly through the mechanical biological treatment of the municipal solids wastes (MSW).

There are numerous benefits to the mechanical and biological treatment of the waste before disposal [Zechmar-Lahl 2000; Robinson et al. 2005]:

- The MBT wastes are stabilized to a substantial extent;
- When landfilled, they produce low-concentration impurities and display biogas potential;
- Depending on the type of treatment technology the volume of the waste can be reduced by 30% and the treated products that are landfilled can even be made as thick as 1,3 Mg/m^3 [Fricke et al. 1993].

The quality of MSW landfills has been researched for several decades and is presented extensively in the literature [McBean et al. 1995; Chen 1996; Stegman and Ehring 1989; Tatsi and Zouboulis 2002]. The leachate is highly concentrated, especially within the first two years of landfilling. Values of the COD fluctuate from 6 to 60 gO_2/dm^3, BOD from 4 to 40 gO_2/dm^3, and the concentration of the total nitrogen and chloride reach values up to 5 g/dm^3.

For ten years or more, work on the leachate from landfills in which MBT wastes are being disposed, has been carried out. The untreated municipal solid waste, industrial waste and other waste have been disposed together with MBT wastes in the majority of the landfills. Results on leachate quantity and leachate chemical composition of the MBT wastes from mono-landfills are still limited [Höring et al. 1999; Leikam, Stegman 1999; Zeschmar-Lahl 2000; Robinson et al. 2005].

The presence of an acetogenic phase of decomposition manifesting a high concentration of organic substance in leachate has not been noted regularly, on MBT landfills. The COD values of leachate from MBT wastes decreases down to around 1000 mgO_2/dm^3 ($BOD<20\ mg/dm^3$), and the TKN concentration does not exceed 200 mg/dm^3[Leikman, Stegman 1999] after approximately 250 days. According to Fricke et al. [1991] and Zeschmar-Lahla [2000] the leachate from MBT wastes contains 80–90% less organic substances than leachates from other waste landfills.

By way of the analysis of available data on composition of leachates treated with various methods, Robinson et al.[2005] noted that the COD of MBT leachates fluctuated from 1000 to 4000 mg/dm^3; generally the BOD was <100 mg/dm^3 and ammonium nitrogen and Kjeldahl nitrogen were considerably lower than those observed in MSW leachate and furthermore depended on the treatment technology.

This paper presents quantitative data on the leachates of untreated wastes and after those after mechanical biological treatment within the 2.5 year period of the measurements.

The objective of the research was to determine the influence of mechanically and biologically treated wastes on the quality of the leachate at landfills as well as on the load of pollutant washed out from the wastes. The results are indispensable in order to:

- Assess the risk to groundwater resulting from the landfilling;
- Properly design leachate management (drainage, transportation and purification) systems;
- Determine the influence of the leachate quality on landfill construction material.

2 MATERIALS AND METHODS

The study was conducted in the area of the Municipal Waste Composting Plant in Zielona Gora (Fig. 1).

Two reinforced concrete bunkers of the composting plant equipped with a leachate intake system were filled with waste (Fig. 1). In bunker I, 238 Mg of MSW, arising from multi-storey buildings with central heating systems, were deposited and in bunker II, 193 Mg of MSW from the same area of waste collection but which had first undergone the composting process in chambers with forced aeration (MBT wastes).

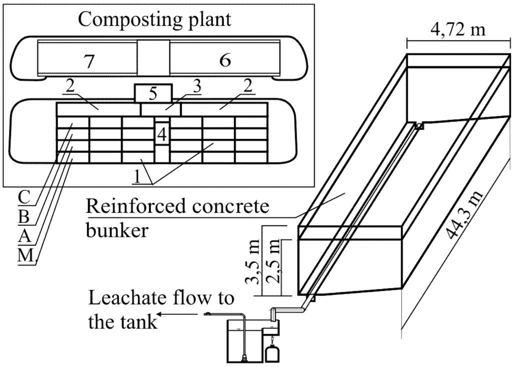

Figure 1. The bunker used in this work. 1 – set of compost courses: M, A, B, C – composting compartments, 2 – bunkers (I, II), 3 – sewage container, 4 – forced ventilation centre (ventilation room), 5 – building for compost treatment, 6 – compost storage, 7 – bio-filter.

The process line of the composting plant consists of four open compartments (M, A, B, C) from where and to the wastes are transferred. The wastes are stored from 7 to 10 days in each compartment. The total composting time is around 5 weeks. Aeration of the wastes is done by gas suction from the bottom of the compartments.

Waste in the bunkers was thickened with a light-weight crawler chain bulldozer, obtaining the bulk densities: MSW – 0.69 Mg/m^3, and for MBT −0.56 Mg/m^3. Waste was not covered with a layer of mineral material. Leachate was collected in the drainage at the bottom of each bunker (Fig. 1).

The process control included the investigation of the morphology of waste loaded in the bunkers, its quantity and analysis of the leachate's chemical composition. The rainfall quantity was also recorded.

The twenty-four hour quantities of the rainfall were determined on the basis of the monthly reports obtained from the Institute of Meteorology situated near the landfills. The twenty-four hour quantities of leachate were determined on the basis of daily readings from the water meters. The leachate's chemical composition was analysed: from the 1st to the 122nd day of the investigation – twice weekly on average; from the 123rd to 365th day – once a week on average and from the 366th to 915th day – once every 3 weeks on average.

The monitoring of leachate quality included three classes of contaminants: organic substances, measured by the following indicators: COD (chemical oxygen demand), oxidizability, total organic carbon, nitrogen forms (organic nitrogen and ammonium nitrogen) and also mineral pollutants (represented mainly by chloride and sulphate).

The Mathematica 4.1 program was used for statistical calculations and to determine relationships between the values.

3 RESULTS

3.1 *The morphological composition of the waste*

The morphological composition of MSW and MBT wastes is presented in Table 1.

The dominant components in MSW were vegetable and animal materials – approximately 40% (m/m) and scrap paper – 25.5% (m/m) (paper −18.9%, and cardboard – 6.6%).

The quota of biodegradable ingredients in MSW was more than 60% higher than in the wastes after the MBT.

In MBT wastes large amounts of fine fractions (less than 8 mm) – 12% (m/m), glass – 14% and plastics and foil −14.4% (m/m) were found.

The average moisture of MSW and MBT wastes was comparable; approximately 40%.

3.2 *Leachate and rainfall quantity*

The average quantities of rainfall (Q_R) and leachate (Q_L) for each month are presented in Figure 2.

The obtained results show very high leachate production in relation to the quantity of rainfall and its high variation in time (Fig. 2).

Table 1. The average group composition of the municipal MST and MBT wastes, in % m/m.

Component	MSW	MBT
Paper	18.9	10.5
Cardboard	6.6	3.4
Vegetable, animal waste	40.2	26.6
Glass	7.7	14.0
Textiles	3.2	6.5
Plastics	5.0	9.5
Foil	2.7	4.9
Ferrous metals	1.6	3.3
Non-ferrous metals	0.2	0.4
Other organic	1.2	0.9
Other non-organic	5.9	8.0
Fraction <8 mm	6.8	12.0

The monthly average quantities of leachate from MSW were from 26.7 to 338% of the monthly rainfall, and from MBT wastes were from 14.0 to 327%. The highest quantities of leachate in relation to rainfall, exceeding by over three times the monthly average quantities of rainfall, occurred in March 2005 ($Q_{L.}/Q_R = 3.4$ for MSW and 3.2 for MBT wastes) (Fig. 2). During this month thawing of a thick snow cover occurred. The high leachate participation in relation to rainfall, reaching approximately 100% of the monthly rainfall, was also noted in February and December 2004 and in January, June and October 2005. The high leachate quota during these months could be related to the high intensity of the rain, including a number of rainstorms.

3.3 *The concentration of pollutants in leachate*

Figures 3–8 show values of chosen quality indicators of MSW leachate and MBT wastes leachate in the course of research.

COD Values of leachate from MSW fluctuated from 470 to 6600 mgO_2/dm^3 and from MBT waste from 350 to 2100 mg O_2/dm^3. The maximum values of COD in leachate from MSW (>2000 mg O_2/dm^3) occurred from the 1st to 23rd day of the measurements. The value of COD of leachate from MBT waste never exceeded 800 mg O_2/dm^3 (Fig. 3).

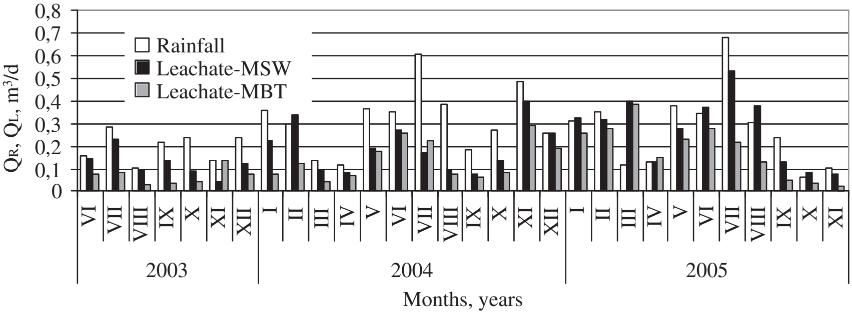

Figure 2. The monthly average quantities of rainfall and leachate specified for MSW and MBT wastes.

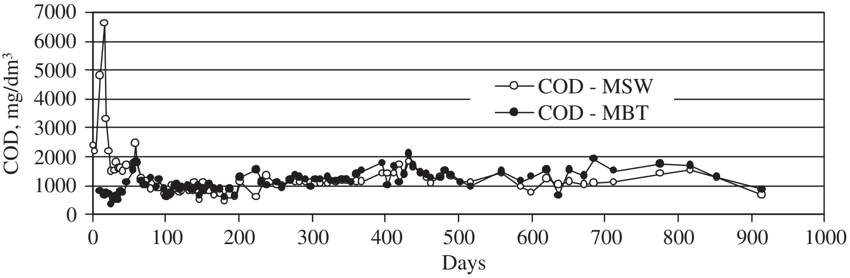

Figure 3. Value of COD of leachate from MSW and MBT wastes.

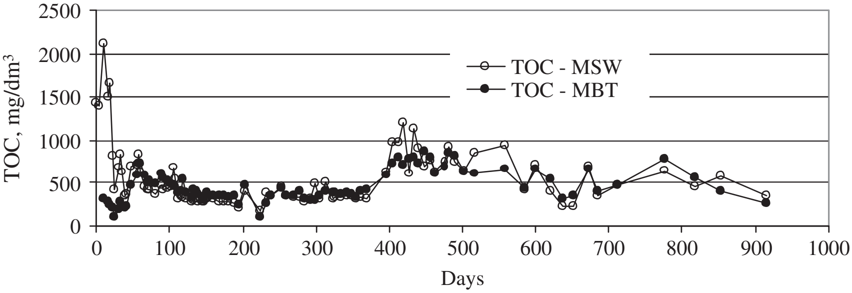

Figure 4. Value of TOC of leachate from MSW and MBT wastes.

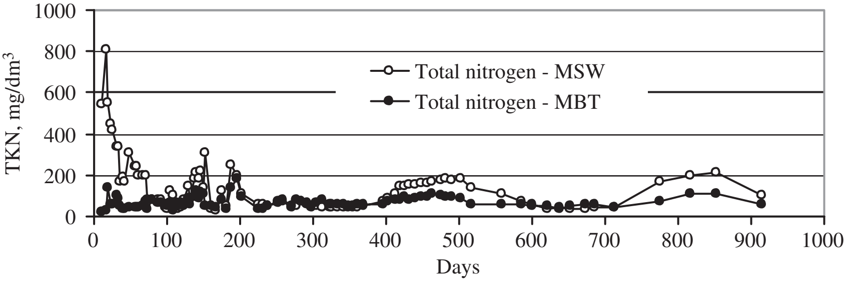

Figure 5. Value of total nitrogen of leachate from MSW and MBT wastes.

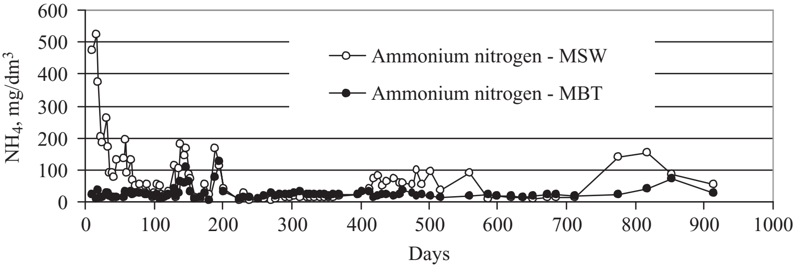

Figure 6. Value of ammonium nitrogen of leachate from MSW and MBT wastes.

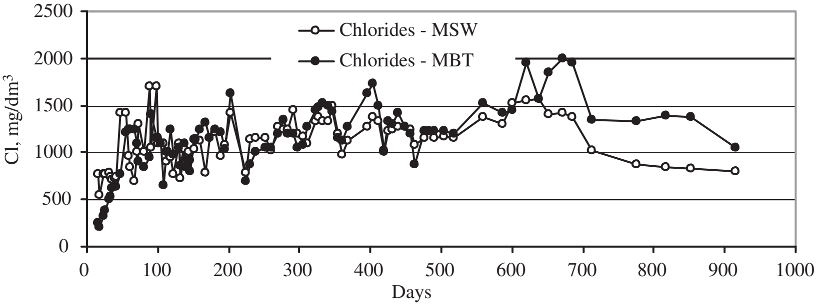

Figure 7. Value of chloride of leachate from MSW and MBT wastes.

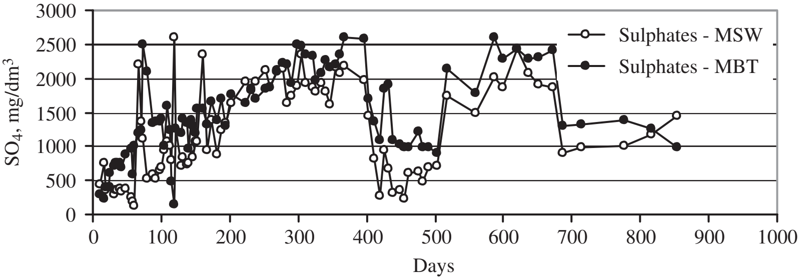

Figure 8. Value of sulphate of leachate from MSW and MBT wastes.

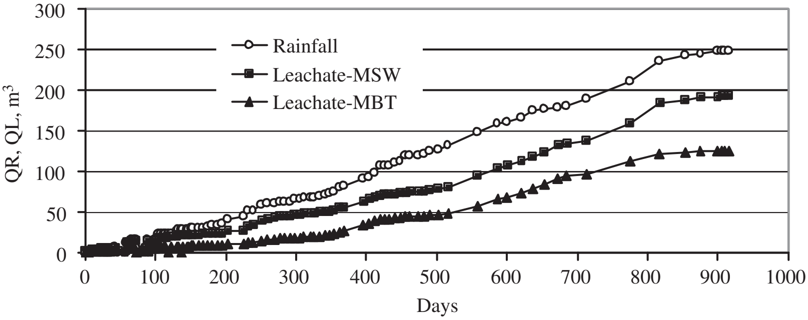

Figure 9. The total quantities of rainfall and leachate determined for MSW and MBT wastes.

The TOC concentration of the leachate from MSW fluctuated from 183 to 2120 mg/dm^3, and in the leachate from MBT waste from 108 to 873 mg/dm^3. Apart from the first 23 days of the research, the TOC concentration in the leachate from MSW and MBT wastes were similar (Fig. 4). Similar to the COD values, the TOC concentration in the leachate from MSW was several times higher at this time.

The total nitrogen concentration in the leachate from MSW fluctuated from 28 to 812 mg/dm^3 and in the leachate from MBT waste from 23 to 184 mg/dm^3. In the first three months of the measurement from 412 to 517 day (July – October 2004) and between 766 and 853 day (July – September 2005) it was noted that the total nitrogen concentration in the leachate from MSW was substantially higher then in the leachate from MBT waste (Fig. 5). The distribution of the ammonium nitrogen was similar (Fig. 6). The ammonium nitrogen concentration in the MSW leachate fluctuated from 3 to 525 mg/dm^3, and in the MBT waste leachate from 4,2 to 123 mg/dm^3.

With a substantial tendency to increase with time, the chloride concentration of the MSW leachate fluctuated from 548 to 1700 mg/dm^3 and in the MBT waste leachate from 206 to 2000 mg/dm^3 (Fig. 7).

The sulphate concentration in the MSW leachate and MBT waste leachate varied from approximately 140 to 2600 mg/dm^3. Up to the 400th day of measurements the sulphate concentration in the leachate generally increased in a linear way. In the period following it fluctuated considerably.

4 DISCUSSION

4.1 *Leachate and rainfall quantity*

Rainfall and leachate total quantities are presented in Figure 9. The total rainfall quantity, which entered each bunker over the course of the work, was 248 m^3.

The total quantities of collected leachate from the bunker with MSW and MBT wastes were very high and amounted to 77.8% and 50.4% of the rainfall quantities respectively.

In principle the results obtained confirmed previous experience resulting from operation of the large scale waste landfills. The leachate quantities are determined mostly by the water balance in the surface layer with a thickness of up to 0.3 m. The MBT waste was more homogeneous, which guaranteed a more even spread of the rainfall (on the whole surface) in the bunker. There were only a few open channels in the surface layer of these wastes, through which the rainfall could flow directly into the deposit, thus excluding their participation in the water exchange between the waste and the atmosphere (evaporation).

Table 2. The average (mean) values, range, standard deviation of chosen quality indicators from MSW and MBT wastes determined for three periods: the first two weeks, two consecutive months and for the remaining time of the research, in mg/dm^3.

	The average values of pollution indicators determined for three periods								
	Two weeks			Two consecutive month			The remaining time		
Pollution indicators No. of samples	Mean	Range (4)	S.D.	Mean	Range (15)	S.D.	Mean	Range (74)	S.D.
MSW									
COD	4000	2200–6600	2097	1895	1500–3300	562	1072	470–1826	287
TOC	1612	1400–2116	338	721	357–1665	329	472	183–1200	235
TKN	679	546–812	123	301	84–550	126	104	28–308	64
Ammonium nitrogen	500	452–548	35	167	75–375	86	48	3–179	44
Chlorides	762	645–763	83	869	547–1428	275	1157	720–1700	217
Sulphates	443	405–466	27	370	193–751	545	1340	226–2595	626
MBT wastes									
COD	725	650–800	78	942	350–1804	456	1175	594–2100	321
TOC	265	207–315	46	353	110–732	209	478	108–873	173
TKN	28	23–33	5	62	33–137	29	71	31–184	27
Ammonium nitrogen	17	11–23	6	21	13–37	8	27	4–126	20
Chlorides	249	230–268	15	693	206–1250	365	1233	650–2000	278
Sulphates	295	268–317	20	643	232–959	285	1701	146–2601	553

In the case of MSW which contains components having large diameters, the contact surface between the water and the mass of the waste, was considerably lower. Approximately 78% of the rainfall which directly infiltrated the deposit, became leaks. The value of this indicator was unexpectedly high. For the MSW landfills, a range of 50% to 60% was the maximum value of the indicator [Canziani R., Cossu R. 1989; Stegman R., Ehring H.J. 1989]. The observed discrepancy between our work and that in the literature, can be explained as follows: our landfill was not covered with a layer of mineral material; the low bulk densities (0,69 Mg/m^3 – MSW; 0,56 Mg/m^3 – MBT) and the overall changes in the morphology of waste over the last 20 years. In older waste the amount of plastics and glass was higher. Nowadays the waste is discarded into containers in plastic bags, which, in the great majority of cases, remain intact during the unloading of the garbage trucks. In this way, the contact of water with the organic fraction of the waste, on which the storage of water depends, is hindered by the waste's own structure.

4.2 *The concentration of the pollutants in leachate*

There are three phases of waste decomposition in the deposit on the landfill [McBean et al. 1995]:

- Aerobic digestion that lasts for as long as there is oxygen available in the waste during landfilling – ca.2 weeks;
- Acetogenic fermentation – 2 – 3 months in high – moisture waste;
- Methanogenic fermentation.

In Table 2 the average (mean) values, range and standard deviation of chosen quality indicators from MSW and MBT wastes determined from three periods are presented: the first two weeks (from 1st to 14th day of investigations), two consecutive months (from 15th to 66th day) and for the remaining time (from 67th to 915th day) of the research.

During the analysis of the pollution concentration in leachate in the three separate periods the following was noted:

- A significant decrease of the content of the organic substances as well as nitrogen concentrations in leachate from MSW;
- A significant increase in the content of organic substances as well as nitrogen concentrations in leachate from MBT waste and also
- An increase of the chlorine and sulphate concentrations in leachates from MSW and MBT wastes.

In the first two weeks of the research the average concentration of organic substance and forms of nitrogen in leachate from MSW waste, were from over twofold (COD, TOC and total nitrogen) to ca. threefold (ammonium nitrogen) higher than the average concentration from the period of two consecutive months. In comparison with the values for the remainder of the test period they were higher: COD and TOC around 4 and 3,5 times, total nitrogen – 6,5 times and ammonium nitrogen – 10 times (Table 2) respectively.

Average chloride and sulphate concentrations from a two-month period were slightly different from the average values for the first two-week period. In the rest of the period a 1.5 fold increase of chloride concentration and threefold increase in sulphate were noted (Table 2).

Changes of the average concentration of the analyzed pollutants in leachates from MBT wastes progressed completely differently. In the MBT leachates the occurrence of high concentration of organic substances and nitrogen compounds in the first period of disposal, which is characteristic of non-treated wastes [Leikam and Stegman 1999], was not noted. In the first two periods the average COD values in the leachates from MBT wastes were lower than $1000\,mgO_2/dm^3$ but grew noticeably with the passage of time. An average COD value found after 250 days of the measurement was $1330\,mgO_2/dm^3$ and maximum – $2100\,mg\,O_2/dm^3$. The values were higher than those presented by Leikam and Stegman [1999] and are more similar to those of Robinson et al. [2005].

Average concentrations of total nitrogen and ammonium nitrogen in the leachates from MBT wastes were lower than the values typical for municipal sewage in the periods mentioned. The average concentration of ammonium nitrogen in the leachates from MBT wastes amounted to a mere $17\,mg/dm^3$ whereas it was $500\,mg/dm^3$ in the leachates from MSW after the first 2 weeks. The low average concentrations of nitrogen forms were a result of the removal of easily biodegradable substances that contained nitrogen (proteins), during the process of composting.

High concentrations of sulphate in the leachates from MBT wastes, higher than those found in the leachates from MSW, were an interesting issue resulting from the tests. Average values of sulphate concentrations in the leachates from MBT wastes were 643 and $1701\,mg/dm^3$ in the period of 2 months and the rest of the period and in the leachates from MSW 370 and $1340\,mg/dm^3$ respectively. Sulphate is reduced to sulphide which precipitates in the form of sparingly soluble ferrum or other metal in the methanogenic MSW bed. Compared to the leachates from MSW wastes, noticeably higher concentrations of sulphates in the leachates from MBT wastes may indicate a discontinuity in the highly anaerobic layer of the waste bed. The increase in heavy metals in the leachates might be a negative effect.

The results of the tests carried out in the laboratory and on a technical scale have proven the conclusions presented in the literature. Bioreactivity in the bed on the landfill is being substantially reduced through the landfilling of effectively composted wastes. As a consequence, concentrations of pollutants in the wastes at the initial stage of landfilling are considerably lower than in the leachates of non-treated wastes.

As the tests have shown, “poor and hard biodegradation resistant” organic components in the MBT wastes (cellulose, lignins, humus compounds) are still posing a problem. The substances are still a source of relatively high COD values in the leachate (around $1000\,mgO_2/dm^3$ and higher) that are comparable to the ones found in the leachates of non-treated wastes [Ketterna 1993, Robinson iin. 2005] being a result of changes in the methanogenic phase on the landfill.

4.3 *Loads of pollutants washed out from MSW and MBT wastes*

In the Figures 10–12 plots of total pollutant loads released in leachate from MSW and MBT wastes in the course of the research, are presented.

In Table 3 the total loads of pollutants removed in leachate from MSW and MBT wastes after two months and over the whole period of research and the values of their quotient are compared.

The relationship of loads in organic substances and the form of nitrogen released from waste in the form of leachate from the time of storage can described accurately using a power function such as:

$$y = Ax^a, a > 0.$$

There in, the speed of increase depends on the exponent “*a*”. When $a = 0.3$ the quantities of washed out pollutants during the first year doubles after 10 years, when $a = 0.5$ they increase 3 times, and when $a = 1$ they rise 10 times.

The emission of organic substances in leachate from MSW was described by functions in which “*a*” equalled 0.20, 0.22 and, for MBT wastes, equalled 0.37, 0.39. The decomposition functions, which describe the removal of total nitrogen are analogous. For these functions $a = 0.15$ applies to the emission of pollutants from MSW and $a = 0.51$ for MBT wastes. Higher values of “*a*” obtained for MBT waste show that washing out of the impurities from MBT waste in the first months of storage is less intense than the washing out from MSW.

The course of elementary chloride and sulphate loads which were removed from waste in leachate since the beginning of storage was significantly different from the dependency determined for the organic substance and nitrogen forms. Over the 2.5 year period of the research, the emission of chloride and sulphate loads in leachate from MSW and MBT wastes was described by the function:

$$y = a\left(\frac{-1}{k}x\exp(-kx) - \frac{1}{k^2}(\exp(-kx) - 1\right) \quad (1)$$

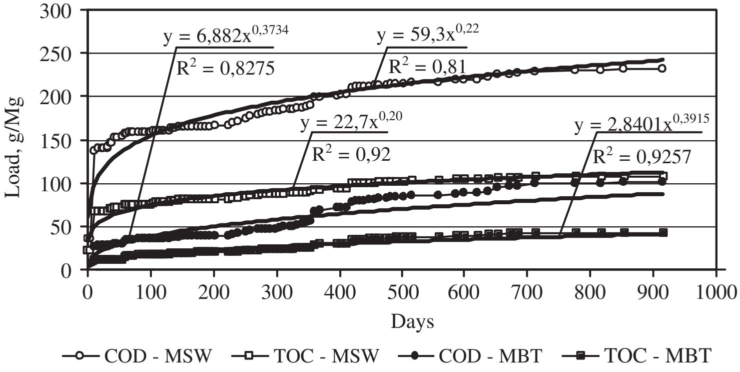

Figure 10. Curves of the total loads of COD and TOC released in leachate from MSW and MBT wastes.

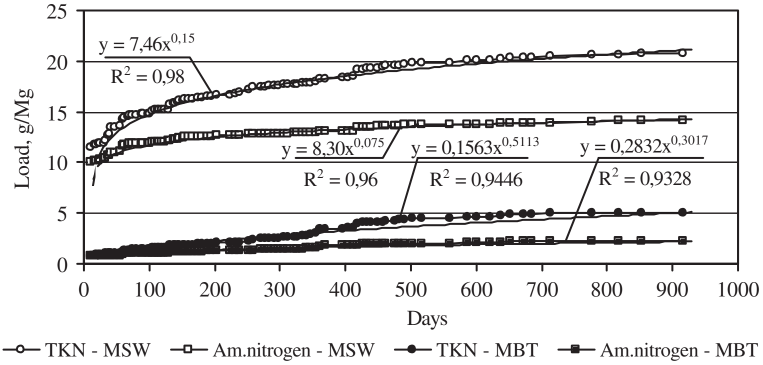

Figure 11. Curves of the nitrogen loads emitted in leachate from MSW and MBT wastes.

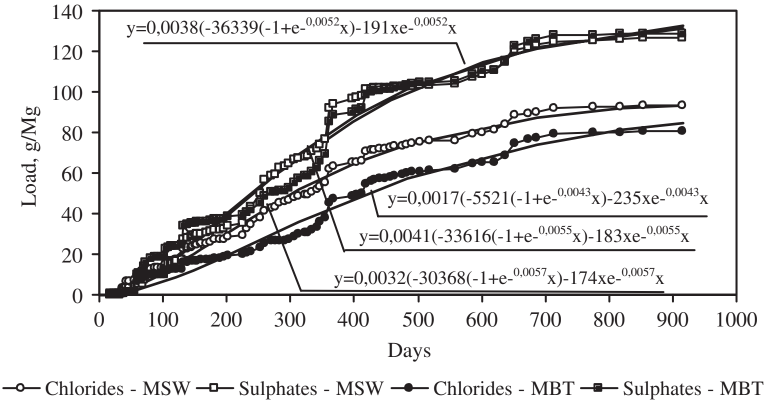

Figure 12. Curves of the total chlorine and sulphate loads emitted in leachate from MSW and MBT wastes.

It is an increasing function which has a limiting value at $x \to \infty$; it can be recognized as a measure of content of water soluble components (chlorides and sulphates) in the waste. The limiting values of the function for MSW were: chlorides – 96.8 g/Mg and sulphate – 137.2 g/Mg; for MBT wastes: chloride 94,0 g/Mg and sulphate – 139,2 g/Mg. Analysing the physical sense of the limits of the function, it appears that the chloride load removed from the wastes within 2,5 years of the test comprised 96.6 and 80.5 % of their maximum

Table 3. Elementary loads of pollutants removed in leachate from MSW and MBT wastes after two months and over the whole period of research and the values of their quotient.

	First 2 months of research			The whole research period		
	Loads, kg/Mg			Loads, kg/Mg		
Pollution indicators	MSW	MBT waste	Ł$_{MBT.}$/Ł$_{MSW}$	MSW	MBT waste	Ł$_{MBT.}$/Ł$_{MSW}$
COD	0,158	0,034	0,22	0,231	0,100	0,43
BOD	0,013	0,003	0,23	0,004	0,001	0,25
TOC	0,074	0,015	0,20	0,108	0,043	0,39
LKT	0,002	0,001	0,50	0,010	0,004	0,40
Total nitrogen	0,014	0,001	0,07	0,021	0,005	0,24
Ammonia nitrogen	0,012	0,001	0,08	0,014	0,002	0,14
Chloride	0,011	0,007	0,64	0,094	0,081	0,86
Sulphate	0,006	0,010	1,70	0,127	0,129	1,02

pollution potential in the MSW and MBT wastes. In the case of sulphate they were 92,6 and 92,7% respectively.

The values of load quotients in pollutants washed out from MSW and MBT wastes (Table 3), confirmed the information from the literature, indicating that the processing of biological waste before its landfilling reduces the amount of pollutants in the washed-out leachate [Fricke et al. 1995; Zeschmar-Lahla 2000].

The load of the pollutants that was removed from the MBT waste leachate was lower than that removed from MSW by:

- Organic substances
  - after 2 months; approximately 78% – COD, 80% – TOC and 77% – BOD$_5$
  - after 2.5 years; approximately 57% – COD, 61% – TOC and 75% – BOD$_5$
- General nitrogen
  - after 2 months: 93%
  - after 2.5 years; approximately of 76%.

In the case of mineral components a reduction in the loads of washed out chloride by approximately 36% was noted after two months and by 14% after 2.5 years. On the other hand, the amount of washed out sulphate after 2 months was 70% higher but after 2.5 years was similar.

5 CONCLUSION

On the basis of the test results we draw the following conclusions:

- When compared to the amount of rainfall, the amount of leachates obtained were surprisingly high and considerably different from the upper values of the rates given in the literature. In the tests, the leachates from MSW constituted 78% of the rainfall volume and 50% of leachates from MBT.
- In the test, in common with the literature, the occurrence of high concentrations of organic substances and nitrogen compounds in the first period of landfilling, well-known in the processing of non-treated wastes, was not noted in the leachates from MBT.
- The COD and TOC values in the leachates from MSW wastes in the methanogenic phase were similar to the values determined in the leachates from MBT and concentrations of total and ammonium nitrogen were only slightly lower.
- The loads of nitrogen and organic substances that had been removed from the leachates from MBT wastes were considerably lower than the load removed from MSW: COC – 57%, TOC – 61%, BOD$_5$ – 77% and total ammonium – 76% within the 2.5-year period of the test respectively.
- The load of chlorides washed out from the MBT wastes was lower by 14% when compared to those that had been removed with the leachates from MSW. The sulphate load behaved similarly.

Further investigations will be necessary to determine the long-term potential of MBT wastes to biological decomposition as well as the nature and fate of the biodegradation resistant COD in the leachates from MBT and their impact on the mobility of heavy metals.

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Biological removal of organics and nitrogen from landfill leachates – A review

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ABSTRACT: In this review the influence of landfill age on temporal changes in organics and nitrogen in leachate will be discussed. Furthermore, the occurrence of hazardous compounds such as BTEX, polyaromatic hydrocarbons, chlorinated aliphatic and aromatic compounds will be systematically examined.

The efficiency of organics removal from leachate in different biological systems in aspect of temporal changes in leachate composition will also be analysed. Moreover, the factors determining the efficiency of nitrification and denitrification in leachate from young and old landfills are pointed out. Newer trends in the technology of nitrogen removal *ex situ* and *in situ* are also discussed and evaluated.

Keywords: Landfill leachate composition, hazardous compounds, organics and nitrogen removal.

1 INTRODUCTION

A typical problem associated with landfills of municipal waste solids (MWS) is leachate production. Leachate is highly variable and heterogeneous. A complete description of the potential pollution in landfill leachate is very complex. It is influenced by the age, content and the management of the landfill at its origin, as well as by the prevailing temperature and rainfall at the site. Moreover, all of these factors interact and may vary considerably, even in the relatively short term, not to mention over the decades of a typical landfill's lifetime.

Leachate migration is controlled by the combination of landfill cap, bottom liner and appropriate drainage and collection systems. The collected leachate should be treated. It is possible in municipal wastewater treatment plants (Boyle & Ham 1974, Ahnert & Ehrig 1992). As the flow rate of leachate increases parallel to the expansion of landfill solid waste, a separate treatment plant will be needed to reduce the transportation cost and pollution load on the central treatment plant. Moreover, stricter regulations for nitrogen discharge and growing concern over the potential effect of recalcitrant and toxic leachate constituents have led to increased demands for separate treatment systems being a part of landfill infrastructure (Albers & Krückeberg 1992).

Leachate has always been considered as problematical wastewater from the treatment point of view, because its quality and quantity changes with time within the same landfill. Limiting concentrations for the discharge of treated leachate, mainly of COD, BOD_5 and nitrogen are of great importance for the choice of the appropriate treatment technology. According to the increasingly restrictive limitations for wastewater discharge, complicated and costly treatment facilities are required.

Current facilities for the treatment of leachate consist mainly of biological and/or physicochemical systems such as coagulation-floculation, adsorption (active carbon), chemical oxidation and membrane technology (Bilstad & Madland 1992, Chiang et al. 1995, Amokrane et al. 1997, Kim et al. 1997, Steensen 1997, Chianese et al. 1999, Zamora et al. 2000, Trebouet et al. 2001, Rivas et al. 2003, Monje-Ramirez & Orta de Velásquez 2004, Wu et al. 2004, Bila et al. 2005, Kurniavan et al. 2006).

In most cases biological treatment is the first stage of wastewater treatment. So far, biological leachate treatment, including those working under aerobic and anaerobic conditions, has been investigated by many authors (Vicevic et al. 1992, Blakey et al. 1992, Welander & Henrysson 1998, Timur & Özturk 1999, Timur et al. 2000, Kennedy & Lentz 2000, Im et al. 2001, Wiszniowski et al. 2001).

Despite this plethora of work, there is still a need to elaborate highly efficient and unified methods of biological leachate treatment. Little is yet known, especially on the removal of hazardous substances, biomass growth, mechanisms of nitrogen removal, mainly at high N/C ratios in leachate.

In this review the influence of operational conditions on organics and nitrogen removal from landfills is pointed out. Newer research trends and further perspectives of leachate treatment are also discussed.

2 LANDFILL LEACHATE FORMATION AND QUALITY

2.1 *Leachate formation*

Leachate is formed when the refuse moisture content exceeds its field capacity, which is defined as the maximum moisture that is retained in a porous medium without producing downward percolation (Blakey 1989, Calace et al. 2001 (after Matejka et al. 1994). Water percolating through the site tends to leach out both organic and inorganic substances (Lema et al. 1988).

El-Fadel et al. (2002) divided the factors influencing leachate formation in landfills into two categories: (i) those that contribute directly to landfill moisture (for example rainfall, snowmelt, ground water intrusion, initial moisture content, recirculation), and (ii) those that affect leachate or moisture distribution within the landfill (refuse age, pre-treatment, compaction, permeability, particle size, density).

In young landfills (<5 years of exploitation), the leachate production is minor – 30–40 mm/year, and percolation through the waste deposits occurs as preferential flow. Water still accumulates in 10-year-old deposits. From landfills of this age, the rate at which drainage water leaves the landfill is rather constant in time, with only small, seasonal fluctuations (Bengtsson et al. 1994).

Ehrig & Stegmann (1992) report that the amount of leachate in young and highly condensed landfills in Germany is from 15 to 25% of annual rainfall, while in old landfills, operated similarly, it runs at 25–50%.

However, according to Ragle et al. (1995), in a 3.7-year-old landfill in Seattle the amount of landfill leachate is about 13%, while in a 16-year-old landfill located nearby, it was 2.6-fold lower.

In Poland, with an annual rainfall of 500 mm the mean amount of leachate in capped landfills runs at 20–50 mm/year, but at a total rainfall of 1200 mm/year it is 75–200 mm/year. In the case of opened landfills, the amount of leachate is 3–7-fold higher. In practice, the amount of leachate depends not only on the quantity of waste but also on the level of compaction of the solid wastes. It is about 40% of rainfall for landfills with low compaction and 25% of rainfall for landfills with high compaction by waste compactor or non-compacted (Rosik-Dulewska 2005).

2.2 *Organics in leachate*

The characteristics of organics and nitrogen in landfill leachate are directly related to the natural processes occurring inside the landfill. Under favourable conditions, generally dictated by the presence of sufficient moisture to support microbial activity, landfills behave like large-scale anaerobic reactors. The fermentative processes are currently relatively well known, at least for the 20–30 years of a landfill's lifetime. Simultaneously, in accordance with biochemical changes, physicochemical processes, including dissolution, precipitation, adsorption, dilution, volatization and others influence leachate quality.

Organic matter in leachate is usually expressed as Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) or Total Organic Carbon (TOC). In addition, some authors carry out determinations of volatile fatty acids content, more refractory compounds like fulvic-like and humic-like compounds and hazardous organic substances.

Leachate produced in younger landfills is generally characterized by the presence of substantial amounts of volatile acids, as a result of the acid phase of fermentation. Harmsen (1983) demonstrated that, in leachate from a landfill at the acid stage of fermentation, acetic and butyric acids prevailed with concentrations of 11,000 mg/l and 9890 mg/l, respectively. The content of caproic, propionic and valeric acids was lower and amounted to 5770 mg/l, 3 760 mg/l and 2510 mg/l, respectively. Ethanol was present at a concentration of 277 mg/l. However, previous investigations of Burrows & Rowe (1975) show that in leachate from municipal landfill several years of age butyric acid accounted for 87%, while valeric and propionic acids made up merely 6% and 7% of the total content of volatile acids, respectively. Among the low molecular weight organic compounds were propanol (43%), ethanol (20%), butanol (17%) and acetone (20%).

The anaerobic phase starts with the growth of methanogenic bacteria. Harmsen (1983) observed in the acid phase of leachate more than 95% of the COD content of 20,000 mg/l consisted of volatile fatty acids and only 1.3% of the COD consisted of a high molecular weight compound (MW > 1000). In the methanogenic-phase of leachate creation no volatile acids were detected, and 32% of the COD (2100 mg/l) consisted of high molecular weight compounds (MW > 1000).

Calace et al. (2001) characterized two kinds of municipal landfill leachate on the basis of the molecular weight distribution of leachate constituents. Leachate was collected from a "old" and "young" municipal waste landfill (10 and 4 years old, respectively). In the sample of leachate from the older landfill the constituents were distributed over a wider range of molecular weights. High molecular weight fractions represented MW > 100,000 Da – 19%, MW from 50,000 to 10,000 Da – 20% and low molecular weight MW < 500 Da −28%. However, in the sample from the younger landfill the fractions were narrower at the lower molecular weights MW > 10,000 Da – 18%, MW from 500 to 10,000 – 12% and MW 500 Da – 70%. The high molecular weight fractions of leachate from the older landfill were found to be complex structures formed by condensed nuclei of carbons substituted by functional groups containing nitrogen, sulphur and oxygen atoms; the low molecular weight fractions of leachate characterized by linear chains substituted by oxygenated functional groups, such as carboxyl and/or alcohol groups.

Chian et al. (1977) found that the majority of the organics in leachate consisted of free volatile fatty acids. The next largest group consists of fulvic-like material of intermediate molecular weight (MW 500–10,000), characterized by a relatively high carboxyl and aromatic hydroxyl group density. A small percentage of the organics consisted of a high molecular weight humic-carbohydrate-like complex (MW 10,000).

Kang et al. (2002) showed certain differences between the leachate humic substances (HS) and commercial humic acid (Aldrich Co). Leachate HS consisted of molecules of smaller sizes and was less aromatic in nature than commercial humic acid. The authors also observed less condensed aromatic rings in molecules of leachate compared to those of the commercial humic acid. Such differences in the molecular size and structural characteristics suggest that the leachate HS were at a lower stage of humification. These results indicate that the leachate HS were in an early stage of humification, and the degree of humification increased as the landfill age increased.

The process of methane production and waste stabilization must continue for over a 10–20 years or longer to reach a steady state. Recently, leachate recirculation was practised in many landfills. Chan et al. (2002) showed that leachate recirculation reduced the waste stabilization time, enhancing gas production and improving leachate quality, especially in terms of COD. The authors suggested that lowering of the leachate concentration depended on the portions of nutrients, minerals or organics being attenuated by the waste and soil in landfill cells. If effective attenuations are high, a lower strength of leachate is expected. Therefore, leachate recirculation rate must be properly adjusted in order to have minimal quantity and low-strength output. The experimental results obtained by Warith et al. (1999) indicated that addition of supplemental materials (buffer, nutrients, sludge) to the leachate during recirculation has a positive effect on the rate of biological degradation of solid waste. Their investigations also indicated that recirculation of the leachate periodically does not increase the concentrations of the heavy metals substantially above the initial concentrations. Benson et al. (2007) showed that leachate recirculation generally produces more concentrated leachate than conventional landfills during the first two to three years of recirculation. Thereafter, the leachate from conventional and recirculation landfills are similar, at least in terms of BOD, COD and pH. The exception is ammonia, which tends to remain elevated in recirculation landfills.

The selection criteria of landfill stabilization are mainly directed towards low biogas and leachate production. Typical old landfills produce leachate catalogued as stabilized and characterized by relatively low chemical oxygen demand (COD), slightly basic pH and the presence of high molecular weight compounds (humic substances).

2.3 *Organic hazardous substances in leachate*

Xenobiotics are organic compounds (XOCs, i.e. organic chemicals with an anthropogenic source) occurring in leachate originating from household or industrial waste disposed of on a municipal solid waste site. A number of these chemicals are released to leachate during the lifetime of the landfill. With regard to the individual organic compounds or group of compounds the investigations concerned mainly hydrophobic, volatile, aromatic and aliphatic organic substances, e.g. BTEX (benzene, ethylbenzene, toluene, xylene), polyaromatic hydrocarbons and chlorinated aliphatic and aromatic compounds. Additionally, compounds containing polar/ionic groups such as phthalates, phenols were analysed (Harkov et al. 1985, Sabel & Clark 1984, Reinhard et al. 1984, Schultz & Kjeldsen 1986, Wenzen et al. 1999, Kulikowska 2002, Baun et al. 2004).

Benzene, toluene, ethylbenzene and xylenes are found in the highest concentrations, reflecting their common usage as solvents in a range of products and waste generating processes, along with the halogenated hydrocarbons tetrachloroethylene, trichloroethylene and dichloroethanes. Another group of chemical substances, represented in large numbers, are phthalates found in plastificators. In leachate, products of phthalic acid degradation are frequently detected (Bauer et al. 1998, Yamamoto et al. 2001, Jonsson et al. 2003, Marttinen et al. 2003, Slack et al. 2005).

Andreottola & Cannas 1992) (after Shridharan & Didier 1988) reported that concentration ranges of benzene and its aliphatic derivatives in leachate can vary considerably from 1 to 630 μg/l (benzene), 1–1680 μg/l (ethylobenzene), 1–11,800 μg/l (toluene), 9.4–240 μg/l (xylene). Among PAHs, acenaphthene occurred at concentrations of 13.9–21.3 μg/l, fluorine 219–32.6 μg/l, naphthalene 4.6–186 μg/l and phenanthrene at 8.1–1220 μg/l.

Buniak et al. (1997) in leachate from municipal landfill in Maélice noticed the presence of 16 PAH compounds, whose total concentration was 7966 μg/l, including 70% of acenaphthylene.

Detailed investigations conducted by Paxéus (2000) in three municipal landfills in the Göteborg area of western Sweden revealed the existence of 209 individual organic compounds with concentrations ranging from less than one up to several hundred μg/l. Among all the identified compounds, 35 are classified as Priority Pollutants:

– aromatic hydrocarbons: chlorobenzene (0.1–62 μg/l), dichlorobenzene (0.1–57 μg/l), toluene (1.0–17 μg/l), ethylbenzene (0.2–179 μg/l), xylenes (0.3–210 μg/l),
– substituted benzenes: styrene (0.1–11 μg/l), naphthalene (0.4–400 μg/l), 1,1’-biphenyl (0.1–22 μg/l), phenanthrene (0.6–52 μg/l),
– phenols: trichlorophenols (0.3–1 μg/l), tetrachlorophenols (0.2–1 μg/l), nonylphenol (3–22 μg/l),
– phthalates: di-ethylphthalate (0–4 μg/l), di-(2-ethylhexyl)phthalate (97–346 μg/l).

Baun et al. (2003, 2004) evaluated the occurrence of XOCs in leachate from both old landfills (uncontrolled landfills) and landfills still in use (engineered landfills). The monitoring program included sampling at 10 Danish landfills. The study also included the analysis of pesticides degradation products, toluene, NPEs and phthalates. The research revealed the presence of 55 different xenobiotic organic compounds and 10 degradation products of these compounds. The group composition of these compounds was as follows:

– aromatic hydrocarbons −18 compounds, in concentrations ranged from <1 to 2 220 μg/l,
– chlorinated hydrocarbons (1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene) in concentrations 2–9 μg/l,
– nonylphenol and derivatives,
– phenols −13 compounds, in concentrations <0.1 to 60.9 μg/l.

From a literature review, it was concluded that in municipal landfill leachate more than 200 organic compounds have been identified (Yasuhara et al. 1997, Paxéus 2000, Schwarzbauer et al. 2002). However, in underground water around landfills more than 1000 chemicals were identified (Christensen et al. 2001, Kjeldsen et al. 2002). This means that the transformation and/or partial degradation of different types of hazardous substances causes the release of intermediate compounds.

2.4 *Nitrogen in leachate*

According to a comprehensive literature review, it is apparent that, apart from organics, nitrogen-containing compounds are the principal pollutants in leachate. Landfilled MSW contain high amounts of organic nitrogen in a non-degradable form as well as readily soluble nitrogen. As a result of anaerobic digestion of MSW putrescibles, around 50% of the nitrogen undergoes solubilization (Jokela & Rintala 2003). According to Ehrig (1989) the release of soluble nitrogen from municipal solid waste into leachate is slow and continues over a long period.

Hydrolysis of soluble protein is catalyzed by several types of proteases that cleave it to amino acids, dipeptides or oligopeptides. Fermentation of amino acid leads to the formation of organic acids and ammonia. Leachate from older landfills is rich in ammonia nitrogen due to hydrolysis and fermentation of the nitrogenous fractions of biodegradable substrates (Carley & Mavinic 1991). Ammonia concentration in leachate from different landfills may vary from tens or hundreds of mg N_{NH4}/l (Henry et al. 1987, Robinson & Maris 1983, Robinson & Grantham 1988, Statom et al. 2004) to 2000–3000 mg N_{NH4}/l (Timur & Özturk 1997) or even over 10 000 mg N_{NH4}/l (Tatsi & Zouboulis 2002) (Table 1).

From investigations conducted in Poland by Kaczorek & Ledakowicz (2002) and Surmacz-Górska et al. (2000) it can be seen that ammonia concentration in leachate achieves a value of 3000 mg N_{NH4}/l. Obrzut (1997) showed that its concentration in leachate collected from 10 landfills in Poland varied between 1.7 and 1520 mg N_{NH4}/l, with a mean value of 398 mg N_{NH4}/l. The investigations of Kulikowska (2002), Koc-Jurczyk (2006) demonstrated that the ammonia concentration increased from about 100 to 600 mg N_{NH4}/l with increased landfill age from the 3rd to 10th year of landfill operation.

2.5 *Temporal variations of BOD_5/COD and N/COD in leachate*

During the design of biological systems with integrated removal of carbon and nitrogen compounds the changes in biodegradability of the leachate are reflected in the BOD_5/COD ratio, while the N/COD ratio in leachate gives information about the possibility of nitrogen removal.

The ranges of organic substances and nitrogen in leachate depend on the waste degradation phase in the landfill. Therefore, some authors have identified the different phases and ascribed them a specific order of magnitude of chemical parameters.

Heyer & Stegmann 2005 (after Ehrig 1990) on the basis of ten-year investigations of leachate from German landfills distinguished between acid and methanogenic phases. For each of them a range of

Table 1. Organics and ammonium nitrogen concentrations in landfill leachates of different age.

Landfill age (years)	COD (mg/l)	BOD_5/COD	N_{NH4} (mg/l)	N_{NH4}/COD	References
<5	5028	0.6	76	0.015	Robinson & Maris 1983
	13,780	0.7	42	0.003	Henry et al. 1987
	5400	0.65	158	0.029	Robinson & Grantham 1988
	58,400	0.69	1720	0.029	Chang 1989
	17,350	0.47	1692	0.098	Avezzu et al. 1992)
	38,000	0.22	2109	0.06	Szpadt 1995
	4100–5000	0.2	2100–3000	–	Chiang et al. 1995
	204–3641	0.05–0.79	29–2505	0.016–0.73	Chen 1996
	14,900	0.46	280	0.19	Timur & Özturk 1997
	16,200–20,000	–	1120–2500	–	Timur & Özturk 1999
	41,507	0.79	1896	0.046	Kang et al. 2002
	1188–1596	–	100–189	–	Klimiuk & Kulikowska 2005
5–10	3750	0.29	36	0.0096	Henry et al. 1987
	3100	0.25	641	0.21	Avezzu et al. 1992
	2150	0.1	790	0.37	Trebouet et al. 2001[1]
	5348	0.5	1826	0.34	Kang et al. 2002
	757	0.14	362	0.48	Kulikowska & Klimiuk 2004
	2483	0.06	n.r.	–	Fan et al. 2006
	875	0.23	657	0.75	Koc-Jurczyk 2006
10–20	1870	0.49	10	0.0053	Henry et al. 1987
	4140	0.46	998	0.24	Avezzu et al. 1992
	6610–30,000	0.17–0.38	1500–11,000	0.1–0.85	Lo 1996
	550	0.03	390	0.71	Trebouet et al. 2001[2]
	685–15,000	–	39–1750	–	Tatsi & Zouboulis 2002
	1367	0.11	892	0.65	Kang et al. 2002
	590–1180	0.31–0.44	71–260	0.12–0.22	Marttinen et al. 2003
	7622–8000*	0.07–0.09	2390–2620	–	Kurniawan et al. 2006
	3038	0.06	n.r.	–	Fan et al. 2006
>20	1000	0.1	340	0.34	Knox 1985
	800–1300	–	460–600	–	Welander et al. 1997
	190–2800	0.07–0.46	53–210	0.07–0.37	Marttinen et al. 2003

n.r. – no result

[1]- intermediary leachate

[2]- stabilized leachate

concentrations (COD, BOD_5, TOC) and AOX with medium values, was given. In leachate from the acid phase of a landfill, concentrations of COD, BOD_5 and TOC were maintained in ranges of 6000–60,000, 4000–40,000 and 1500–25,000 mg/l, respectively. The concentration of AOX varied between 540 and 3450 μg/l. However, leachate from landfill in the methanogenic phase contained several times or even several ten times lower concentrations of organics COD (500–4500 mg/l), BOD_5 (20–550 mg/l), TOC (200–5000) mg/l and AOX (524–2010 μg/l).

Some authors attribute the specific phase of process with the time of landfill operation, for which they assign concentration parameters.

Amokrane et al. (1997) separated three periods of landfill operation, for which they assigned characteristic values of BOD_5, COD and TOC and ratios between them. According to the authors, in young landfills with ages < 5 years, the concentration of organics (COD) is above 10,000 mg/l and the BOD_5/COD ratio > 0.5. In landfills aged between 5–10 years the COD amounts to $<10{,}000$ mg/l and BOD_5/COD ratio from 0.1 to 0.5. However, in landfills older than 10 years COD and BOD_5/COD ratio are 5000 mg/l and 0.1, respectively.

Farquhar (1989) reported on the extent of the variation of leachate quality with landfill time exploitation. According to the author, organics concentration (COD) ranges from 15,000 to 40,000 mgO_2/l (BOD/COD ratio – 0.6) for landfills in operation for less than 5 years; and from 10,000 do 20,000 mgO_2/l (BOD/COD from 0.1 to 0.2) for landfills aged between 5–10 years. The concentration of organic substances and BOD/COD ratio decreased with time giving COD < 1000 mgO_2/l at BOD/COD ratio of 0.05 for landfills aged over 20 years. The ranges of ammonia concentration varied from close to zero to about 1 250 mg N_{NH4}/l, similar to organic nitrogen. The concentration of nitrate (V), in general, did not exceed 9.8 mg N_{NO3}/l, and nitrate (III) 1.5 mg N_{NO2}/l.

The values of organics concentration as COD, ammonia, BOD_5/COD and N_{NH4}/COD ratio according to different authors are given in Table 1.

From the presented data it follows that the highest changes of COD and BOD_5 occurred during the first 5 years of landfill operation. In numerous cases the COD was reported to be below or equal to 5000 mg O_2/l.

Usually, in leachate from young landfills the BOD/COD ratio amounts to about 0.6 with occasional exceptions. Chen (1996) on the basis of investigations on the composition of nine young landfills in the central region of Taiwan (age $<$ 5 years) shows that BOD/COD ratio vs. landfill age shows a sharp decrease within approximately one year and then progressively levels off with the increase in landfill age. This observation indicates that the reactions of biodegradable organics are rapid during ca. the first one and a half years and then a steady state is reached. Another reason for the decreasing ratios of BOD/COD is probably due to rainwater washing.

In many countries sewage sludge is disposed of in landfills. According to Davis & Hall (1997), Bergs & Lindner (1997) and Yagout (2003) the share of sludge waste in total waste disposed in the landfill site amounted to about 40% – 60%. The nitrogen and phosphorus content in sludges can be even as high as 5% d.m. and 1.5%, respectively (Bień, 2002), i.e. several times higher in comparison with their content in municipal waste, where the values usually do not exceed 1% d.w. and 0.7% d.w., respectively (Skalmowski 2001). Therefore, it can be presumed that sludges disposed of in landfills in large quantities might influence the nutrient content of leachate, and thereby the N_{NH4}/COD and P/COD ratios.

In leachate from landfills exploited for shorter than 5 years, significant changes of ammonia concentration can be seen, and, in consequence, variable values of N_{NH4}/COD ratio from 0.003 (Henry et al. 1987) to 0.73 (Chen 1996).

Along with increasing landfill age a strong decrease of BOD_5 and COD, as well as a distinct decline of BOD_5/COD ratio, is observed, which is confirmed by literature data (Table 1).

Between the 5th and the 10th year of landfill exploitation the fluctuations of organics concentration (COD) are not so high, however values of BOD/COD ratio changed to a large extent from 0.06 to 0.5. For the leachate from older landfills, exploited $>$10 years, there is a tendency for a successive decrease in BOD_5/COD values, the range of results remains still quite high from 0.03 to 0.49.

Analysis of leachate from a municipal landfill in Hong Kong with an age of 10–20 years showed that in leachate from landfills, the concentration of organics ranged from 6610 to 30,000 mg COD/l and N/COD ratio from 0.1 to 0.71 (Lo 1996).

From the data presented in Table 1 it can be seen that for landfills operating from 5 to 20 years, with only few exceptions, the tendency to high N/COD ratio strengthened.

There are a few results concerning leachate composition from landfills exploited for $>$20 years. In these, there appears to be a tendency towards residual low organic concentrations.

2.6 *Organics removal*

The variable nature of leachate contaminants ensures that some types of biological and/or physicochemical treatment processes should be preferentially employed. In general, biological processes are most effective for leachate from young landfills whereas from older landfills – physicochemical.

Numerous studies have been performed to evaluate the removal of organic substances in biological treatment systems. High concentrations of organic substances and high BOD_5/COD ratio in the leachate from a young landfill suggest the application of anaerobic pre-treatment prior to aerobic processes.

Modern reactors are used extensively for leachate treatment. Among them suspended-growth processes such as Upflow Anaerobic Sludge Blanked reactors (UASB) and attached-growth processes such as Downflow Stationary Fixed Film reactor (DSFF) or Upflow Stationary Fixed Film reactor (USFF) were tested. Some authors also employed Anaerobic Sequencing Batch Reactors (ASBR). The results of leachate treatment in anaerobic conditions with the type of reactor, technological parameters and effects of treatment gained by different authors are shown in Table 2.

The results of the presented data show that methane fermentation was applied to leachate treatment containing considerable concentrations of organic substances. The values of COD often exceeded 10,000 mg/l and BOD_5/COD ratio was on average 0.6, which explains the high efficiency of COD and BOD_5 removal.

The advantage of anaerobic processes is the lower production of biomass in comparison to aerobic processes. The biomass production coefficient Y determined during methane fermentation in SBR was 0.1 g VSS/g COD while the specific biomass decay rate k_d – 0.01 d^{-1} (Timur & Özturk 1999). Similar values are given by Kennedy et al. (1988) for leachate from a 15 year old municipal landfill in Halifax, (Canada), for which the Y value changed in the range from 0.05 to 0.09 g VSS/g COD.

The influence of hydraulic retention time (HRT) in aerobic conditions on activated sludge production in SBR was investigated by Klimiuk & Kulikowska (2006). Leachate characterized by a low

Table 2. Efficiency of anaerobic landfill leachate treatment.

Anaerobic methods	Landfill age and/or organics in leachate	Operational conditions	Removal efficiency	References
Anaerobic filter	COD – 13,780 mg/l	organics loading 1.45 kg/m^3·d	COD – 95%	Henry et al. 1987
	BOD_5 – 9660 mg/l	organics loading 2.89 kg/m^3·d	COD – 68%	
	COD – 3750 mg/l	organics loading 1.26 kg/m^3·d	COD – 95%	
	BOD_5 – 1100 mg/l	organics loading 3.14 kg/m^3·d	COD – 60%	
	COD – 1870 mg/l	organics loading 1.35 kg/m^3·d	COD – 90%	
	BOD_5 – 930 mg/l	organics loading 2.66 kg/m^3·d	COD – 88%	
Modified anaerobic sludge bed filter (upflow system combining a sludge bed and a filter)	landfill age – 1.5 year COD – 58,400 mg /l BOD_5 – 40,065 mg /l	organics loading $<$ 13 kg COD/m^3·d organics loading 21.77 kg COD/m^3·d	COD – 92% COD – 70%	Chang 1989
Anaerobic upflow fixed-film reactor	COD – 9254 mg /l BOD_5 – 5340 mg /l	organics loading 1.5 kg COD_5/m^3·d HRT 5.8d	COD – 72%. BOD_5 – 80%	Vicevic et al. 1992
Anaerobic up-flow blanket filter	landfill age – 15 years COD – 19,480 mg/l	organics loading 4.8–14.5 kg COD_5/m^3·d HRT 4 – 1.5d	COD – 96.3–95.8%	Kennedy et al. 1988
Downflow stationary film	landfill age – 15 years COD – 19,480 mg/l	organics loading 5.2 – 14.7 kg COD_5/m^3·d HRT 4.2 – 1.5d	COD – 90.9–93.4%	
Upflow anaerobic sludge blanket (UASB) reactor	COD – 11,450–33,440 mg/l BOD_5 – 7910–24,130 mg/l	organics loading 113.6–19.7 kg COD_5/m^3·d HRT 1.0 – 3.2d	COD – 65.7–99.2% BOD_5 – 69.2–96.1%	Blakey et al. 1992
Anaerobic stabilization	COD – 12,760 mg/l BOD_5 – 4995 mg/l	HRT 8.8 months	COD – 84.3% BOD_5– 78.7%	Zaloum & Abbott 1997
Continuous flow upflow anaerobic sludge blanket (UASB)	COD – 3210–9190 mg/l	HRT 12 h	COD – 77%	Kennedy & Lentz 2000
Anaerobic sequencing batch reactor (ASBR)	COD – 1875–15,400 mg/l	organics loading – 0.19–10 kg COD/m^3·d HRT 1.5 – 10d	COD – 83.7–73.3%	Timur et al. 2000
Anaerobic sequencing batch reactor (ASBR)	COD – 3800 mg/l COD – 15,940 mg/l	organics loading 0.4 kg BOD_5/m^3·d organics loading 9.4 kg BOD_5/m^3·d	COD – 85% COD – 64%	Timur & Özturk 1999
Anaerobic sequencing batch reactor (AnSBR)	COD – 3210–9190 mg /l	HRT 24 h	COD – 86%	Kennedy & Lentz 2000
Up-flow biofilm anaerobic reactor packed with inert media (Saran 1000)	COD – 21,300–26,900 mg/l BOD_5 – 9250–11,650 mg/l	organics loading 2.6–19.2 kg COD/m^3·d	COD – 90%	Im et al. 2001
Anaerobic hybrid bed filter (AHBF)	COD – 3955–14,950 mg/l	organics loading – 0.78–7.41 kg COD/m^3·d HRT 0.9 – 5.1d	COD – 87.0–59.3%	Timur et al. 2000
Up-flow sludge blanket reactor (UASBR)	COD – 10,250–25,250 mg/l	organics loading – 3.7–10.7 kg COD/m^3·d HRT 1.7 – 2.35d	COD – 94.0–92.0%	

concentration of organics (BOD_5 and COD), did not exceed 517 and 1348 mg O_2/1, respectively. The theoretical yield coefficient (Y) and specific biomass decay rate (k_d) were 0.616 mg VSS/mg COD and 0.032d^{-1}, respectively. Activated sludge production expressed as the observed coefficient of biomass production (Y_{obs}) increased appropriately with HRT decreasing. In the reactors working with only an aeration phase, the Y_{obs} changed from 0.04 mg VSS/mg COD (HRT = 12d) to 0.32 mg VSS/mg COD (HRT = 2d).

Effective leachate treatment in anaerobic reactors can be carried out even at low temperatures. Kettunen & Rintala (1998) noted that a UASB reactor created for the treatment of municipal landfill leachate (COD 1500 – 3200 mg/l) could operate at a temperature as low as 13°C. Despite changes in leachate quality, 65–75% of COD and up to 95% of BOD_7 were removed at 18–23°C with organic loading rates of 2–4 kg COD/m^3·d. At 13–14°C, 50–55% of COD and 72% of BOD_7 removal were obtained with organic loading 1.4–2 kg COD/m^3·d. Methane yield averaged 320 ml CH_4/g COD_{removed}.

The literature results show that anaerobic reactors ensure high efficiencies of organic substances removal, especially from leachate arising in young landfills. In the case of leachate from mature landfills these are less effective in comparison to aerobic reactors. Gourdon et al. (1989) compared the efficiency of leachate treatment in anaerobic and aerobic conditions. The concentration of organic compounds in leachate (COD) was 1930 mg/l, but the concentration of organic carbon was 640 mg/l (TOC). In anaerobic conditions the authors used a fixed-film reactor with heat-expanded vermiculite as a packing medium (3 × 4 mm) at 35°C, while in aerobic conditions – a trickling filter filled with plastic packing medium (10 × 10 mm) at 20°C. The effectiveness of organic compound removal (COD) in aerobic conditions was 69% but in anaerobic conditions it was lower – about 33.2%. The efficiency of TOC removal was 70 and 35.9%.

During the methanation phase, the leachate contains relatively a low concentration of degradable organic substances, but a high concentration of ammonia in the effluent generally requires the removal of both residual organics and ammonia nitrogen.

In Table 3, the results of leachate treatment obtained by several authors in aerobic conditions are shown. Methods studied in leachate treatment include suspended growth systems, such aerated lagoons, conventional activated sludge processes and sequencing batch reactors (SBR). From the presented results it can be noted that the subjects of the study were leachate characterized by low BOD_5/COD ratios.

It can be seen that the authors, to achieve suitable results by their treatment, applied a long leachate retention time in the activated sludge. The essential factor was assumed to be a sufficiently aged sludge. Robinson & Maris (1983) treated landfill leachate (COD 5000 mg/l, BOD 3000 mg/l) using aerobic biological continuous-flow reactors at a low temperature. They showed that with an SRT of 1 day, about 65% of the BOD and 62% of the COD of leachate were removed. Higher SRT values provided better removals – an SRT of 20 days yielded concentrations of BOD of less than 20 mg/l and of COD down to 155 mg/l.

In SBR reactors, the COD in treated leachate strongly depends on the operational conditions. Kulikowska (2002) has proved that for leachate from young landfills (BOD_5/COD = 0.35–0.39) the most important factor influencing COD removal was the HRT – when the HRT was decreased from 12d to 2d the process efficiency dropped from 83.5% to 70.5%.

Koc-Jurczyk (2006) showed that in the case of leachate from the same landfill, but at a longer time of landfill exploitation (BOD_5/COD = 0.23), organic compounds (COD) removal in SBRs was less efficient and did not exceed 24%.

Drzewicki (2003) investigated activated sludge biocenosis in SBRs treating landfill leachate. He showed that the quality of activated sludge is equal to 5–4 points of SBI (Sludge Biotic Index) for sludge age >20 days and HRT 3 days or longer. According to Madoni (1994) the numerical value of SBI is in the range of 10–0 points. SBI points correspond to four quality classes of activated sludge. Activated sludge is characterized by 10–8 points and belongs to the I class. A smaller number of points correspond to classes: 7–6 points (II), 5–4 points (III) and 3–0 points (IV).

Many researchers have employed systems with attached growth of microorganisms for leachate treatment such as trickling filters or rotating biological contactors. Martienssen et al. (1995) treated municipal landfill leachate using activated sludge bioreactor, fluidized bed biofilm reactor and packed-bed column reactor (trickling filter). Among the three biological treatment technologies investigated, the fluidized bed biofilm reactor was the best with respect to TOC removal. More than 90% of TOC were removed at a loading of less than 0.5 kg/m^3·d. At TOC loading 4 kg/m^3·d, its removal was 80%.

A new type of attached growth system includes the suspended carrier biofilm and moving bed biofilm processes. Some research has also been conducted on inserting an activated carbon-like biomass carrier (Table 3).

More recently, in the landfill leachate treatment, the combination of a biological activated sludge treatment and membrane filtration for biomass separation named a membrane bioreactor has been used. Chen & Liu (2006) applied a membrane bioreactor with airlift bioreactor and gravity flow to landfill leachate

Table 3. Efficiency of aerobic landfill leachate treatment.

Aerobic methods	Landfill age and/or organics in leachate	Operational conditions	Removal efficiency	References
Aerated lagoons	COD – 5 518 mg/l BOD$_5$ – 3670 mg/l	retention period >10d organics loading – 0.3 kg COD/m^3·d	COD – 97.2%	Robinson & Grantham 1988
Aerated lagoons	COD – 11,216–12359 mg/l BOD$_5$ – 5015–5294 mg/l	organics loading – 1.0 kg COD/m^3·d	COD – 87% BOD$_5$ – 95%	Ehrig & Stegmann 1992 (after Cossou 1981)
Aerated lagoons	COD – 9785 mg/l BOD$_5$ – 5162 mg/l	organics loading – 0.21 kg COD/m^3·d	COD – 96.4% BOD$_5$ – 99.5%	Ehrig & Stegmann 1992 (after Klingl 1981)
Activated sludge	COD – 15,800 mg/l	HRT 10d HRT 5d	COD – 97% COD – 46.5%	Cook & Foree 1974
Activated sludge bioreactor	COD – 2000–2600 mg/l	organics loading – 1 150 mg TOC/l·d organics loading < 450 mg TOC/l·d	TOC – 74% TOC > 83%	Martienssen et al. 1995
Aerobic biological process in continuous flow reactor	landfill age – 2 years COD – 5518 mg/l BOD$_5$ – 3670 mg/l	temp. 10^{0}C. SRT 10d	COD – 92% BOD$_5$ > 98%	Robinson & Maris 1983
Biological activated carbon fluidized bed process	COD – 86–221 mg/l BOD$_5$ – 1–26 mg/l DOC – 81–151 mg/l	HRT 24–96 h	DOC – 42–58%	Imai et al. 1995
Moving-bed biofilm process (SBR with free-floating polyurethane carriers)	COD – 5000 mg/l BOD$_5$ – 1000 mg/l	HRT 20–24d	COD – 65% BOD$_5$ – 95%	Loukidou & Zouboulis 2001
Granular activated carbon (GAC) moving-bed biofilm process (SBR with GAC)	COD – 5000 mg/l BOD$_5$ – 1000 mg/l	HRT 20–24d	COD – 81% BOD$_5$ – 95%	
Aerobic RBC Fixed-Film Reactor	COD – 9254 mg /l BOD$_5$ – 5340 mg/l	organics loading – 2.8 kg COD$_5$/m^3·d HRT 2.9d	COD – 86% BOD$_5$ – 95%	Vicevic et al. 1992
Fluidized bed biofim reactor	COD – 2 000 ÷ 2 600 mg/l	organics loading – 4 200 mg TOC/l·d organics loading < 450 mg TOC/l·d	TOC – 84% TOC > 94%	Martienssen et al. 1995
Packed-bed column reactor (trickling filter)	COD – 2 000 ÷ 2 600 mg/l	organics loading – 300 mg TOC/l·d organics loading < 125 mg TOC/l·d	TOC – 59% TOC > 85%	
SBR treating raw leachate	COD – 12 760 mg/l BOD5 – 4 995 mg/l	HRT 20d SRT 50d	COD – 91.2% BOD5 – 99.7%	Zaloum & Abbott 1997
SBR treating anaerobic pretreated leachate	COD – 1 240 mg/l BOD5 – 805 mg/l	HRT 4.6d SRT 50d	COD – 87.7% BOD5 – 99%	
SBR treating anaerobic pretreated leachate	COD – 2 205 mg/l BOD5 – 1 010 mg/l	HRT 3.2d SRT 50d	COD – 94.6% BOD5 – 99.5%	
SBR treating raw leachate	COD – 1 237 mg/l BOD5 – 457 mg/l	HRT 2–12d mixing and aeration phases in the SBR cycle, short filling period	COD – 70.5–82.9% BOD5 – 98.2–99.3%	Klimiuk & Kulikowska 2005
SBR treating raw leachate	COD – 1 380 mg/l BOD5 – 539 mg/l	HRT 2-12d mixing and aeration phases in the cycle, filling over the reactionperiod	COD – 76.7–83.1% BOD5 – 97.6–99.2%	
SBR treating raw leachate	COD – 1 188 mg/l BOD5 – 451 mg/l	HRT 2-12d aerobic conditions, filling over the reaction period	COD – 75.7–79.5% BOD5 – 97.5–99%	
SBR treating raw leachate	COD – 875 mg/l BOD5 – 204 mg/l	HRT 1.1–3d aerobic conditions	COD – 9–24% BOD5 – 89–95%	Koc-Jurczyk 2006

treatment. They showed that more than 95% BOD_5 was removed with less than 35 mg/l of BOD_5 in the effluent at less than 1.71 $kg/m^3 \cdot d$ of BOD_5 loading rate. When dissolved oxygen was maintained in the range of 2.3–2.8 mg/l and the loading rate of ammonium nitrogen was kept at 0.16–0.24 $kg/m^3 \cdot d$, the N_{NH4} in the effluent was less than 15 mg/l. However, the removal efficiency of soluble chemical oxygen demand (SCOD) varied between 70 and 96%. Besides, the results indicated that organics in the leachate were composed of a high molecular weight (MW) fraction and a low MW fraction. The high MW fraction is not biodegradable, but can be decreased with a microfiltration membrane. Most of the low MW fraction is biodegradable, but the residue of the low MW fraction is able to permeate through the membrane, resulting in high soluble COD in the effluent from the MBR. Laitinen et al. (2006) treated landfill leachate in a SBR and a submerged membrane bioreactor (MBR). The average quality of the leachate was 475 mg/l suspended solids, 1240 mg/l BOD_7, 10 mg/l phosphorus and 210 mg/l ammonium nitrogen. The SBR process was operated with hydraulic retention time (HRT) from 4 to 8 days and MBR with HRT around 3 days. Solid retention times (SRTs) in SBR were from 10 to 40 days and in MBR from over 35 to over 60 days. The authors showed that in MBR effluent the concentrations were much lower than in SBR, e.g. suspended solids, BOD_7 and COD in SBR effluent were 290 mg/l, 190 mg/l and 500 mg/l, respectively, while in MBR effluent 1.2 mg/l, 8.3 mg/l and 340 mg/l.

The efficiency of harmful substance removal from leachate carried out by Klimiuk & Kulikowska (2004) in activated sludge operated as a single and a two-stage SBR. Raw leachate contained specific hazardous organics, among them BTEX (175.8 μg/l), chloroorganics (55.7 μg/l), chlorobenzenes (0.75 μg/l), PAHs (1.97 μg/l) and PCBs (0.001 μg/l). In the effluent, the concentrations of BTEX (as a sum of compounds) were 1.6 μg/l (single SBR system) and 0.8 μg/l (two-stage SBR system), which responds to a removal efficiency of over 99%. The effluent contained PAHs at the level of 0.793 μg/l in the single system and 0.377 μg/l in a two-stage system. In the effluent from single and two-stage SBR system chloroorganics and chlorobenzenes were not detected. In addition, the effluent from two-stage SBR system did not contain benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene. From the work of Koc-Jurczyk (2006) it can be seen that the BTEX concentration in raw leachate was 20.4 μg/l. After biological treatment in SBR reactors (HRT = 3 days), this was reduced to 4.6 μg/l, which corresponds to the average efficiency of this compound removal (77.5%). In the case of benzene, of which the concentration in raw leachate was 4.6 μg/l, the removal efficiency was the highest and reached 97.8%. The lowest efficiency (20%) was obtained for ethylbenzene. In raw leachate, sixteen standard PAHs were found. PAHs with five or less rings were effectively removed by activated sludge, but PAHs containing six rings like dibenzo(a,h)anthracene and benzo(g,h,i)perylene or fluorene and acenaphthalene only with low efficiency.

2.7 *Nitrogen removal*

The introduction of legal restrictions to the range of permissible concentrations of ammonium nitrogen in leachate has meant that, in the last ten years, the attention of many researchers has turned to nitrogen removal. According to Albers & Krückeberg (1992), Leitzke (1996), Kaczorek et al. (2002) even though, when physical and chemical processes like ozonation or reverse osmosis in leachate treatment are applied, preliminary nitrogen removal using a biological technology is economically justified.

In the case of nitrogen removal from activated sludge, nitrification and denitrification processes were extended in time. The influence of operational conditions on nitrification for given types of biotreatment systems was investigated. Additionally, the researchers focused on denitrification with internal and external carbon sources.

Literature reviews show that nitrogen removal from leachate can be via biosynthesis and denitrification and/or simultaneous nitrification and denitrification. Robinson & Maris (1983) at SRT greater than 5 days found that the ammonia concentration in the effluent was less than 1 mg/l. According to the authors, removal of ammonia was principally caused by its conversion to organic nitrogen during the growth of biomass. Similarly, Bull et al. (1983) showed that 60% of total nitrogen removal from leachate was the consequence of its consumption for new cell growth. Klimiuk & Kulikowska (2005) proved that in SBRs working with mixing and aeration phases in the cycle, the percentage of nitrogen consumed for biomass production was over 30%.

In activated sludge, the growth of nitrifying bacteria is favored by long sludge age, high oxygen concentration and low organic carbon/ammonium nitrogen ratio. In the initial stage of landfill exploitation, organic acids, which appear at high concentrations in leachate, can inhibit the rate of ammonium oxidation, which, in consequences leads to a decrease of nitrification efficiency (Takai et al. 1997). On the other hand, in leachate from landfills in the methane phase, the lack of a carbon source can cause a decrease in the denitrification efficiency. The type and concentration of available organic compounds decide the rate of denitrifying bacteria growth.

Surmacz-Górska et al. (2000) proved that, during the treatment of leachate from a 4 year old municipal landfill in Siemianowice Slaskie, the high organics concentration in leachate was the main factor inhibiting nitrification in activated sludge. In leachate of low organic content (COD 1500 mg O_2/l) the ammonium nitrogen efficiency was 90%, but when the COD increased to 6548 mg O_2/l, the nitrification was inhibited.

One way of increasing nitrification in comparison with activated sludge only, is the introduction of moving carriers to activated sludge. It extends the retention time of microorganisms and increases the biomass content in reactor.

Welander et al. (1997) investigated nitrification in reactors fitted with a suspended-carrier biofilm. The leachate contained 460–600 mg/l ammonium nitrogen, 800–1300 mg/l of COD and 30–140 mg/l of BOD_7. The authors studied the effects of temperature and HRT on the volumetric nitrification rate in three reactors filled with three different types of carrier media (polyethylene carriers and macro porous cellulose). The nitrification rate showed a weak dependence on the temperature, the rate at 5°C was approximately 77% of the rate at 20°C. The HRT had a stronger influence on the rate of nitrification, showing a considerable increase in nitrification rate with decreasing HRT. The highest nitrification efficiency (99.6%) and maximum nitrification rate (40 g $N_{NH4}/m^3 \cdot h$) were obtained for a macro-porous cellulose media at 20°C and HRT 14 h.

The efficiency and rate of nitrification in various types of biological beds were also investigated. Knox (1985) analysed the ammonium nitrogen oxidation in trickling biofilters and in activated sludge. Leachates from 60-year old municipal and industrial landfills in Pitsea in Great Britain were tested. The trickling biofilter had a 16.5 m^3capacity with cylinders made of plastic Flocor R type as the medium. The specific surface of biofilter medium was 230 m^2/m^3. The activated sludge system consisted of an aeration tank with a volume of 8.1 $m^3$and a sedimentation tank with a volume of 9.3 m^3. The author obtained complete nitrification in both systems. The maximum nitrification rate was 131 mg/g d.m.·d in the activated sludge, and, in the bed – 309 mg/m^2·d. In landfill leachate, technological problems connected with nitrogen removal can be caused by insufficient concentrations of organic substances. In order to achieve complete denitrification it is necessary to introduce an external carbon source. Such solutions are commonly applied for leachate (Shiskowski & Mavinic 1998, Calli et al. 2005). Methanol is usually used as carbon source, although maltose and acetate have also been tested (Doyle et al. 2001).

Nitrogen removal was tested in pre-denitrification or post-denitrification systems. Currently, simultaneous nitrification and denitrification is an object of intense research. Pre-denitrification is more effective if low amounts of leachate are treated. The denitrification rate depends on the BOD_5/N ratio in the influent. Using the post-denitrification process, very low nitrate values in the effluent can be reached. However, in this case the degradable organics in the leachate cannot be used as a carbon source.

Martienssen & Schöps (1997) studied the nitrogen removal in a continuous system with pre-denitrification. The organics concentration in leachate expressed as COD was 2560 mg O_2/l and ammonium nitrogen concentration – 463 mg N_{NH4}/l. In samples without methanol at the retention time of 1.5 days and loading rate of 1150 mg TOC/l·d, the ammonium nitrogen efficiency was about 60%, but total nitrogen was less than 50%. After the introduction of methanol, at C/N ratio = 3/1, the ammonium nitrogen concentration in the effluent decreased to 5 mg N_{NH4}/l but nitrite and nitrate did not exceed 10 mg N_{NO2}/l and 20 mg N_{NO3}/l, respectively.

Shiskowski & Mavinic (1998) used a continuous flow activated sludge system with pre-denitrification for nitrogen removal from leachate at the methane phase of landfill (COD – 375 mg/l, BOD_5 – 30 mg/l, ammonium nitrogen – 200 mgN/l). The research was carried out at retention times of 1.72 and 3.43 h in an anoxic and an oxygen chamber and with activated sludge age in an oxygen chamber – for 13 days, respectively. After introduction of methanol to the anoxic chamber, after 70 days of operation, they achieved complete ammonium nitrogen removal in the oxygen chamber and almost total nitrate and nitrite reduction in the anoxic tank. The authors proved that this system required the application of equipment with dosing, because excess of methanol can move from the anoxic tank to the oxygen tank causing nitrification inhibition. Similarly, Shiskowski & Mavinic (1998) (after Azevedo 1993), showed that, in a continuous flow system where nitrification follows denitrification, there is a danger of "leaking" methanol from the anoxic to the aerobic reactor and, as a consequence, nitrification inhibition.

Klimiuk & Kulikowska (2004) investigated the efficiency of organics and nitrogen removal from municipal landfill leachate in activated sludge operated as single and two-stage SBR. Leachates from mature landfills are characterized by a high N/COD ratio (>0.5). In a single activated sludge system at the hydraulic retention time (HRT) 3 days and at methanol dosage of 8 mg COD/mg N_{NO3} complete ammonium nitrogen removal was obtained. The ammonium concentration in the effluent was 0.15 mg N_{NH4}/l and nitrate – 23.5 mg N_{NO3}/l. At the hydraulic retention time of 2 days, nitrate nitrogen concentration in the effluent decreased to 2.79 mgN_{NO3}/l. The concentration of ammonium nitrogen was 0.35 mgN_{NH4}/l. However, a sporadically high concentration of ammonium appeared. In a two-stage SBR system (1° nitrification, 2° denitrification), a HRT of 2d was sufficient to achieve complete nitrification. In the effluent ammonium and nitrate concentrations were 0.08 mg N_{NH4}/l and 320 mg N_{NO3}/l, respectively. In the anoxic reactor at HRT 1d and methanol dosage of 3.6 mg COD/mg N_{NO3} complete denitrification was obtained.

Borzacconi et al. (1999) treated raw leachate (COD 30,000 mgO_2/l and N_{NH4} 1000 mg/l) in systems comprising of a denitrifying reactor – upflow sludge bed (USB), UASB – anaerobic reactor and nitrifying RBC. In the first stage, raw leachate and UASB outlet were tested as possible carbon sources, using KNO_3 as a nitrate source. Using raw leachate and UASB outlet with COD/N_{NO3} ratios of 4 and 12, respectively, denitrification efficiencies of about 90% were reached in the USB reactor operated alone. A sludge yield of 0.16 g VSS/g COD was obtained. In the second stage the USB reactor was integrated into the carbon and nitrogen removal system. A portion of the aerobic reactor effluent was recycled into the denitrification stage and some raw leachate was also added as an additional C source. For the anoxic reactor operating in the complete system, denitrification efficiencies of 90% were also achieved.

Literature data indicate that the duration of the maturation phase of landfill exploitation is the longest. Leachate from this stage is characterized by a low concentration of available organics and a high concentration of ammonia nitrogen. Therefore, denitrification process is ineffective. In recent years new mechanisms of nitrogen removal have been discovered and described. These are known as partial nitrification (as a pre-step for conventional denitrification or Anammox), Anammox and Canon (Mulder et al. (1995), van de Graaf et al. (1995), Hellinga et al. (1998), Strouss et al. (1999), Sliekers et al. (2002).

Partial nitrification is the oxidation of wastewater ammonium to nitrite, but not to nitrate. The removal of nitrogen via nitrite may be achieved by reducing the activity of *Nitrobacter* and correspondingly giving *Nitrosomonas* species growth a advantage. As was suggested by the inhibition of nitrite oxidation to nitrate a saving of organic substances of up to 40% could result. This would be of particular interest in biological nitrogen removal from wastewater with an unfavorably high N/COD ratio.

Partial nitrification can be the first stage in a conventional denitrification system or Anammox. The Anammox process, called anaerobic ammonium oxidation, needs a preceding partial nitrification step, which converts half of the wastewater ammonium to nitrite.

Now, the oxidation of nitrite to nitrate can be prevented by making use of the different growth rates of ammonia and nitrite oxidizers at sufficiently high temperatures and/or at a hydraulic retention time higher than the growth rate of nitrite oxidizers but lower than ammonia oxidizers. An example is the Single Reactor High Activity Ammonia Removal Over Nitrite process ("SHARON"). SHARON operates at a high temperature (30–40°C) and pH (7–8). The process is performed without sludge retention (Hellinga et al. 1998). SHARON still makes use of denitrification with added methanol. Methanol is supplied periodically, while the aeration is switched off.

Koc-Jurczyk (2006) observed partial nitrification in SBR and SBBR (SBR with PCV sponge filler) at HRT 1.1d, T = 20°C, pH 8–8.24. The ammonium nitrogen concentration in leachate was an average 796 mg N_{NH4}/l, N/COD = 0.7. At the end of the cycle the nitrite concentration in treated leachate was 631 mg N_{NO2}/l in SBR and 633 mg N_{NO2}/l in SBBR. The efficiency of second step nitrification was low and the nitrate concentration (V) in the effluent did not reach 82 mg N_{NO3}/l and 71 mg N_{NO3}/l in SBR and SBBR, respectively.

Another interesting concept is the combination of partial nitrification and Anammox in a single, aerated reactor. The name Canon (Completely Autotrophic Nitrogen Removal Over Nitrite) refers to the two groups of bacteria which cooperate in the process. The nitrifiers oxidize ammonia to nitrite, consume oxygen and so create an anoxic condition, which the Anammox process needs (Schmidt et al. 2003). To increase the effectiveness of the process and nitrate nitrogen (V) removal, the introduction of organic substances is recommended as an external carbon source (Hao & van Loosdrecht 2004).

Koc-Jurczyk (2006) showed that in SBBR (SBR with PCV sponge filter) with a mixing phase integrated into the cycle, at HRT 3 days, nitrogen removal was 448 mg N_{NH4}/cycle, which corresponds to 74% of ammonium concentration in the influent. Nitrogen consumption for biosynthesis did not reach 7%. The residue in the treated leachate was mainly ammonium nitrogen (19%) and organic nitrogen (6%).

Klimiuk & Kulikowska (2005) investigated nitrogen removal from municipal landfill leachate in SBR reactors. The influence of hydraulic retention time (HRT), sludge age (SRT), method of leachate dosage (short filling period of SBR and filling during reaction period), and operational conditions with and without a mixing phase in the SBR cycle, was explored. Ammonia nitrogen and organics concentrations (as COD) in raw leachate were 100.3–141 mg/l and 1188–1596 mg/l, respectively. The authors showed that the highest efficiency of ammonium removal was obtained in highly aged sludge and when a short filling period of leachate were applied. In these conditions, at HRT of 3–12d and SRT of 20–51d, the ammonium concentration in the effluent did not exceed 1 mg/l. Nitrogen removal proceeded mainly in the aeration phase as a result of ammonium losses and, to a lower extent, dissimilative nitrate reduction over the mixing phase.

Recently, anaerobic-aerobic systems adapting the methanogenesis and denitrification processes were studied as a feasible method for treating the immature and mature leachate from municipal landfill sites.

Jokela et al. (2002) tested a low-cost method for the removal of nitrogen from landfill leachate. Nitrification was studied in a laboratory and on-site pilot aerobic biofilters. Three types of laboratory reactors were used: an upflow filter (UF) with crushed brick as a medium, a downflow filter (DF) with a bulking agent (wood chips) of mature compost as a medium and suspended carrier biofilm process (SCBP) with commercial carriers. In addition, an on-site pilot study of the upflow nitrification filter with crushed brick as a filter medium was tested. Denitrification was studied in a laboratory anoxic/anaerobic column filled with landfill waste. The authors showed that in all laboratory reactors over 90% effectiveness of nitrification was obtained with loading rates 100–130 mg N_{NH4}/l·d at 25°C. In an on-site pilot study the same level of nitrification (over 90%) was achieved with a loading rate of 50 mg N_{NH4}/l·d at 5–10°C. In the denitrification column, the total oxidized nitrogen (TON) in nitrified leachate usually declined below detection limit.

Im et al. (2001) tested an experimental treatment system, which consisted of an up-flow anaerobic biofilm reactor adapting the simultaneous methanogenesis and denitrification process, an aerobic activated sludge reactor and clarifier. Six experiments were carried out to evaluate the degradation rate of organic and nitrogen compounds. The loading rate varied by diluting influent and increasing influent flow rates. The range of organics loading in the anaerobic reactors was 2.6–19.2 kg COD/m^3·d and N_{NH4} loadings into the aerobic reactors was 0.23–1.25 kg/m^3·d. The leachate was characterized by BOD_5/COD and C/N ratios of 0.44 and 14, respectively. Denitrification and methanogenesis were successfully carried out in the anaerobic reactor while the organic removal and nitrification depended on hydraulic retention time. The maximum organic removal rate was 15.2 kg COD/m^3·d in the anaerobic reactor, while the maximum NH_4-N removal rate and maximum nitrification rate were 0.84 kg N_{NH4}/m^3·d and 0.50 kg N_{NO3}/m^3·d in aerobic reactor, respectively. The gas production rate was 0.33 m^3/kg COD and the biogas composition of CH_4, CO_2 an N_2 were kept relatively constant. 66–75%, 22–32% and 2–3%.

In the past, oxygen has not been added to landfills, thus nitrification has not typically occurred *in situ*. However, more recently, air addition has been practiced.

Berge et al. (2006) evaluated an aerobic reactor *in situ*, or partially *in situ* (microcosm studies) nitrogen removal and demonstrated the potential efficiency of such processes in landfills. The results suggest that ammonia removal via nitrification and denitrification may occur simultaneously in a single reactor with a low C/N ratio.

Mertoglu et al. (2006) monitored the composition of nitrifying bacteria in an aerated landfill bioreactor filled with municipal solid waste incineration bottom ashes and shredded incombustible wastes. N_{NH3} decreased from 250 to about 30 mg/l within 250 days of operation. To confirm the nitrification activity in the aerated bioreactor intensive amounts *Nitrosomonas*-like ammonia oxidiers and *Nitrospira* related nitrite oxiders were identified with 16S rRNA based hybridization assays.

He & Shen (2006) evaluated the performance of nitrogen removal in a vertical aerobic/anoxic/anaerobic laboratory scale bioreactor landfill system with fresh municipal solid waste. In the experiment two bioreactors were used (R1 and R2). Both systems were identical except that system R1 contained intermittent aeration at the top of landfilled waste by an aeration pump. The population of nitrifying bacteria for the landfill bioreactor with the intermittent aeration system reached between 10^6 and 10^8 cells/dry g waste. The population of denitrifying bacteria increased by between 4 and 13 orders of magnitude compared with conventional anaerobic landfill waste layers. The N_{NO3} concentration of leachate was very low in both experimental landfill reactors. Leachate N_{NH4} and total nitrogen concentrations for the landfill reactor with intermittent aeration system were 186 and 289 mg/l, respectively, while they were still kept above 1000 mg/l for the landfill reactor without an intermittent aerobic system.

3 CONCLUSIONS

The composition and concentration of constituents in leachate from a landfill municipal waste solid is difficult to predict Although generally with landfill age concentration of organics (as COD) and BOD/COD ratios decrease and N/COD ratio increase, the range of values for landfills with ages less than 5 years varies from 204 to 58,400 mg/l (COD), from 0.2 to 0.79 (BOD/COD), and from 0.003.to 0.73 (N/COD). However, for landfills with ages of 5–20 years it is between 550–30,000, 0.03–0.49 and 0.0053–.085, respectively. On the basis of leachate analysis from landfills in North-East Poland we conclude that recirculation causes fast increase of N/COD ratio from 0.1 in the 3rd year to 0.75 in the 10th year of exploitation and decrease of BOD_5/COD from 0.37 to 0.23, respectively.

The investigations on hazardous substances allowed for the determination of the wide ranges of compounds such as BTEX, polyaromatic hydrocarbons and chlorinated aliphatic and aromatic compounds. The limited number of investigations on analysis of hazardous substances in leachate from landfills of different ages makes the determination of their changes in time impossible. There is a need for advanced investigations on toxic compounds removal in leachate treatment systems, and leachate toxicity as well.

The design of a treatment plant for leachate should first be considered after their total quantitative and qualitative diagnosis. Organics removal in biological systems depends on reactor type, retention time of leachate and sludge age. The removal of ammonia from leachate is currently practiced *ex situ*. However, mature leachate contains a relatively low concentration of degradable organic material but a high concentration of ammonia, so the N/COD ratio can change in a wide range from 0.0053 to 0.85. At unfavourable ratios external carbon sources (e.g. methanol) are used. However, the *ex situ* treatment of concentrated leachate can be difficult and costly.

Nitrogen removal at unfavorable C/N ratio is possible by simultaneous nitrification and denitrification. Using such systems as the Canon or Anammox processes needs further investigations owing to the still insufficient stability of the whole process.

The construction of leachate treatment plants at the landfill site, thus enabling nitrification in the leachate and subsequently its recirculation to the landfill, to be carried out, seems to be appropriate trend to *in situ* nitrogen removal form leachate.

The development of an *in situ* removal technique can be also an attractive alternative. Landfill bioreactors are a new trend in waste management in which *in situ* conditions are controlled by adding moisture by leachate circulation and/or air.

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Management of Pollutant Emission from Landfills and Sludge – Pawłowska & Pawłowski (eds)

Landfill leachate treatment at a pilot plant using hydrophyte systems

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ABSTRACT: Constructed wetlands can provide an effective and economical solution to landfill leachate treatment. In this report the performance of a CW for leachate treatment, consisting of two horizontal flow constructed wetlands (HF-CW) beds, working at the municipal landfill in Gdansk-Szadolki in the period 2004–2005 is discussed. The plant has been operating since 2001. Clogging problems and surface flow occurred in the system because of insufficient hydraulic conductivity of the filter bed material. Neither the treatment efficiency nor effluent pollutant concentrations meet the design criteria, though quite high efficiencies of PAH (over 70% for both beds), N_{tot} and N-NH_4 (61.7% for bed I and 51.6% for bed II) removal are obtained. The depletion of total alkalinity and pH increase confirm that a/the nitrification process took place in the beds.

Keywords: Constructed wetlands, landfill leachate, treatment, hydraulics.

1 INTRODUCTION

Treatment of landfill leachate has recently become one of the most important environmental problems. The reasons for this are fluctuating composition and quantity of the leachate as well as high concentrations of specific pollutants (PAH, AOX, PCB, heavy metals) and very high ammonia nitrogen and COD concentrations. Discharging leachate to municipal WWTPs is usually expensive and results in destabilization of biological treatment processes. Also, the on-site treatment plants constructed at the landfills, using highly effective treatment methods, require very high financial expenditures, both during construction and operation. Thus, natural treatment systems for landfill leachate treatment using hydrophyte plants are gaining popularity. Hydrophyte treatment systems have the potential to remove micropollutants present in the leachate as well as heavy metals. Roots of emergent macrophytes, like *Phragmites australis*, grow in an anaerobic environment and thus are capable of tolerating low oxygen concentrations, elevated concentrations of iron and manganese, as well as organic acids and other breakdown products of organic matter (Peverly et al., 1995). Many authors also report the capability of emergent macrophytes to take up heavy metals (Hawkins et al., 1997; Crites et al., 1997; Vymazal, 2003; Karathanasis and Johnson, 2003; Weis et al., 2004; Obarska-Pempkowiak et al., 2005). According to Peverly et al., (1995) *P. australis* grows well in the presence of high concentrations of N-NH_4^+ (300 mg/l), BOD (300 mg/l), Fe (30 mg/l), Mn (1.5 mg/l) and K (500 mg/l).

In the recent years several constructed wetlands (CWs) for leachate treatment were constructed in Europe and the USA, though the use of constructed wetlands is still in the development stage (Maehlum, 1995; Peverly et al. 1995; Kowalik et al., 1996; Bulc et al., 1997; Martin et al., 1999; Kadlec, 2003). The benefits of CWs application are low costs, simple and inexpensive operation and maintenance as well as good treatment efficiency.

In the article the hydraulics and treatment performance of a CW for the landfill leachate treatment plant at Szadolki near Gdansk is discussed.

2 MATERIALS AND METHODS

A constructed wetland for leachate treatment was built at the municipal landfill in Gdansk-Szadolki in 2001. It consists of two parallel HF-CW beds (subsurface, horizontal flow of sewage) (Fig. 1). The area of each bed is 50 × 50 m and the depth –0.6 m. The beds were inhabited with common reed (*Phragmites australis*).

According to the design project the leachate treated in the beds ought to be discharged to Kozacki Stream flowing through the landfill area. However, since the efficiency of treatment is below expectations, the leachate is recirculated to one of the landfill's compartments.

In 2004 and 2005 seven series of analyses of pollutant concentrations in the leachate were performed. Leachate samples were collected at the inflow to the CW system and at the outflow of each of two beds and the efficiencies of pollutants removal were

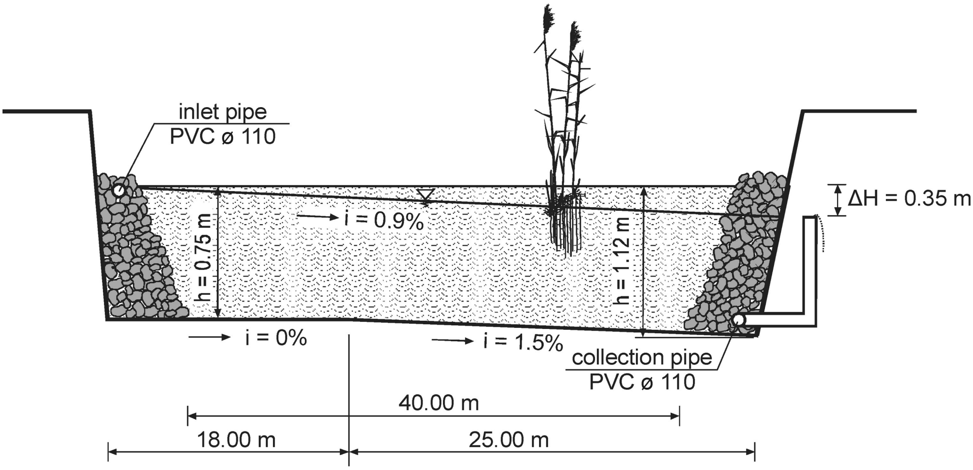

Figure 1. Cross section of constructed wetland at Szadolki.

calculated. The concentrations of the following pollutants were measured: TSS, BOD_5, COD_{Cr}, $N\text{-}NH_4$, N_{tot}, TOC, PAH, total alkalinity, Fe and Mn. The analyses were performed according to Polish Standard Methods. Based on the pump capacity and its working period the quantity of leachate waters from the landfill area in the period 2002–2005 was evaluated.

In November 2004 granulometric analyses of filtration beds media and permeability coefficients were performed. Two types of soil samples were collected from randomly chosen sampling points at the beds I and II: the disturbed-structure samples for grain size analyses (from the depth below 30 cm) and the undisturbed-structure samples for the measurement of the permeability coefficient (from the depth 30–40 cm). The analyses were carried out at the laboratory of Geotechnics Department of the Gdansk University of Technology, according to Polish Norm PN-88/B-0481 Construction soils – soil samples analyses. Permeability coefficients were measured with the apparatus ITB-ZWk2.

3 RESULTS AND DISCUSSION

3.1 *The hydraulics of beds*

The CW plant at Szadolki was designed according to the guidelines of Kickuth (1981) who recommended fine-grained soils as filter bed materials. Kickuth was convinced that the initial low hydraulic conductivity of the medium would increase due to root penetration. Unfortunately, in many CWs built in the 1980s, where this approach was applied, clogging of the beds occurred. This resulted in surface flow of sewage and deterioration of treatment efficiency (Brix and Schierup, 1989). Hence medium and coarse sands are currently considered to be the better filter bed materials (Peverly et al., 1995).

Also in the CW Szadolki clogging took place at both beds resulting in flooding and surface flow of leachate. Since the design criteria for the surface flow beds are different than for subsurface flow ones, the expected treatment efficiency was not achieved. Moreover, *P. australis* started to die off due to permanent flooding, so the chance for hydraulic conductivity improvement due to root penetration vanished. It was determined that the quantity of leachate from the landfill area varied from 6 to 240 m^3/day.

In the design project of the CW system at Szadolki neither the grain size nor permeability coefficient were defined.

Since the grain size distribution was considered to be the main reason for the beds flooding, granulometric analyses and permeability coefficient measurements were undertaken. The results of soil analyses are presented in Table 1.

Permeability coefficients of both beds were very low in comparison to the recommended values (International Water Association Specialist Group on The Use of Macrophytes in Water Pollution Control, 2000; Reed et al., 1995).

Based on the results of filtration medium analyses, the hydraulic conductivity of the beds I and II in Szadolki was calculated from the law of mass conservation and the Darcy law:

$$Q_S = F \cdot v$$
$$v = k \cdot I$$

where:
Q_S – flow rate [m^3/s]
F – the cross-section area of the bed perpendicular to the flow direction [m^2]

Table 1. The results of filtration medium analyses from CW Szadolki.

		Bed I			Bed II		
		Sample number			Sample number		
Parameter	Unit	A20	B20	C30	D30	E30	F30
The depth of sample collection	cm	20–30	20–30	30–40	30–40	30–40	30–40
Effective grain size	mm	0.0011	0.0007	0.0024	0.0016	0.001	0.0012
Coefficient of graining non-uniformity $U = d_{60}/d_{10}$	–	449	583	174	252	694	356
Permeability coefficient	m/s	$k_{10} = 5.77 \cdot 10^{-5}$ m/s			$k_{10} = 2.55 \cdot 10^{-5}$ m/s		
	m/d	$k_{10} = 4.98$ m/d			$k_{10} = 2.20$ m/d		

v – flow velocity [m/s]
k – permeability coefficient [m/s]
$I = \Delta H/L$, hydraulic gradient [-].

$$F = h \cdot W$$

where:
h – bed depth [m]
W – bed width [m]

Then the flow rate for each of the beds is equal to:

$$Q_S = F \cdot v = h \cdot W \cdot k \cdot I = h \cdot W \cdot k \cdot \Delta H/L$$

The geometrical parameters of the beds (depth, width, length, etc.) are given in the Fig. 2. The values of permeability coefficients for the beds I and II are given in Table 1.

The calculated flow rates are 0.527 m^3/d for bed I and 1.193 m^3/d for bed II. The total hydraulic capacity of the CW system (the sum of flow rates of both beds) is equal to 1.72 m^3/d. In contrast, the hydraulic loading of the beds, evaluated based on the pump capacity and pump working period for the years 2002–2004, varied from 6 to 240 m^3/d. The hydraulic capacity of the beds is very small in comparison to the hydraulic loading of the beds, which resulted in surface flow of sewage and flooding of the beds.

The minimal permeability coefficient enabling the subsurface flow of leachate was calculated from the formula:

$$k = \frac{Q_S \cdot L}{h \cdot W \cdot \Delta h}$$

The minimal effective grain size assuring the re-quired permeability coefficient was calculated from the Hazen equation:

$$k = \frac{(d_{10})^2}{100}$$

where: k[m/s], d_{10}[mm]

on the condition that the coefficient of grain non-uniformity:

$$U = \frac{d_{60}}{d_{10}} \leq 5$$

The minimal permeability coefficients and corresponding effective grain sizes calculated for three different hydraulic loadings Q_s are given in Table 2.

3.2 *Treatment efficiency*

The quality of leachate discharged to the CW at Szadolki is presented in Table 3. The landfill leachate discharged to the analysed reed beds contained from 63.2 to 380 mg/l suspended solids (average 150.3 mg/l). The pH of leachate was stable and varied from 7.4 to 7.5. The concentration of BOD_5 fluctuated from 41 to 2118.5 mg O_2/dm^3 (average 792.375 mg O_2/l).

The TOC varied from 181.0 to 621.9 mg/l (average 410.5 ± 221.0 mg/l) and COD from 503 to 4380.2 mg O_2/l (average 1615.8 ± 1645.1 mg O_2/l). The high COD/BOD_5 ratio (the average value 2.2) indicated that, in comparison to domestic sewage, the leachate contained higher concentrations of refractive substances that cannot be biochemically decomposed.

The concentrations of toxic heavy metals (Cu, Pb, Cd and Cr) were quite low – slightly above the detection level, so the potential environmental hazard is minimal. Among the analysed metals only the Fe concentrations were high. High concentrations of Fe probably contributed to the beds clogging. The analyses indicated the presence of PAH in concentrations from 238.0 to 2680 ng/dm^3 (average 1127.3 ng/l). The analysed leachate also contained high concentrations of nitrogen, mainly N-NH_4^+ ions (average 301.8 mg N/l). The chloride concentration was very high (748.9 mg/l), which was the most probable reason of *P. australis* die off (Sim et al., 2006; Howard & Rafferty, 2006).

The leachate composition was very unstable, a fact indicated by the very high standard deviation values and large differences between the minimal and maximal values. The most unstable parameters were BOD_5, COD, TOC, TSS, $N\text{-}NH_4^+$ and PAH.

The reed beds I and II applied for landfill leachate treatment significantly differed in treatment efficiency. The bed I more effectively removed organic substances and nitrogen compounds, while the bed II achieved higher efficiency of iron and manganese removal.

High efficiency of PAH removal was observed – over 70% at both beds (Fig. 3). Also the N_{tot} and $N\text{-}NH_4^+$ removal efficiency at the bed I was high, though at the bed II it was lower. The decrease of N_{tot} and $N\text{-}NH_4^+$ concentrations as well as the decrease of total

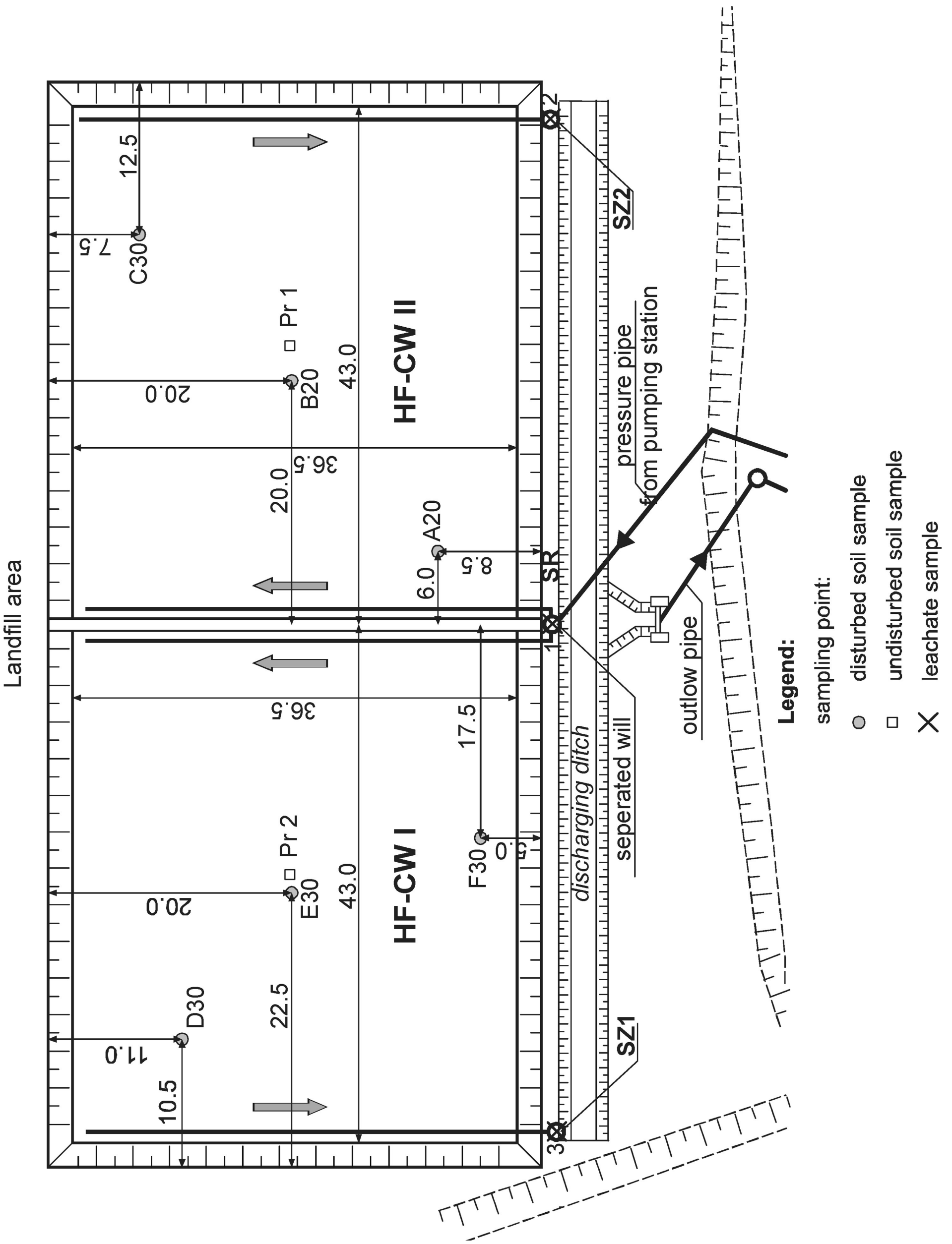

Figure 2. The scheme of HF-CW for municipal landfill leachate in Szadolki.

alkalinity and pH in the effluent indicate nitrification process took place.

The additional tank at the beginning of treatment process would enable qualitative and quantitative averaging of the unstable discharge of the leachate.

The reed beds I and II applied for landfill leachate treatment differed significantly in treatment efficiency. Bed I removed organic substances and nitrogen compounds more effectively, while the bed II achieved higher efficiency of iron and manganese removal.

High efficiency of PAH removal was observed – over 70% at both beds (Fig. 3). Also the N_{tot} and $N\text{-}NH_4^+$ removal efficiency in the bed I was high, though in the bed II it was lower. The decrease of N_{tot} and $N\text{-}NH_4^+$ concentrations as well as the decrease of total alkalinity and pH in the effluent indicate that nitrification took place.

The efficiency of organic substance removal (especially COD) in CW Szadolki was low in comparison to other CW for leachate treatment. Maehlum (1995) reported the BOD5 and COD removal efficiencies in the plant at Esval (Norway) of 91% and 88%, respectively. Also TOC removal efficiency was high (71%). Iron was removed at 88%. The CW in Esval had similar construction to CW Szadolki (two HF-CW beds working in parallel), but in Esval the leachate was pretreated in an aeration lagoon and the effluent of HF-CW beds was polished in a surface flow bed. The major difference between Esval and Szadolki was the filter bed material – in Esval gravel (10–20 mm diameter) was used. The treatment plant in Esval works in a cold climate (average February temperature −12°C), thus it should be possible to achieve similar treatment efficiencies in Poland, if the CW is properly designed.

Table 2. The minimal permeability coefficients enabling the subsurface flow of leachate and the corresponding minimal effective grain size d_{10} calculated for different hydraulic loadings.

Hydraulic loading Q [m^3/d]	Minimal permeability coefficient k [m/s]	Minimal effective grain size d_{10} [mm]
50	$1.2 \cdot 10^{-3}$	0.35
100	$2.4 \cdot 10^{-3}$	0.50
200	$4.8 \cdot 10^{-3}$	0.70

Other literature reports confirm that pollutant removal efficiencies (especially organic substances) can be significantly higher than in CW Szadolki. In Dragonja (Slovenia) removal efficiencies of COD, BOD5, ammonia nitrogen and iron were as follows: 68%, 46%, 81% and 80%, respectively (Bulc et al., 1997).The quality of treated leachate discharged to the surface water ought to meet the same standards as treated wastewater. According to the Polish Environment Department Regulation of the 8th July 2004, the demands for the treatment plant's effluent quality depend on the size of the plant (the person equivalent PE). The flow in Szadolki places this plant in the range below 2000 PE (the limits: BOD_5 –40 mg O_2/dm^3, COD –150 mg O_2/dm^3, TSS –50 mg/dm^3; the concentrations of the total N and P are limited only if the sewage is discharged to the lakes or artificial retention tanks). The effluent from the CW Szadolki did not meet these demands (the average BOD_5 –350 mg O_2/dm^3, COD –1044 mg O_2/dm^3, TSS – 176 mg/dm^3).

Table 3. The quality of leachate discharged to the CW treatment plant Szadolki.

Parameter	Average (for 7 analyses) ± standard deviation		Maximum	Minimum
TSS [mg/l]	150.3	± 134.05	380	63.2
BOD_5 [mg O_2/l]	792.4	± 968.92	2118.5	41
COD_{Cr} [mg O_2/l]	1615.8	± 1645.06	4380.2	503
TOC [mg/l]	410.5	± 221.01	621.9	181
$N\text{-}NH_4^+$ [mg/l]	301.8	± 205.69	523	40.3
N_{tot} [mg/l]	432.7	± 92.45	551	342
$P\text{-}PO_4^{3-}$ [mg/l]	1.8	± 1.47	2.73	0.11
PAH [ng/l]	1127.3	± 1349.39	2680	238
Chlorides [mg/l]	748.9	± 162.61	922	531.8
Total alkalinity [mval/l]	57.9	± 13.46	71.7	39.5
SO_4^{2-} [mg/l]	34.6	± 34.05	72	5.4
Fe [mg/l]	22.6	± 13.95	38.12	11.17
Mn [mg/l]	0.98	± 0.69	1.76	0.42
Cu [mg/l]	0.2	± 0	0.2	0.2
Pb [mg/l]	0.3	± 0	0.3	0.3
Cd [mg/l]	0.1	± 0	0.1	0.1
Hg [mg/l]	0.001	± 0	0.001	0.001

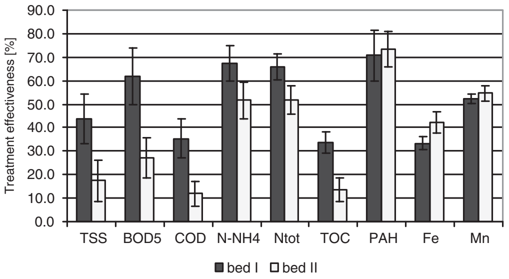

Figure 3. Average treatment efficiency with SD – bed I and bed II.

Therefore the treated leachate could not be discharged to the receipient (Kozacki Stream) but was recirculated to one of the landfill's compartments.

4 CONCLUSIONS

The quality of leachate inflowing to the CW Szadolki is very unstable. An additional tank at the beginning of the treatment process would enable qualitative and quantitative averaging of the unstable discharge of the leachate. The CW for leachate treatment in Szadolki provides quite good treatment efficiencies of BOD_5 (bed I), PAH, N_{tot} and $N\text{-}NH_4^+$. Treatment efficiencies of other parameters were much lower than reported for other landfill leachate treatment CW systems. The reason for this was clogging and flooding of the beds as well as *P. australis* die off in response to high salinity of treated leachate. Operational problems leading to decreased treatment efficiency are due to low hydraulic conductivity of the beds. Also lack of preliminary removal of Fe contributes to the clogging of beds.

In spite of the unsatisfactory treatment results obtained in the CW Szadolki, constructed wetlands have potential to provide an effective and economical solution to landfill leachate treatment if they are properly designed and operated.

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Management of Pollutant Emission from Landfills and Sludge – Pawłowska & Pawłowski (eds)

Deammonification in an aerobic Rotating Biological Contactor (RBC)

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ABSTRACT: Leachate from landfills is a highly complex polluted wastewater. Landfill leachate with a high concentration of ammonium nitrogen is generally difficult to treat, efficiently. Furthermore, it can be very expensive when there is lack of an easily biodegradable carbon source. Combination of the nitrification/denitrification with the Anammox process can be a very attractive alternative. For the purpose of this study, a Rotating Biological Contactor (RBC) was used. The main objective of the research was to investigate the performance of the Anammox process that occurs together with heterotrophic denitrification in the same RBC. During the operation period, the acclimation of biofilm to the Anammox process was successful at temperature not exceeding 20°C. Apparently, the process was not affected by a high concentration of nitrite up to 100 g NO_2-N m^{-3}. Additionally, it was shown that the Stover-Kincannon model could be used for description of the ammonium and nitrite removal rates.

Keywords: Anammox, biofilm, denitrification, leachate, nitrification, nitrogen removal.

1 INTRODUCTION

In Europe the number of permitted or legal landfills appears to have declined because of the implementation of the EU Landfill Directive (1999/31/EC) (Kohler N. & Perry 2005). Nevertheless, landfilling using municipal waste is still a very important issue in the waste management system in Europe and the rest of the world.

One of the major aspects associated with landfilling of solid wastes is related to the discharge of leachate into the environment. Leachate from landfills is a highly polluted and complex wastewater containing high concentrations of ammonia nitrogen, organic materials and inorganic contaminants such as heavy metals and inorganic salts. The composition of leachate from municipal landfill depends on waste composition and age, landfill surface, landfill operation and climatic conditions. As a consequence, leachate composition is highly affected by waste characteristics and local conditions (Borzacconi et al. 1999). This pollution is also a result of biological, chemical and physical processes occurring in the landfill. According to the Landfill Directive, it is necessary to treat contaminated water and leachate collected from the landfill to the appropriate standard required for their discharge. The common solution of treating leachate together with municipal sewage in the municipal sewage treatment plant has been questioned due to the effects of leachate on the biological sewage treatment process. It has been indicated that inhibitory compounds in the leachate may disturb the biological sewage treatment process (Welander et al. 1997). Technologies intended for leachate treatment can be classified as follows (i) biological methods, (ii) chemical and physical methods. However, taking into account the changing nature of leachate and, in order to meet strict quality standards for direct discharge of leachate into surface water, the development of integrated methods of treatment, i.e. a combination of chemical, physical and biological steps, is required (Wiszniowski et al. 2006).

Since municipal solid wastes contain about 4% proteins (Price et al. 2003), ammonia nitrogen is produced during the decomposition of organic nitrogen. Treatment of leachate to remove ammonium nitrogen is an important aspect of leachate management. Physical/chemical or biological processes can be used to remove ammonia. However, physical/chemical processes have several disadvantages like odor, air pollution, high cost of chemicals (Bae et al. 1997). Biological methods are the simplest and cheapest way to treat such wastewater. However, landfill leachates with high concentrations of ammonium

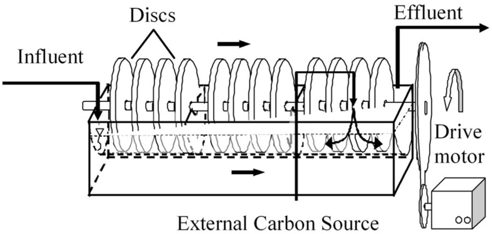

Figure 1. Flow scheme of the RBC.

Table 1. Characteristics of the rotating biological contactor.

Parameter	Value
No. of stages	3
No. of discs per stage	4
Total number of discs	12
Disc diameter [m]	0.225
Total surface area available for growth [m^2]	2.61
Disc submergence [%]	41
Liquid volume [m^3]	0.014
Volume-disc area ratio [m^3 m^{-2}]	5.36

nitrogen are generally difficult to treat efficiently. Furthermore, it can be very expensive when easily biodegradable carbon is not available. Interest in finding new solutions and improving existing technologies is growing rapidly. A combination of the classical nitrification/denitrification with the Anammox process may be a very attractive alternative for such wastewater.

The aim of the presented research was to investigate biological nitrogen removal from landfill leachate via a combination of nitrification/denitrification with the Anammox process in a rotating biological contactor.

2 MATERIALS AND METHODS

A lab-scale rotating biological contactor (RBC) with partially immersed discs was used. The RBC consisted of three equally sized stages. For each stage there were four discs fixed to the centre shaft. The effective disc area in each stage was 0.87 m^2 and the disc submergence was 41%, providing a volume-disc area ratio of 5.36 m^3 m^{-2}. A developed surface area for biofilm was provided with doormat (PE) fixed to discs. The discs rotated into wastewater and air alternately, and that way the biofilm sorbed pollutants and was aerated. The RBC unit was covered by polystyrene foam to prevent the growth of algae by light exclusion. The scheme of the RBC is shown in Figure 1 and the design characteristics of the RBC are listed in Table 1.

Table 2. Characteristics of the inflow leachate.

Parameter	unit	max	min	av	st. dev.
NH_4-N	g m^{-3}	658.8	176.0	421,0	148,8
NO_2-N	g m^{-3}	830,0	215,4	524,1	181.0
NO_3-N	g m^{-3}	109,5	0	42,8	25,0
COD	g m^{-3}	1700	200	669,3	298,0
pH	–	8,6	7,0	8,1	0,4

The contactor was fed with landfill leachate from the municipal landfill in Gliwice (Poland). The composition of the leachate after the AS reactor was adjusted with $NaNO_2$ and NH_4Cl in order to reach an nitrite-to-ammonium ratio of 1.32:1 (Strous et al. 1998). The characteristics of the inflow is presented in Table 2.

Nitrogen loading rates applied to the first stage of the RBC were gradually increased from 3 to 6 g N m^{-2}d^{-1}. Three research periods can be differentiated based on the increasing nitrogen concentration in the influent (period I: day 1 to 36; period II: day 36 to 91; period III: day 91 to 176). Additionally, an appropriate dose of sodium bicarbonate $NaHCO_3$ was added to neutralize the alkalinity decrease during the nitrification process. Glucose, as an external carbon source, was introduced in the third part of the contactor in order to denitrify nitrites and nitrates after the nitrification and Anammox process. During the research, samples were collected from the influent, effluent and each stage of the contactor twice per week. The efficiency of the biological treatment was followed in terms of the general parameters such as: COD (dichromate method), ammonia (Kjeltec System 1026 Tecator), nitrite, and nitrate. Moreover, the process was monitored by measuring other parameters: flow rate, pH, temperature and dissolved oxygen (DO). No specific heating was applied and the temperature was kept constant at 17 ± 2.4°C.

2.1 *Denitrifying bacteria analysis*

Material used for microbiological analysis was collected from three stages of the contactor. Two 10 g samples of biofilm were prepared from each stage. One of them was used for determination of dry mass. The second sample was inserted into Erlenmeyer flask containing 90 ml of 0.85% NaCl and then was vigorously shaken on the rotary shaker for 15 min. Afterwards the sample was left for 2 min. to allow sedimentation of large particles and was then used for preparing various dilutions. Suspensions prepared in this way were used for isolation of denitrifying bacteria. For titer determination of denitrifying bacteria liquid Giltay medium was used. Inoculated samples were incubated at 26°C for 48 hours. After incubation from positive samples 0.1 ml of inoculum was taken and transferred onto nutrient agar plates for isolation of pure denitrifying

Table 3. List and description of probes used for the analysis.

Probe	Target organisms	Probe sequence	Target site	%FA	Ref.
NEU	Most halophilic and halotolerant Nitrosomonas spp.	CCC CTC TGC TGC ACT CTA	653–670	40	1
CTE-competitor NEU		TTC CAT CCC CCT CTG CCG	653–670		1
Claster 6a192	Nitrosomonas oligotropha lineage	CTT TCG ATC CCC TAC TTT CC	192–211	35	2
Competitor claster 6a192		CTT TCG ATC CCC TGC TTC C	192–211		2
Ntspa662	Genus Nitrospira	GGA ATT CCG CGC TCC TCT	662–679	35	3
Competitor Ntspa662		GGA ATT CCG CTC TCC TCT	662–679		3
NIT3	Nitrobacter spp.	CCT GTG CTC CAT GCT CCG	1035–1052	40	4
Competitor NIT3		CCT GTG CTC CAG GCT CCG	1035–1052		4
EUB338	Most Bacteria	GCT GCC TCC CGT AGG AGT	338–355	35	5
EUB338 II	Planctomycetales	GCA GCC ACC CGT AGG TGT	338–355	35	6
EUB338 III	Verrucomicrobiales	GCT GCC ACC CGT AGG TGT	338–355	35	6
Pla46	Planctomycetales	GAC TTG CAT GCC TAA TCC	46–63	30	7
Amx820	anaerobic ammonium-oxidizing Bacteria, Candidatus 'Brocadia anammoxidans' and Candidatus 'Kuenenia stuttgartiensis'	AAA ACC CCT CTA CTT AGT GCC C	820–841	40	8

Ref: 1 – Wagner et al., 1995, 2 – Adamczyk et al., 2003, 3 – Daims et al., 1996, 4 – Wagner et al., 1996, 5 – Amann et al., 1990, 6 – Daims et al., 1999, 7 – Neef et al., 1998, 8 – Schmid et al., 2001.

bacteria cultures. Inoculated plates were incubated at 26°C for 48 hours. After incubation, single cultures of bacteria were isolated and purified on Petri dishes with nutrient agar. Pure strains were used for inoculation of the liquid Giltay medium to recheck their ability for denitrification and their morphology, Gram reaction and oxidase reaction were determined. For identification of oxidase-positive bacteria strains API 20 NE (standardized system for non-enteric bacteria strains) was used and for oxidase-negative bacteria strains API 20 E (standardized system for enteric bacteria strains).

2.2 *FISH – Fluorescent in situ Hybridization*

Detached biofilm samples were fixed with paraformaldehyde solution (4% paraformaldehyde in phosphate-buffered saline (PBS), pH 7.2) at 4°C for 3 hours and washed subsequently in PBS. Fixed samples were stored in PBS: ethanol (1:1) solution at −20°C. *In situ* hybridization was performed as described previously by (Daims et al. 2005). 16S rRNA targeted fluorescence labelled oligonucleotide probes; the sequences and targeted sites are listed in Table 3.

The probes EUB338, EUB338 II and EUB338 III were mixed together (EUB338 mix) in proportion 1:1:1 in order to detect all bacteria.

The probes, chosen from the probeBase database (Loy et al. 2003), were 5′ labeled with the dye FLUOS (5(6)-carboxyfluorescein-*N*-hydroxysuccinimide ester), Cy3 or Cy5. Both the probes and unlabeled competitor oligonucleotides were obtained from Biomers, Ulm, Germany.

Prior to microscope observations samples were embedded in Citifluor (Citifluor Ltd, UK) to reduce the fluorochrome fading (bleaching). A scanning confocal microscope (Zeiss LSM 510) equipped with an Ar-ion laser (488 nm) and two HeNeLasers (543 nm and 633 nm) were used to examine the microbial community. Image processing was performed using the standard software package delivered with the instrument (Zeiss LSM version 3.95).

3 RESULTS AND DISCUSSION

The RBC was run for six months at 17 ± 2.4°C which was much lower than the optimum temperature of 37°C reported for the Anammox process (Schmidt et al. 2003). However, Siegrist et al. (1998) observed a significant nitrogen loss (ranging from 27 to 68%) in RBC during the treatment of stabilised leachate at temperatures ranging from 15 to 20°C, but they were not sure whether it resulted from the Anammox process or from autotrophic denitrification.

An average nitrite-to-ammonium ratio in the influent amounted to 1.29:1 ensuring the Anammox reaction. The inorganic nitrogen removal efficiency in the first stage of the contactor was 58 ± 17% on average during the whole operating time and it was comparable during subsequent periods I, II and III (58, 55 and

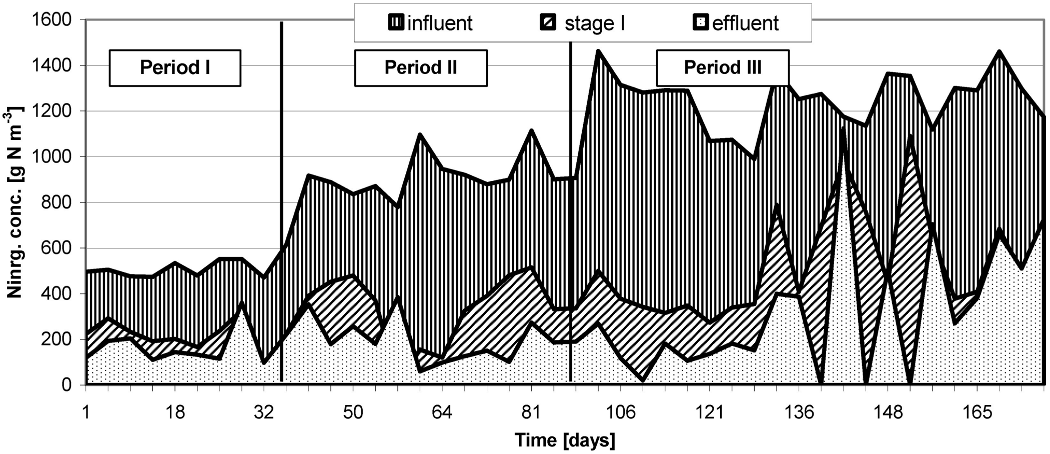

Figure 2. Inorganic nitrogen removal in RBC.

57% respectively) (Figure 2). This indicates that the nitrogen removal efficiency was independent of the nitrogen load in the applied range. Most probably the Anammox process was the main cause of nitrogen removal. Some conditions were particularly conducive to Anammox occurrence, namely: (i) the presence of nitrite and ammonia in an optimal ratio, (ii) long period of system operation, (iii) efficient biomass retention (biofilm system), (iv) unfavourable biodegradable organic carbon to nitrogen ratio ($COD_{eli}/N_{eli,inorg}$ amounting to 0.8 on average) for heterotrophic denitrification.

The process of nitrogen removal predominated in the first stage of the contactor, providing 88 and 95% ammonium and nitrite nitrogen removal, respectively during the whole period of operation. The ammonium, nitrite and inorganic nitrogen removal efficiencies in the first stage of the RBC unit are shown in Figure 3A.

The maximum ammonium and nitrite removal rates were 3.0 and 3.9 g N $m^{-2}d^{-1}$, respectively (0.56 and 0.73 kg N $m^{-3}d^{-1}$, respectively). The maximum inorganic nitrogen removal rates were 5.8 g N $m^{-2}d^{-1}$ (0.93 kg N $m^{-3}d^{-1}$) with an average value of 2.8 g N $m^{-2}d^{-1}$. In Figure 3B an example of nitrogen profiles in the RBC unit in period I (day 18), period II (day 53) and period III (day 116) are shown. The aeration of treated medium resulted in the DO concentration amounting to 2.6 ± 0.7 g O_2 m^{-3} in the first stage of the contactor. In the second stage the DO concentration rose to 4.8 ± 0.9 g O_2 m^{-3} probably as a result of earlier consumption of substrates for nitrification in the first stage and there was no reaction in the second stage of the contactor. The aerobic conditions, in stage I, were conducive to nitrification proceeding in the system, and resulted in nitrate production amounting to 50% of nitrogen inflow. According to the stoichiometry of the Anammox reaction (Strous et al. 1998), nitrate production should be equal to 11% of nitrogen inflow, and the difference was caused by presence of nitrite oxidizers in the biofilm. *Nitrobacter* and *Nitrospira* were the species responsible for oxidation of nitrite to nitrate and they competed for substrate with the Anammox bacteria. The average ratio of nitrite-to ammonium removal rates was equal to 1.4 and varied from 0.7 to 2.5, which was caused mainly by nitrifiers competing with the Anammox bacteria. The occurrence of nitrification is also confirmed by the drop in pH from 8.1 in the influent to 7.1 in stage I.

Between the 130th and the 150th day of the experiments, a temporary breakdown of the process performance was observed. It is difficult to explain, because no operating problem was noticed. It is conceivable that the Anammox bacteria are inhibited (reversibly) if exposed to aerobic conditions (Schmidt et al. 2003). For two weeks before this breakdown, the ammonium concentration in stage I dropped to much below 20 g NH_4-N m^{-3}; this could lead to the process inhibition due to the deeper penetration of oxygen into the biofilm. This phenomenon was also observed by Siegrist et al. (1998). It could be also caused by the increase of nitrite nitrogen up to 90 g m^{-3} on the 123rd day of the experiment, however, on the contrary high peaks of nitrite concentration on the 67th and 71st days (around 90 g m^{-3}) did not cause such problems. According to Schmidt and co-workers (2003) the Anammox process is irreversibly inhibited by nitrite at concentrations exceeding 70 g N m^{-3} for several days. This could mean that the process is insensitive to short-term high nitrite concentrations in the reactor (even up to 100 g NO_2-N m^{-3} for several hours). It resulted in only a temporary decrease of nitrogen removal rates. Therefore, the breakdown of the process efficiency could be due to the overlap of these two phenomena: deeper oxygen penetration into the

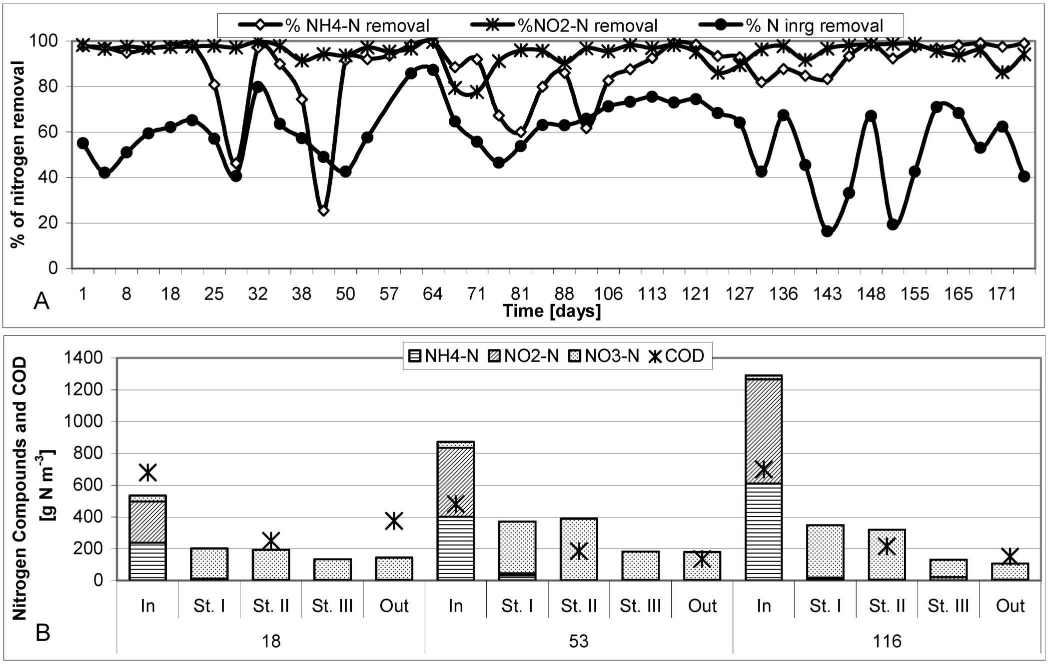

Figure 3. A) Ammonium, nitrite and inorganic nitrogen removal efficiency in the first stage of the RBC B) Example of nitrogen profile in the RBC (days: 18, 53 and 116).

Table 4. Identified nitrifiers and Anammox bacteria.

	Nitrosomonas oligotropha lineage	Most halophilic and halotolerant Nitrosomonas spp.	Nitrobacter spp.	Genus Nitrospira	Anaerobic ammonium-oxidizing bacteria, Candidatus 'Brocadia anammoxidans' and Candidatus 'Kuenenia stuttgartiensis'
Stage I	−	+ + +	++	+ + +	+ + +
Stage II	+	++	++	++	+
Stage III	+	+	−	+	−

scale: (−) – absence; (+) – few; (++) – middle; (+ + +) – high availability.

biofilm due to low ammonium concentration in the bulk liquid, as well as high nitrite concentration.

The final nitrogen removal was performed in the stage III of the RBC unit by using a supplementary biodegradable organic (glucose) as an external carbon source for denitrification. The average COD/N was equal 6.2 ± 0.7. The removal of nitrate entering the third stage of the contactor was 34% on average which corresponded to a nitrogen removal rate of $0.68\,\mathrm{g\ NO_3\text{-}N\,m^{-2}d^{-1}}$. The average efficiency of inorganic nitrogen removal achieved in the whole RBC was 77%.

Microbial analysis (FISH) confirmed the presence of nitrifiers in the biofilm (Table 4). The presence of the Anammox bacteria belonging to *Candidatus Brocadia anammoxidans* and/or *Candidatus Kuenenia stuttgatiensis* in the first two stages of the contactor was also proved, confirming the main role of the Anammox process in the nitrogen removal in the first stage of the RBC.

Referring to studies of Egli et al. (2003), it was proved that within the RBC biofilm depth, ammonium oxidizing bacteria are on the outer layer, and the Anammox bacteria were only detected in the lower part of the biofilm, defined by penetration depth of the oxygen into the biofilm.

Using commercial identification kits API 20NE and API 20E, in the biofilm from all three stages of

Table 5. Identified denitrifying bacteria strains.

Bacteria identified	Stage I	Stage II	Stage III
Acinetobacter calcoaceticus	+	−	−
Pseudomonas fluorescence	+	+	−
Alcaligenes xylodoxidans	+	−	−
Pseudomonas alcaligenes	−	++	−
Proteus vulgaris	−	+	−
Aeromonas salmonicida	−	−	++
Aeromonas hydrophila	−	−	++
Pseudomonas earuginosa	−	−	+
Shigella spp	−	−	+
Acinetobacter lwoffi	−	−	+

++ – Dominating strain

the reactor, the denitrifying bacteria strains have been identified (Table 5).

Microbial analysis in the stage I of RBC revealed the presence of denitrifying bacteria such as: *Acinetobacter calcoaceticus*, *Pseudomonas fluorescence* and *Alcaligenes xylodoxidans*, followed by: *Pseudomonas fluorescence*, *Pseudomonas alcaligenes*, *Proteus vulgaris* in stage II (Table 5). However, the biodegradable organic carbon to nitrogen ratio was unfavourable for heterotrophic denitrification. Therefore, heterotrophic denitrification could not be responsible for nitrogen removal in the first stage of the RBC. The presence of *Nitrosomonas* spp. in the biofilm suggested that part of the nitrogen loss could be also attributed to denitrifying Nitrosomonas cells located in the lower part of the biofilm. They could use ammonium as electron donors and nitrite as electron acceptor in case of oxygen lack. (Bock et al. 1995, Helmer & Kunst 1998).

The results confirmed presence of *Pseudomonas* considered as a species responsible for denitrification. It is in agreement with the recent results of Ju et al. (2005) who found that *Pseudomonas earuginosa* is able to denitrify under aerobic condition when DO concentration exceeded 1 g O_2 m^{-3}. Likewise, in an early observation, Bang et al. (1995) reported the presence of aerobic denitrification in the RBC reactor even when the DO concentration exceeded 3 g O_2 m^{-3} in the treated medium. *Aeromonas salmonicida, Aeromonas hydrophila* were the dominating denitrifying strains in the third stage of the contactor. They are Gram-negative, ubiquitous organisms. They are widespread in the mixed liquor of activated sludge plant when they are involved in the degradation of organic matter. They are known as incompletely denitrifying heterotrophic bacteria showing strong reduction of nitrates to nitrites (Drysdale et al. 1999). Moreover, some authors have observed that these bacteria preferred oxic conditions for growth but were still able to produce nitrites from nitrates reduction while simultaneously utilising oxygen as a final electron acceptor. The domination of denitrifiers responsible for partial denitrification of nitrates only to nitrites and the presence of nitrite oxidizers in the stage III may be an explanation of the low effeciency of nitrate removal. The average oxygen concentration in the bulk liquid was 3.0 ± 1.5 g O_2 m^{-3}; this created favourable conditions for nitrifiers that oxidized nitrites produced by Aeromonas spp.

Figure 4. Photos of the biofilm in the denitrification part of the RBS reactor.

Glucose appears to be the least efficient carbon source in comparison with the methanol and acetic acid used in previous research. Efficiencies of 83 to 97% in nitrogen removal respectively were achieved for the both organic carbon sources (unpublished data). Additionally, it seems that with glucose as an external carbon source, intensive biofilm growth accompanied nitrate reduction and aerobic degradation. In the third stage of the RBC very intensive growth was observed, and discs were completely covered with a white, fluffy biofilm (Figure 4)

Moreover, different denitrifying bacteria strains were noticed when methanol and acetic acid were applied (unpublished data). For biofilm fed with methanol the following bacteria strains have been identified: *Aeromonas hydrofilla*, *Aeromonas* salmonicida (dominating strain), Aeromonas mausoucida, Pseudomonas aeruginosa (dominating strain), Pseudomonas fluorescence and for biofilm fed alcaligenes and Aeromonas sorbia.

Additionally, analysis of data indicated that the Stover-Kincannon model described the process of ammonium and nitrite removal well for the first stage of the RBC, where nitrification and the Anammox process took place. The Stover-Kincannon with acetic acid: *Plesiomonas shigellides*, *Pseudomonas* model, for a rotating biological contactor, assumes that the suspended biomass is negligible in comparison to

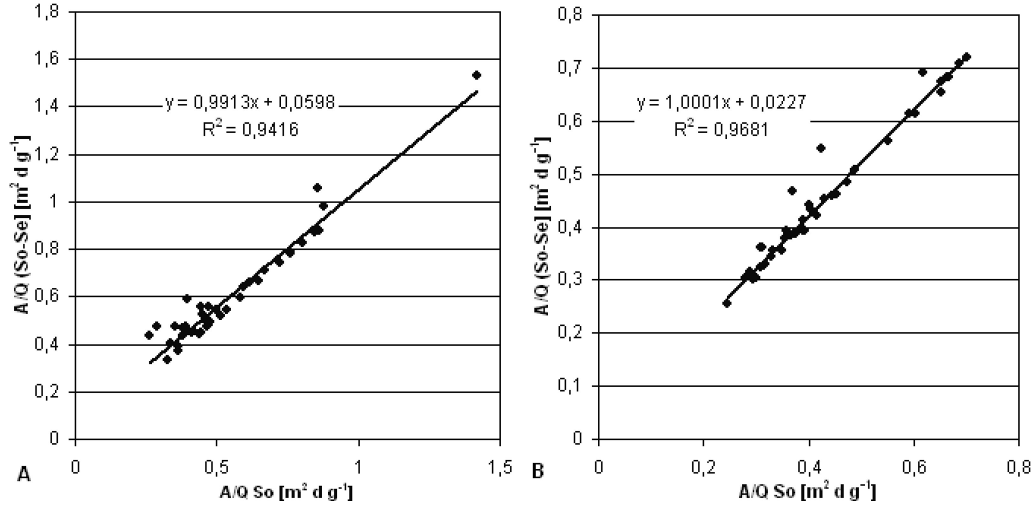

Figure 5. Stover-Kincannon plots for A) ammonium nitrogen and B) nitrite nitrogen.

the attached biomass and expression for the substrate removal rate is as follow (Wilson 1993; Ahn & Forster 2000):

$$r_A = \frac{U_{max}\dfrac{Q}{A}S_i}{K_B + \dfrac{Q}{A}S_i} \tag{1}$$

The equation 1st can be linearised as:

$$r_A^{-1} = \frac{K_B}{U_{max}} \cdot \frac{A}{QS_i} + \frac{1}{U_{max}} \tag{2}$$

where: r_A is the substrate utilization rate ($g\,m^{-2}d^{-1}$), S_i is the inflow substrate concentration ($g\,m^{-3}$), U_{max} is the maximum utilization rate constant ($g\,m^{-2}d^{-1}$), K_B saturation value constant ($g\,m^{-2}d^{-1}$), A is the surface area of the discs (m^2), Q is the inflow rate (m^3d^{-1}).

If r_A is taken as $A/(Q(S_i\text{-}S_e))$ (where S_e is the effluent substrate concentration ($g\,m^{-3}$)), which is the inverse of the load removal rate and this is plotted against the inverse of the total loading rate ($A/(Q\,S_i)$), K_B/U_{max} is the slope and $1/U_{max}$ is the intercept point of the straight line. The Stover-Kincannon plots for ammonium nitrogen in Figure 5A and for nitrite nitrogen are shown in Figure 5B.

From the plots shown in Figure 5A and 5B, the values of U_{max} and K_B were estimated as 16.72 and 16.58 g $N\,m^{-2}d^{-1}$ respectively for ammonium nitrogen and 44.05 and 44.06 g $N\,m^{-2}d^{-1}$, respectively for nitrite nitrogen in the first stage of the contactor where the nitrification and Anammox processes took place. However, it appeared that the Stover-Kincannon model was not appropriate for the process of the inorganic nitrogen removal (correlation coefficient $R = 0.62$). This suggested the existence of different enzyme systems acting in the nitrogen transformations. Probably the lower correlation was due to participation of other microorganisms in nitrogen conversion. For instance *Nitrosomonas is* able to deammonify and, perhaps to a small extent, heterotrophic denitrifiers able to use small amounts of biodegradable carbon in the influent.

The obtained maximum removal rates for ammonium and nitrite nitrogen in the first stage of the contactor were much lower than values obtained from the Stover-Kincannon model. This indicated that there is a possibility of attaining higher reaction rates for ammonium and nitrite removal, especially when both nitrogen forms were almost completely removed in the first stage of the RBC, and there was no reaction in the second stage of the contactor.

4 CONCLUSIONS

- Removal of total nitrogen has been achieved with a combination of different processes: nitrification, Anammox and heterotrophic denitrification processes in one RBC. Moreover, it is also possible that some part of nitrogen was removed due to autotrophic denitrification by *Nitrosomonas spp.*,
- It was possible to obtain the maximum removal rates for ammonium and nitrite nitrogen amounting to 3.0 g N $m^{-2}d^{-1}$ (0.56 kg N $m^{-3}d^{-1}$) and 3.9 g N $m^{-2}d^{-}1$ (0.76 kg N $m^{-3}d^{-1}$) respectively, moreover the maximum inorganic nitrogen removal rates (5.0 g N $m^{-2}d^{-1}$ (0.93 kg N $m^{-3}d^{-1}$)) has been achieved.
- It was shown that the Stover-Kincannon model can be used to describe the ammonium and nitrite removal rates in the RBC. The estimated values of

the maximum substrate utilization rates (16.72 and 44.05 for ammonium and nitrite nitrogen respectively) showed the possibility of a still higher nitrogen load to the RBC.

- It was proved that RBC with the Anammox process can be successfully operated even at temperatures below 20°C.
- The process was insensitive to short-term high nitrite concentrations in the reactor of up to 100 g NO_2-N m^{-3} for several hours.

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Treatment of nitrogen-rich streams originating from the dewatering of digested sludge

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ABSTRACT: This paper provides a review of novel approaches to the treatment of nitrogen-rich streams originating from the dewatering of digested sludge. These internal flows are characterized by a very low flow rate, high temperatures and a high concentration of ammonium. Separate treatment of these internal flows significantly reduces the N-load to the main treatment plant. Nitrogen removal in side-stream processes thus offers considerable potential for the upgrading of WWTPs needing to meet stricter effluent standards. A number of innovative biologically-based treatment approaches have been developed in recent years for treating return liquors. This paper compares different biological alternatives for nitrogen removal in side streams, including processes which are based on the concept of bioaugmentation (the InNitri and BABE processes), partial nitrification (the SHARON and Anammox processes) or combined partial nitritation/Anammox deammonification. An overview of the most important microbiological conversions for nitrogen removal is also presented.

Keywords: Nitrogen-rich side-stream treatment, deammonification.

1 INTRODUCTION

An increasing awareness of the need for sustainable water management is resulting in efforts to reduce the load of nutrients discharged from wastewater treatment plants (WWTPs). More-stringent standards on effluents play a decisive role where the choice of the most appropriate technology for wastewater handling is concerned. One important factor having a negative effect on wastewater treatment in the biological nitrification/denitrification step is the recirculation of the nitrogen-rich stream originating from the dewatering of digested sludge. The internal reject waters involved are characterized by a very low flow rate (0.5–2% of the total for the WWTP) (Galí *et al.*, 2005), high temperatures (15–35°C) (Fux & Siegrist, 2004; van Loosdrecht & Salem, 2005), high organic content (1000–1300 g TOC m^{-3}) and a high concentration of ammonium (700–1000 g NH_4^+-N m^{-3}) (Dapena-Mora *et al.*, 2005). Nitrogen removal in side-stream processes thus offers considerable potential for the upgrading of WWTPs needing to meet stricter effluent standards. The treatment of internal-process flows reduces the N-load to the main stream of a WWTP significantly. It is with this prospect in view that a number of innovative biologically-based approaches to the treatment of return liquors have been developed in recent years.

This paper reviews the treatment approaches in question, and compares different biological alternatives for nitrogen removal from side streams. An overview of the most important microbiological conversions for nitrogen removal is also presented.

2 BIOCHEMICAL CONVERSION OF NITROGEN

The classical Biological Nitrogen Removal (BNR) process is performed in two sequential stages. The first is aerobic nitrification and takes place via two steps: oxidation of ammonium -the product of protein breakdown – over nitrite (nitritation) to nitrate (nitratation). The second stage – conversion of nitrate or nitrite to nitrogen gas – is anoxic denitrification, and requires the presence of an organic carbon source. During the BNR process, a negligible part of the ammonium is transformed to ammonia in the gaseous phase. Moreover, ammonia is partly used by activated sludge and biofilm bacteria and contributes to their biomass. No organisms oxidize ammonium directly to nitrate, which is to say that there are distinct groups of aerobic chemolithoautotrophic bacteria which either oxidize ammonium to nitrite or nitrite to nitrate. Each step is performed by different bacterial genera which use ammonia or nitrite as an energy source and molecular oxygen as an electron acceptor, while carbon dioxide is used as a carbon source. The most commonly recognized genus of bacteria that carries out ammonia oxidation is *Nitrosommonas*. However, the nitritation step is also capable of being carried out by: *Nitrosococcus*, *Nitrosolubus*, *Nitrosovibrio* and *Nitrosospira*. These ammonium oxidizers are genetically diverse, but related to each other in the β-subclass of the Proteobacteria. Nitrite oxidizers are phylogenetically more widespread than ammonium oxidizers. *Nitrospira*, *Nitrospina*, *Nitrococcus* and *Nitrocystis* are known to be involved in the nitritation step. However, the most important nitrite oxidizer genus is *Nitrobacter*, which is closely related genetically within the α-subclass of the Proteobacteria (Rittmann & McCarty, 2001; Teske *et al.*, 1994). Equations for the synthesis and oxidation of ammonium are as follows (Metcalf & Eddy, 1991):

$$55NH_4^+ + 76O_2 + 109HCO_3^- \rightarrow C_5H_7O_2N + 54NO_2^- + 104H_2CO_3 + 57H_2O \quad (1)$$

$$400NO_2^- + NH_4^+ + 4H_2CO_3 + HCO_3^- + 195O_2 \rightarrow C_5H_7O_2N + 3H_2O + 400NO_3^- \quad (2)$$

The overall synthesis and oxidation reaction in nitrification can be represented as follows:

$$NH_4^+ + 1.83O_2 + 1.98HCO_3^- \rightarrow 0.021C_5H_7O_2N + 0.98NO_3^- + 1.041H_2O + 1.88H_2CO_3 \quad (3)$$

Denitrification comprises the reduction of nitrate to nitrogen gas via the intermediates: nitrite, nitric oxide (NO) and nitrous oxide (N_2O). All steps are catalysed by several different reductases (Zumft, 1997). The oxidized nitrogen compounds (NO_2^- and NO_3^-) are reduced to gaseous dinitrogen by heterotrophic microorganisms that use nitrite and/or nitrate instead of oxygen as electron acceptors, and organic matter as carbon and energy source. Denitrifiers are common among the Gram-negative α and β classes of the Proteobacteria, including: *Pseudomonas*, *Micrococcus*, *Paracoccus*, *Thiobacillus* and *Alcaligenes*. Some Gram-positive bacteria (such as *Bacillus)* and a few halophilic Archaea (such as *Halobacterium*) are also capable todenitrify (Ahn, 2006). The combined equation for dissimilatory denitrification and synthesis using methanol as an electron donor is as follows:

$$NO_3^- + 1.08CH_3OH + 0.24H_2CO_3 \rightarrow 0.056C_5H_7O_2N + 0.47N_2 + 1.68H_2O + HCO_3^- \quad (4)$$

The denitrification process is engaged in by various chemoorganotrophic, lithoautotrophic and phototrophic bacteria and some fungi. Sludge digester effluent has a very unfavorable COD:N ratio for heterotrophic denitrification, and the addition of an external carbon source is required. However, a novel microbial process, in which ammonium is converted to nitrogen gas with nitrite as the electron acceptor provides for completely autotrophic nitrogen-removal, without external COD addition. Many of the different biochemical routes for nitrogen transformation to nitrogen gas are shown in Table 1. Examples of such biochemical reactions are: aerobic denitrification, heterotrophic nitrification, anaerobic ammonium oxidation or denitrification by autotrophic nitrifying bacteria.

The detection of new organisms responsible for nitrogen removal is introducing considerable complications into depictions of the N-cycle. The nitrogen web from the conventional N-cycle (entailing N-fixation, nitrification and denitrification) through nitrite as an intermediate, anaerobic ammonium oxidation to Anammox process is shown in Fig. 1 (Jetten, 2001; van Loosdrecht, 2004). During nitrification ammonium oxidation to hydroxylamine is catalyzed by ammonia monooxygenase using O_2 or NO_2 as a source of oxygen, hydroxylamine oxidation to nitrite is catalyzed by hydroxylamine oxidoreductase and nitrite oxidation to nitrate by oxidoreductase. Denitrification steps are catalyzed by: nitrate, nitrite, nitric oxide and nitrous oxide reductases. Anaerobic ammonium oxidation is catalyzed by putative nitrite reductase, hydrazine forming enzyme and hydrazine oxidoreductase. Ammonification is catalyzed by nitrite reductase (Jetten, 2001).

Advanced microbial methods such as Fluorescent *in situ* Hybridization (FISH), dot-blot rRNA hybridization, and 16S rDNA clone library construction (Egli *et al.*, 2003) are of considerable help in determining the bacteria responsible. Analysis of the complex interactions of the different microorganisms in biofilms requires a technique that determines, not only the composition, but also the spatial distribution, of the community. This requirement necessitates the application of a non-invasive microscopic method. Confocal Raman microscopy (CRM) has been shown to be suitable for microbial analyses in several recent investigations. It provides, not only specific spectral fingerprints for unique identification, but also distributions of different microorganisms inside a biofilm-without destroying it (Pätzold & Kuentje, 2006).

3 OVERVIEW OF PROCESSES WITH NITROGEN-REMOVAL IN SIDE STREAMS

The diversity of different organisms involved has combined with various technological options to lead to a wide variety of novel applications in the last few years.

Conventional nitrification/denitrification technology consumes considerable amounts of resources: more than 0.045 g O_2 g^{-1} N and around 0.04 g COD g^{-1} N. These values imply a need to aerate the medium for nitrification, and to supply an external source of carbon for denitrification. Sludge-digested liquids

Table 1. Reactions for biochemical conversions of nitrogen forms (modified after Płaza *et al.*, 2003 and Gut, 2006).

No.	Reaction	Process	Genus or species of microorganisms	References
1a	$C_5H_7O_2N + 4H_2O \rightarrow 2.5CH_4 + 1.5\ CO_2 + HCO_3^- + NH_4^+$	Ammonification (anaerobic)	Bacteria	Rittmann and McCarty (2001); Henze *et al.* (2002); Ahn (2006).
1b	$C_5H_7O_2N + 5O_2 \rightarrow 4CO_2 + HCO_3^- + NH_4^+ + H_2O$	Ammonification (aerobic)	Bacteria	
2	$4CO_2 + HCO_3^- + NH_4^+ + H_2O \rightarrow C_5H_7O_2N + 5O_2$	Assimilation (growth)	Bacteria, Algae	
3	$NH_4^+ + 1.5O_2 + 2HCO_3^- \rightarrow NO_2^- + 2CO_2 + 3H_2O$	Nitritation	*Nitrosomonas,* *N. eutropha,* *N. europea,* *Nitrosospira,* *Nitrosococcus,* *Nitrosovibrio,* *Nitrosolubus*	
4	$NO_2^- + 0.5O_2 \rightarrow NO_3^-$	Nitratation	*Nitrobacter,* *N. agilis,* *Nitrospira,* *Nitrococcus,* *Nitrocystis*	
3 + 4	$NH_4^+ + 2O_2 + 2HCO_3^- \rightarrow NO_3^- + 2CO_2 + 3H_2O$	Nitrification	Nitrifying bacteria	
5	$C + 2NO_3^- \rightarrow 2NO_2^- + CO_2$	Denitratation	Dentrifying heterotrophic bacteria	
6	$3C + 2H_2O + CO_2 + 4NO_2^- \rightarrow 2N_2 + 4HCO_3^-$	Denitritation	Dentrifying heterotrophic bacteria	
5 + 6	$5C + 2H_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2$	Denitrification	Heterotrophs: *Pseudomonas,* *Bacillus,* *Alcaligenes,* *Paracoccus*	
7	$NH_4^+ + 0.75O_2 + HCO_3^- \rightarrow 0.5NH_4^+ + 0.5NO_2^- + CO_2 + 1.5H_2O$	Partial nitritation	Ammonium – oxidizing bacteria	Van Dongen *et al.* (2001a).
3 + 4 + 5 + 6	$4NH_4^+ + 8O_2 + 5C + 4HCO_3^- \rightarrow 2N_2 + 9CO_2 + 10H_2O$	Conventional nitrogen removal	Bacteria	Rittmann and McCarty (2001); Henze *et al.* (2002).
3 + 6	$4NH_4^+ + 6O_2 + 3C + 4HCO_3^- \rightarrow 2N_2 + 7CO_2 + 10H_2O$	Modified nitrogen removal	Bacteria	
8	$O_2 > 0$ $NH_4^+ + 2HCO_3^- + 1.5\ O_2 \rightarrow NO_2^- + 2CO_2 + 3H_2O$ $0.5O_2 + NO_2^- \rightarrow NO_3^-$ $O_2 = 0$ $NH_4^+ + NO_2^- \rightarrow 2H_2O + N_2$	Deammonification in biofilm	*Nitrosomonas*-like *Planctomycete*-like	Broda (1977); Rosenwinkel *et al.* (2005).

have a very unfavorable COD:N ratio for denitrification, so an external C source must be added. In addition, as the alkalinity of the supernatant is only sufficient for nitrification, alkalinity must be added, or regained by denitrification. However, higher temperatures and ammonia concentration allow for several alternatives where biological removal of nitrogen is concerned. First, there are better options involving a complete cessation of nitrification at the nitrite level, saving oxygen and the C-source. The N-rich sludge-liquids can also be used in side-stream cultivation of nitrifiers, which are subsequently inoculated into the

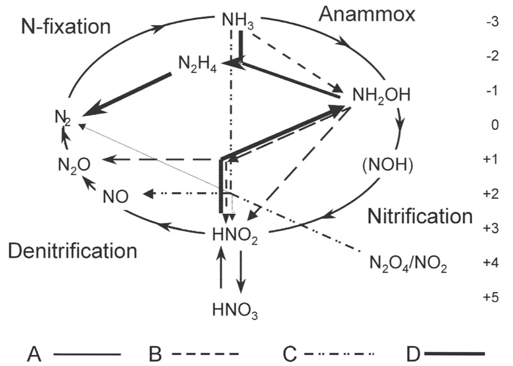

Figure 1. The nitrogen web: A-Conventional N-cycle (nitrification, denitrification, N-fixation), B-*Nitrosomonas* aerobic denitrification or aerobic deammonification, C-*Nitrosomonas* denitrification, D-Anaerobic ammonium oxidation (Anammox).

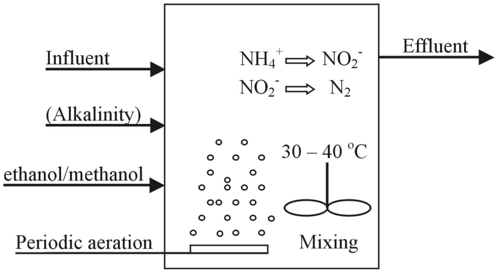

Figure 2. The SHARON reactor.

main-stream process. Such forcing of biological conversion via the nitrite route can be achieved via two approaches:

- making use of the difference in temperature dependency between ammonia and nitrite oxidation (ammonia oxidation is more sensitive to temperature),
- keeping the oxygen concentration low (van Loosdrecht and Salem, 2005).

In recent years several available techniques for treatment of the rejection water from sludge dewatering have been evaluated, including laboratory and pilot scale tests. The SHARON process (Single reactor system for High activity Ammonia Removal Over Nitrite) is the first successful technique by which nitrification/denitrification with nitrite as an intermediate under stable process conditions has been achieved. The SHARON process has been developed and tested at laboratory scale at Delft University (Hellinga *et al.*, 1998). The company Grontmij Water & Waste Management joined Water Authorities HDSR (Utrecht) and ZHEW (Rotterdam) in developing the detailed full-scale design of the two SHARON systems (van Kempen *et al.*, 2001).

The SHARON process (Fig. 2) is based on the higher maximalgrowth rate of ammonia- oxidizers relative to that of nitrite oxidizers at higher temperatures. At such elevated temperatures as 30–35°C – under which the aerobic retention time is low at around 1d – these ammonia-oxidizers are retained selectively, while the slower-growing nitrite-oxidizers are washed out. Aeration in the SHARON reactor is switch on and off intermediately for fulfilling oxic and anoxic conditions respectively for nitrification and denitrification. The denitrification process in the SHARON reactor could be a tool for controlling the pH or getting denitrification (Hellinga *et al.*, 1998). The SHARON process may be operated without biomass retention. This means that the sludge age (SRT) equals the hydraulic retention time (HRT). In such a case, the required sludge retention time (SRT) is the design criterion. If biomass retention is applied, aeration time will become the limiting factor for reactor design (van Loosdrecht & Salem, 2005). The proper choice as regards retention or non-retention depends on the final economic balance between reactor volume and retention equipment.

The stoichiometry of the SHARON reaction is represented by equations as follows (Lai *et al.*, 2004):

$$NH_4^+ + 1.5O_2 + 2HCO_3^- \rightarrow NO_2^- + 2CO_2 + 3H_2O \quad (5)$$

$$NO_2^- + 0.5CH_3OH + 0.5CO_2 \rightarrow 0.5N_2 + 0.5H_2O + HCO_3^- \quad (6)$$

Alkalinity is obtained more cheaply from methanol added for denitrification than from bicarbonate or hydroxide.

The mixed microbial community present in the SHARON biomass was investigated with molecular techniques (Logemann *et al.*, 1998). Analysis of the clones revealed that the dominant clone (69%) was highly similar to *Nitrosomonas eutropha*, which has been described in the literature as a fast-growing nitrifier able to grow at high ammonium and nitrite concentrations (van Dongen *et al.*, 2001b).

SHARON technology proved a very suitable treatment system by which to remove the bulk of the nitrogen from different types of wastewater released by the digestion of organic waste streams and manure. On account of the high ammonia uptake rate and efficient N-removal over nitrite, investment and operational costs are very attractive when set against those of other biological treatment options. In combination with a conventional post-treatment system SHARON technology is very efficient. The aerobic nitrogen uptake rate of the tested combination of treatment systems is very high (0.63–1.0 kg NH_4^+–N m^{-3} d^{-1}) compared with a fully-conventional treatment system (maximum 0.3 kg NH_4^+–N m^{-3} d^{-1}) (Jetten, 2001).

The ANAMMOX process (acronym for: ANaerobic AMMonia OXidation) was first discovered in a wastewater treatment plant in Delft, The Netherlands, and today anammox activity has been reported from several other treatment plants (Strous *et al.,* 1999; Schmid *et al.*, 2000; Egli *et al.*, 2001). Recently the process has also been shown to occur in nature, in marine sediment and anoxic water columns (Thamdrup & Dalsgaard, 2002; Dalsgaard *et al.* 2003; Rysgaard *et al.*, 2004). Anammox is carried out by lithoautotrophic bacteria belonging to the order *Planctomycetales*, including *Candidatus Brocadia anammoxidans*, and *Candidatus Kuenenia stuttgartiensis* identified by the Fluorescent in situ Hybridisation method (FISH) (Egli *et al.*, 2001; Jetten *et al.*, 2001). The biodiversity of Anammox bacteria was extended by the discovery of the genus *Scalindua* (Schmid *et al.*, 2003). Two species were found: *Candidatus Scalindua brodae* and *Scalindua wagneri*. The genus *Scalindua* has been also detected in the marine ecosystems of the Black Sea and *Candidua* was named *Scalindua sorokinii* (Kuypers *et al.*, 2003). Very recently, Anammox bacteria were found in the leachate of a landfill. For this purpose, it has been possible to apply several novel tools, including FISH, dot-blot rRNA hibridization, and 16S rDNA clone library construction (Egli *et al.*, 2003). The Anammox process converts ammonium directly into dinitrogen gas under anaerobic conditions, with nitrite as an electron-acceptor in the absence of any organic C-source. The stoichiometry of the process can be summarized by the equation without cell synthesis (van Dongen *et al.*, 2001a; Constantine *et al.*, 2005) or with cell synthesis (van Dongen *et al.*, 2001a; Fux, 2003) respectively:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \qquad (7)$$

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- \rightarrow 1.02N_2 + 0.26NO_3^- + 0.066CH_2O_{0.5}N_{0.15} + 2.03H_2O \qquad (8)$$

The intermediates in this process are hydrazine and hydroxylamine (Fig. 3) (Verstraete and Philips, 1998; Jetten *et al.*, 2001).

The detailed biochemistry of the process is still under investigation (Fig 4). It remains to be determined whether the reduction of nitrite and the oxidation of hydrazine occur at different sites of the same enzyme (Fig. 4A), or whether the reactions are catalysed by different enzyme systems connected via an electron transport chain (Fig. 4B).

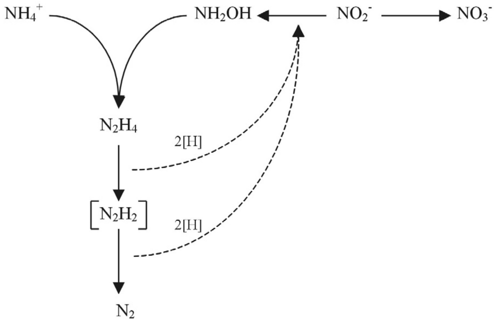

Figure 3. Possible pathway for the Anammox process (after van de Graaf *et al.*, 1996).

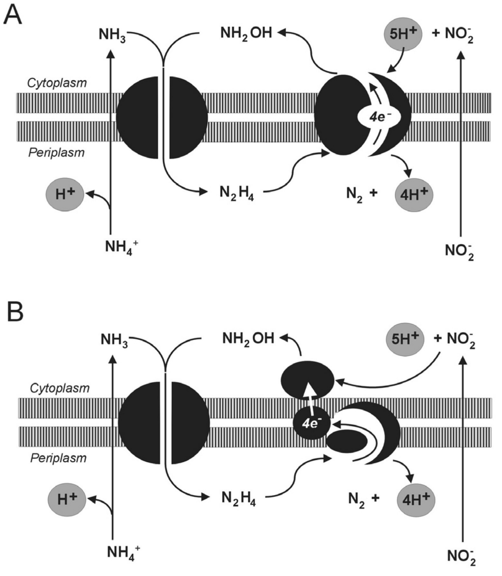

Figure 4. Possible reaction mechanisms and cellular localization of the enzyme systems involved in anaerobic ammonium oxidation (after Jetten *et al.*, 1999).
A: Ammonium and hydroxylamine are converted to hydrazine by a membrane-bound enzyme complex, hydrazine is oxidized in the periplasm to dinitrogen gas, nitrite is reduced to hydroxylamine at the cytoplasmic site of the same enzyme complex responsible for hydrazine oxidation with an internal electron transport.
B: Ammonium and hydroxylamine are converted to hydrazine by a membrane-bound enzyme complex, hydrazine is oxidized in the periplasm to dinitrogen gas, the generated electrons are transferred via an electron transport chain to a nitrite-reducing enzyme in the cytoplasm.

Compared with oxygen-nitrifiers like *Nitrosomonas eutropha* (which also reduce nitrite or nitrogen dioxide with ammonium or hydroxylamine as electron-acceptor, but have very low ammonium oxidation of 2 μmol NH_4^+ $min^{-1}g^{-1}$ protein), Anammox bacteria are much more effective in ammonium oxidation. These bacteria have a highly unusual physiology, in that they live by consuming ammonia in the absence of oxygen. Anammox is highly exergonic and linked to the energy metabolism of the organisms involved.

Also, the Anammox organisms grow with CO_2 as the sole carbon source, using nitrite as the electron donor here to produce cell material in line with the following equation (after Ahn, 2006):

$$CO_2 + 2NO_2^- + H_2O \rightarrow CH_2O + 2NO_3^- \quad (9)$$

The ammonium oxidation rate for Anammox bacteria reaches $45 \pm 5\ \mu$mol NH_4^+ $min^{-1}g^{-1}$ protein (Jetten *et al.*, 1999; Fux *et al.*, 2002). Anammox bacteria have a very low growth rate (of 0.069 – 0.072 day^{-1}) (Trigo *et al.*, 2006), and, as nitrate cannot be used by their organisms, the process needs an initial partial-nitritation step. Due to the slow growth rate of the Anammox bacteria, the reactors used to carry out the Anammox process must guarantee almost complete biomass retention inside the system, especially during the start up. (Strous *et al.*, 1998; Płaza *et al.*, 2002; Szatkowska *et al.*, 2004; Lai *et al.*, 2004; Trela *et al.*, 2004; Gut *et al.*, 2005). In other to achieve this aim, the used reactors were biofilm systems e.g.: fixed bed reactor, fluidised bed reactor, gas-lift reactor, rotating biological contractor (RBC),), or sequential batch reactors Mulder *et al.*, 1995; Fux *et al.*, 2002; Sliekers *et al.*, 2003; Dapena-Mora *et al.*, 2004a; Dapena-Mora *et al.*, 2004b; Dapena-Mora e*t al.*, 2006). In practice, the Anammox process is preceded by a SHARON reactor in which this partial nitritation step takes place (van Dongen *et al.*, 2001b). The SHARON-Anammox combined process is as shown in Fig. 5. The Kaldnes carrier, etc generalized reaction in the combined SHARON-Anammox process is (Tomaszek, 2006 after van Loosdrecht, 2006 www.bt.tudelft.nl):

$$2.3NH_4^+ + 2.95O_2 + 1.2CO_2 \rightarrow 1.2CH_{1.8}O_{0.2} + N_2 + 0.3NO_3^- \quad (10)$$

The SHARON-Anammox system can be applied for the treatment of industrial wastewater with a high nitrogen load and salt concentration, with an appropriate control of the NO_2^--N/NH_4^+-N ratio. The Anammox reactor bacterial population distribution does not change significantly, despite the continuous entry into the system of aerobic ammonium oxidizers coming from the SHARON reactor (Dapena-Mora *et al.*, 2006). An overview of some technical applications of partial nitritation/autotrophic anaerobic ammonium oxidation nitrogen elimination was given by Fux and Siegrist, (2004). The partial-nitritation Anammox process, also defined as the deammonification process, offers remarkable advantages:

- no N_2O and CO_2 production,
- no organic carbon source, and therefore less excess sludge production,
- reduced oxygen demand for partial ammonium oxidation to nitrite,
- reduced operational costs.

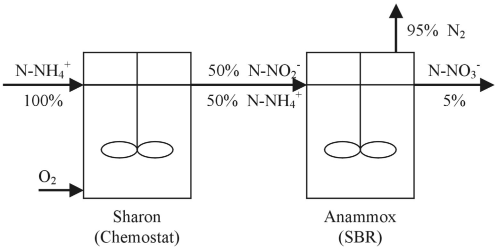

Figure 5. The SHARON – Anammox process.

The concept of the CANON (Completely Autotrophic Nitrogen removal Over Nitrite) process also represents the combination of partial nitritation and Anammox. Here, oxygen-limited conditions are obligatory if cooperation between the aerobic and anaerobic bacteria is to be obtained, but a biofilm provides for accumulation of nitrite in the outer (aerobic) part of the biofilm layer at the same time as the Anammox reaction is ongoing in the inner (anaerobic) part. The overall N removal stoichiometry can be summarized by the following equations (Ahn, 2006):

$$NH_4^+ + 0.75O_2 + HCO_3^- \rightarrow 0.5NH_4^+ + 0.5NO_2^- + CO_2 + 1.5H_2O \quad (11)$$

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 0.066CH_2O_{0.5}N_{0.15} + 2.03H_2O \quad (12)$$

$$NH_4^+ + 0.85O_2 \rightarrow 0.44N_2 + 0.11NO_3^- + 1.43H_2O + 0.14H^+ \quad (13)$$

The process takes place in a single aerated reactor, implying that the two groups of bacteria (*Nitrosomonas*-like aerobic microorganisms and Planctomycete-like anaerobic bacteria) cooperate in the whole process (Sliekers *et al.*, 2002). Nitrifiers oxidize ammonium to nitrite, consume oxygen and so create the anoxic conditions the Anammox process needs. The interaction of aerobic and anaerobic ammonium-oxidizing bacteria under oxygen limitation results in an almost complete conversion of ammonium to dinitrogen gas, along with small amounts of nitrate (Third *et al.*, 2001). The CANON process has quite sensitive operational characteristics in terms of dissolved oxygen, nitrogen load, biofilm thickness and temperature (van Loosdrecht, 2004). The CANON process is completely autotrophic, therefore avoiding COD addition, which is often required for the heterotrophic denitrification in traditional systems. In addition, the entire nitrogen removal can be achieved in a single reactor with very low aeration (the autotrophic process consumes 63% less oxygen), greatly reducing space and energy requirements. Unlike other autotrophic nitrogen removal systems, such as the SHARON-Anammox process, wherein nitrite is generated in a separated reactor, there is no requirements for nitrite addition in the CANON process (Third *et al.*, 2001). Recent studies have shown that the CANON biomass is very resilient to disturbances in wastewater composition, such that by proper control the process may be a good alternative to existing nitrification-denitrification systems for the treatment of liquid waste rich in ammonia (Third *et al.*, 2001; Nielsen *et al.*, 2005).

An integration of nitritation and Anammox in a biofilm reactor also takes place in the OLAND (Oxygen-Limited Autotrophic Nitrification and Denitrification) process. This is possible when oxygen and nitrite are both made limiting, so that nitrite oxidizers may be effectively excluded from the N-removal process (Hao *et al.*, 2002). The OLAND process was first described for a mixed culture of nitrifying bacteria (Kuai & Verstraete, 1998), but was afterwards examined in more detail in the mixed-community biofilm of an RBC (Pynaert *et al.*, 2002). A mature OLAND biofilm under high NH_4^+ loading rate consists primarily of two major groups of bacteria responsible for autotrophic N removal. The aerobic ammonium-oxidizing bacteria (*Nitrosomonas* sp.) convert NH_4^+ to NO_2^- with oxygen as an electron acceptor, and the anaerobic ammonium-oxidizing bacteria – a close relative of *Kuenenia stuttgartiensis*-subsequently oxidize NH_4^+, with NO_2^- as the electron acceptor (Strous *et al.*, 1998). The overall N removal stoichiometry can be summarized by the following equations (Kuai & Verstraete, 1998; Verstraete & Philips, 1998):

$$0.5NH_4^+ + 0.75O_2 \rightarrow 0.5NO_2^- + H^+ + 0.5H_2O \quad (14)$$

$$0.5NH_4^+ + 0.5NO_2^- \rightarrow 0.5N_2 + 2H_2O \quad (15)$$

$$NH_4^+ + 0.75O_2 \rightarrow 0.5N_2 + H^+ + 1.5H_2O \quad (16)$$

The detailed mechanism underpinning these processes is not well understood as yet. The main difference between the OLAND and CANON processes is that the former uses the denitrification activity of conventional aerobic nitrifiers, whereas the latter incorporates the Anammox process (Ahn, 2006 after Jetten, 2001). However, it seems possible that the OLAND process will be based on the CANON concept, and hence on the cooperation between aerobic nitrifiers and anaerobic ammonia-oxidizers under conditions of oxygen limitation (Schmidt *et al.*, 2003). Because Planctomycete-like bacteria are also responsible for the nitrogen removal in this process, the isotopic analysis of the resulting gas given in equation 17 (Wyffels *et al.*, 2003) results in an overall nitrogen stoichiometry similar to that already discussed for the Anammox process.

$$NH_4^+ + 1.43NO_2^- \rightarrow 1.09N_2 + 0.008N_2O + 0.3NO_3^- + \text{biomass} \quad (17)$$

Wyffels *et al.*, (2004) demonstrated the feasibility of a two-stage combined membrane-assisted bioreactor (MBR) for the treatment of nitrogen-rich wastewater with the oxygen-limited autotrophic nitrification denitrification (OLAND) process. The combination in a two-stage OLAND process of oxygen-limited partial nitritation and autotrophic denitrification (or alternatively, anaerobic ammonium oxidation) has been shown to be feasible for the treatment of sludge reject water using MBR with complete biomass retention. Windey *et al.*, (2005) demonstrated the feasibility of treating high-salinity ammonium-rich wastewater in a rotating biological contractor operated under OLAND conditions after adaptation to high salinity.

Bioaugmentation was postulated as an option for upgrading existing WWTPs by the treatment of nitrogen-rich flows (Salem *et al.*, 2003; Salem *et al.*, 2004). A side-stream nitrifier-bioaugmentation allows nitrification to proceed in the mainstream system at substantially reduced SRT. The process then requires less secondary treatment tankage than a traditional nitrification system. The InNiri and BABE processes (Figs. 6 and 7) are based on the concept of bioaugmentation. Both processes use a side stream to nitrify and generate an enriched population of nitrifying bacteria that are subsequently used to increase the capacity of the mainstream secondary treatment process. The

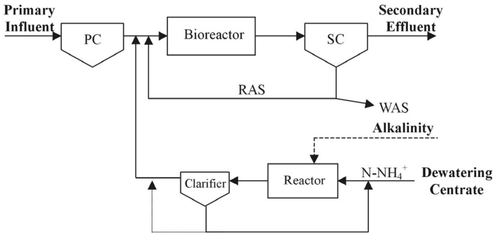

Figure 6. The InNitri process. PC – primary clarifier, SC – secondary clarifier, RAS – return activated sludge, WAS – waste activated sludge.

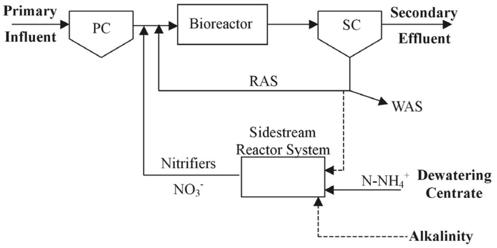

Figure 7. The BABE process.

BABE process differs from the InNitri process in that a side-stream reactor includes a portion of the return activated sludge from the main stream as an additional input stream (Constantine *et al.*, 2005). The BABE process better ensures that the nitrifying biomass is well-suited to growth. As a result of the seeding of the main nitrification reactor with a separately cultivated culture (Płaza *et al.*, 2001), nitrification capacity can be increased substantially by the side-treatment of supernatant, due to both the decreased influent load on the WWTP and the enhanced activity of nitrifiers. One of the main advantages of the full-scale application of the Babe process that treats nitrogen-rich reject water is about a 60% reduction in costs (van der Zandt *et al.*, 2005).

4 SUMMARY AND CONCLUSIONS

The treatment of nitrogen-rich streams via side-stream processes can be applied cost effectively in upgrading WWTPs. The addition to the mainstream treatment plant of dewatering liquids treated in side-stream processes may allow WWTPs to reach new and more stringent limits for total nitrogen in effluent. The InNitri and BABE processes based on the concept of bioaugmentation may be used when the main stream treatment process is characterised by SRT-limited nitrification, or denitrification limited by the anoxic retention time. In comparison with InNitri, the BABE process has lower supplementary requirements as regards alkalinity. If denitrification limits the main treatment process (aeration or COD limiting), the SHARON process could be used. Advantages of this include: a significant saving in oxygen and COD, and relatively simple operation and maintenance. The choice of the process by which sludge water is treated is usually case-specific, the treatment option depending on local conditions, the composition of sludge liquids and economic analysis (comparison of the relative capital and operating costs of each system).

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Possibility of practical utilization of waste and sewage sludge

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Addition of sewage sludge to raw material used in LECA production

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ABSTRACT: Sewage sludge as porosity-causing agent can be added to raw material used in LECA production. The effect of sewage sludge addition upon fusibility and texture of sinters obtained from clay and sewagebased mixture was investigated. Laboratory experiments have been confirmed by industrial tests. The source of the clay was Budy Mszczonowskie deposit mined by the ceramic plant "Keramzyt". The sewage sludge was collected from the municipal waste water treatment plant Sitkówka-Nowiny located near Kielce. The fusibility of ceramic sinters was determined by high temperature microscopy and their texture by a scanning electron microscope. The positive effect of sewage sludge upon the porosity, insulating properties and bulk density of LECA was observed. On the basis of a standard test conducted on the industrial sample the ecological value of sewage sludge utilization is discussed.

Keywords: Sewage sludge utilization, lightweight expanded clay aggregate.

1 INTRODUCTION

Sewage sludge contains 30–85% of organic matter which can be treated as a source of energy and material. Due to organic substances undergoing destruction during sintering, sewage sludge can be used as an expanding agent in the production of light weight expanded clay aggregate (LECA).

LECA is obtained by sintering the expanding ceramic material. The aggregate formation process can be described as follows: when clay is sintered at high temperature (1100 to 1200°C) both solid and liquid phases appear and, owing to the high viscosity of the resulting liquid, emitted gases are retained in pores. Such retention of gaseous phase in pores causes the swelling of granules (Ehlers 1958, Riley 1951). According to the literature, the swelling size of granules is dependent upon the rate at which the temperature of sintering increases as well as on the chemical and mineralogical composition of the raw material (Ehlers 1958, Riley 1951, Parsons 1960).

LECA is a ceramic, durable, incombustible, inactive composite of wide application. It is mainly used in the building industry as a lightweight aggregate. Owing to its low thermal conductivity sinter is a particularly good thermal insulator. In addition, LECA is used to insulate ceilings, floors, walls, inner walls of ducts and kilns. It is also employed as filler for lightweight concrete and asphalt mass as well as a filter medium in water treatment. Work on phosphorus removal from waste water by means of LECA has been carried out (Johansson 1997).

Mæhlum et al. (1995) pointed out that the combination of a high hydraulic conductivity, porous structure and high P-adsorption capacity makes LECA interesting as a filter media, P-adsorbent and insulating material in on-site wastewater treatment systems. The main components in LECA which react with phosphate are Al- and Fe-oxides (Johansson 2006).

From work conducted by Ber et al. (2006) it follows that LECA is a good material for covering liquid manure storage facilities to reduce gaseous emissions, especially for odour and ammonia. Results presented by other researchers (Balsari et al. 2006,) indicate that a significant reduction of ammonia emission from the liquid surface of store swine manure can be achieved by a layer of LECA, 10 cm thick. LECA is also used in trickling filters nitrifying sewage (Lekang & Kleppe 2000) and in hydroponics providing for alimentary and oxygen balance and plant moisture.

LECA is burnt in industrial rotary kilns. If the raw material does not comply with technological requirements, swelling additives like brown coal and waste oil are applied, which improve expanding factor, broaden the expanding interval and decrease the temperature of maximal expanding. The increasing expanding factor brings about the desired decrease of bulk density and the growth of LECA's porosity; this results in higher insulating power.

Examples of the usage of ash obtained after sintering sewage sludge for ceramic building materials are described in the literature (Wiebusch & Seyfried, 1997; Park & Moon, 2003; Suzuku et al., 1997). Some authors (Tay 1987; Lin & Weng, 2001; Weng et al., 2003) presented examples of using dried sewage sludge as a raw material to manufacture bricks but no description of utilising the organic substances contained in sludge as an expanding additive for ceramic mass have been found.

The aim of this work was to test the use of sewage sludge in the production of lightweight expanded clay aggregate as a swelling agent. The test was conducted in a laboratory kiln and the results were further confirmed in an industrial furnace.

Different kinds of sludge are generated at different stages of sewage treatment including raw sludge, chemically deposited sludge, thickened or activated sludge. In the process of sewage sludge treatment dewatered, stabilized sludge is obtained. It contains (depending upon the method of dewatering and stabilization) 20–42% of dry mass, about 60% of organic matter in dry mass, and inorganic components including: SiO_2, $Fe2O_3$, CaO, $P2O_5$, $Al2O_3$ and K2O (De la Guardia 1996, Werther & Ogada, 1999). The presence of organic matter, phosphorus and potassium makes the sludge potentially suitable for agricultural use (De la Guardia 1996). However, as the sludge contains heavy metals in biota, its chemical composition frequently makes it unacceptable for agricultural use. The admissible quantities of heavy metals in the sludge for agricultural use together with the amount of metals in the soil are specified in the directive 86/278/CEE (Council Directive of 12 June 1986).

In the European Union sewage sludge is usually disposed of in landfills. This is not however, the optimal solution to the sludge disposal problem. According to the disposal directive (1999/31/EC) the content of biodegradable substances in the disposed waste has to be gradually reduced to 35% in 2016. Thermal utilization requires considerable financial outlays in installations necessary to protect the environment and human health against harmful gaseous, solid and liquid combustion products.

The amount of the sewage sludge is steadily increasing due to the growing number of sewer system users and technological changes in waste water treatment. According to Werther & Ogada (1999) currently approx. 10 million tonnes of dry mass per year are generated in the European Union.

The present authors assume that, owing to the mechanism of formation of the porous texture of ceramic sinter and the content of organic matter in the sewage sludge, the sludge might be used as an additive in the production of lightweight expanded clay aggregate.

While the metal loading of sludge disqualifies its use in agricultural, it should not pose any threat to ceramic mass. Heavy metals when sintered with clay become embedded in the structure of the ceramic material and partly undergo vitrification. Consequently, their leaching is lower in comparison to that of metals from the sludge and does not exceed the permissible standards (Lin & Weng 2001, Weng et al. 2003 & Liew et al. 2004). Furthermore, the organic matter in sewage sludge is decomposed which allows energy recovery. The calorific value of the dry sludge is comparable with that of brown coal. Treatment of sewage sludge in this way does not generate solid wastes as is the case in sewage sludge incineration or co-combustion with other wastes (Werther & Ogada 1999).

Table 1. Operational parameters in the ceramic plant PKL "Keramzyt" in Mszczonów (industrial test).

Parameter	Value
Raw materials:	
raw clay "Budy Mszczonowskie"amount	120 Mg
clay humidity	18.8%
sewage sludge amount	21 Mg
sludge humidity	80.3%
humidity of raw mass	22–28%
Maximum temperature in rotary kiln	1170°C
Temperature in rotary kiln – input side	550°C
Temperature in rotary kiln – output side	200°C
Time of retention of ceramic mass in kiln	45 min.
Time of retention of ceramic mass in maximum temperature	10 min.
Kiln atmosphere oxidizing	
Total mass of aggregate	75 Mg

2 MATERIALS AND METHODS

The research consisted of two stages: laboratory experiments and industrial tests. On the basis of the laboratory experiments the optimum quantity of sewage sludge causing the maximum swelling of the ceramic aggregate was established. Under laboratory conditions the sintering temperature in the electric kiln was limited to 1170°C, (maximum allowed temperature of the industrial kiln). Both in the laboratory and industrial kiln oxidation was observed (Table 1).

The criterion applied to determine the optimum content of sewage sludge in the raw material used in LECA's production was the porosity of sinters analyzed by means of SEM (Figs 1–3) and the porosity of the aggregate obtained (Fig. 4).

After the optimum content of sewage sludge in the raw material had been determined the industrial tests were conducted in the industrial kiln used in the production of lightweight aggregate. The usability of sewage sludge as the agent expanding the ceramic mass in the process of heat treatment was verified under industrial conditions. The effect of the sewage sludge upon technological parameters of the production process was analysed. The evaluation of the emission of gases from coal-burning furnace/kiln was also discussed.

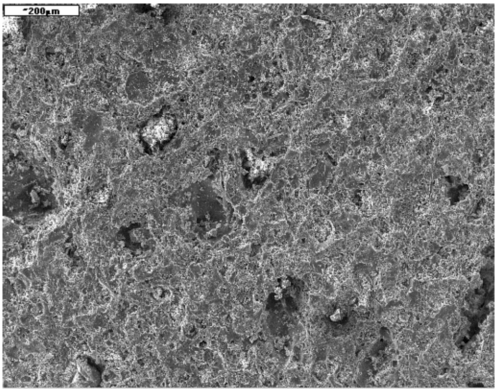

Figure 1. SEM image of clay sample sintered at 1170°C (magnification 100x).

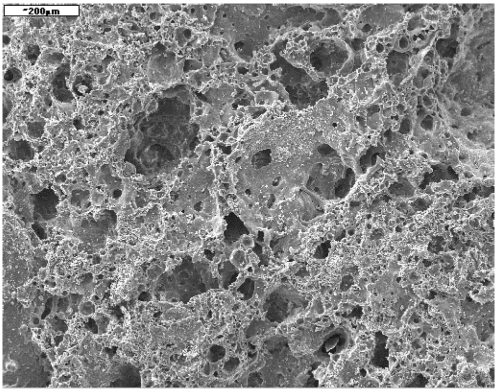

Figure 2. SEM image of sample with 10% sewage sludge sintered at 1170°C (magnification 100x).

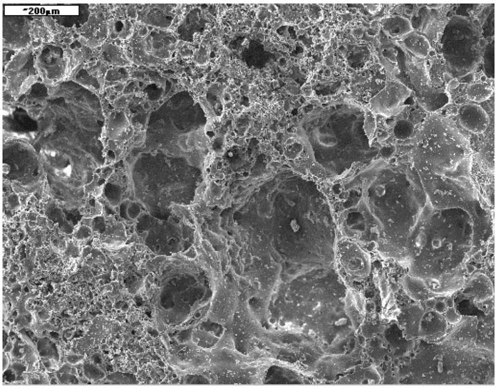

Figure 3. SEM image of sample with 20% sewage sludge sintered at 1170°C (magnification 100x).

The usability of the aggregate obtained for the lightweight concrete production was examined in compliance with the Polish standard.

The raw material used in the present work was clay from the deposit "Budy Mszczonowskie". Alone, the clay has a low expanding capacity. The additive was sewage sludge collected from storage at the sewage treatment plant Sitkówka – Nowiny near Kielce.

As specified, in sewage sludge treatment technology, the sludge undergoes mechanical thickening, stabilisation in an anaerobic sludge digester and dewatering in centrifuges before storage.

2.1 *Laboratory research*

Preparation of samples for laboratory experimental work was based on ceramic clay and dried sewage sludge derived from the treatment plant. The water content of the sludge sample was 48.7% and the pH 7.15. The content of the organic matter was 53.2% (in dry mass).

The sludge, after drying off at a temperature of 105°C, was ground in a mortar to attain a loose state. The clay was also dried off and ground. The amount of sludge in the ceramic mass for LECA preparation was the variable parameter.

Mixtures of clay containing 5, 10, 15, 20% of dried sewage sludge were subsequently prepared. The masses were mixed with water until a plastic consistence was obtained. Next, roll shaped barrels (diameter 10 mm; height 10 mm) were moulded by means of a hand press. The roll shaped barrels were dried off at 105°C and sintered in the laboratory electric kiln "Nabertherm" at 1170°C. The sintering temperature satisfied the conditions for the industrial furnace (the experiment was confirmed there on the technical scale). After thermal processing, the granules had a smooth, vitrified surface.

The texture of the obtained ceramic sinters was examined using a scanning electron microscope (ISM – 5400, Technics Ltd, Japan) (Figs 1–3).

A density analyser (GeoPycTM 1360, Micrometric, USA), was used to determine the dependent variables including total porosity and bulk density of the sinters. The results are presented in Figure 4.

The effect of added sludge on the melting temperature of the ceramic sinter was analysed. The test was conducted in a high temperature microscope which allowed the observation of the mould's shape as a function of temperature (Fig. 5). The temperature was steadily increased by 8°C/1 minute.

2.2 *Industrial tests*

Repeating experiments previously carried out in the laboratory under industrial conditions is always connected with the risk of inconsistency (scale effect). In the case discussed here the conditions in which

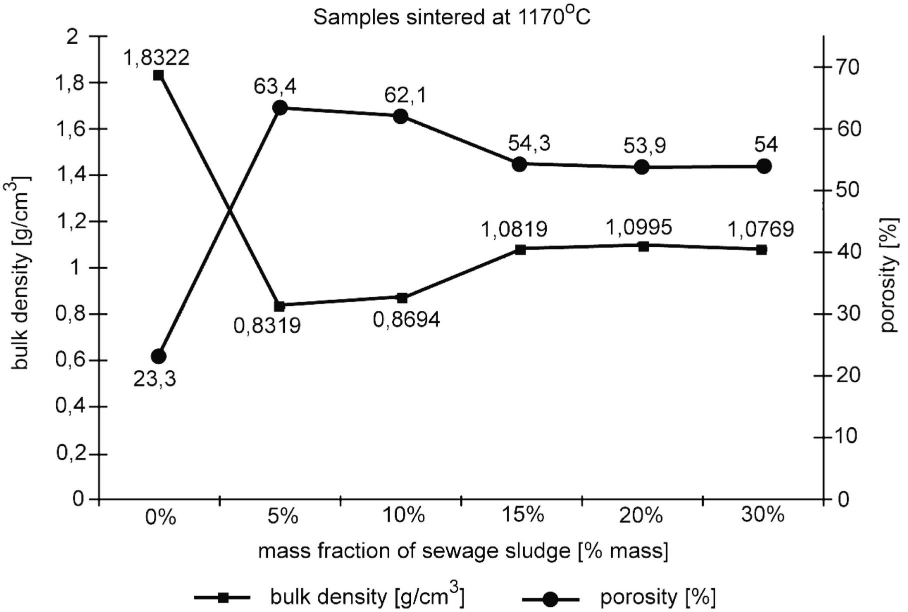

Figure 4. The effect of sludge content in ceramic mass on porosity and bulk density of aggregate sintered in 1170°C under laboratory conditions.

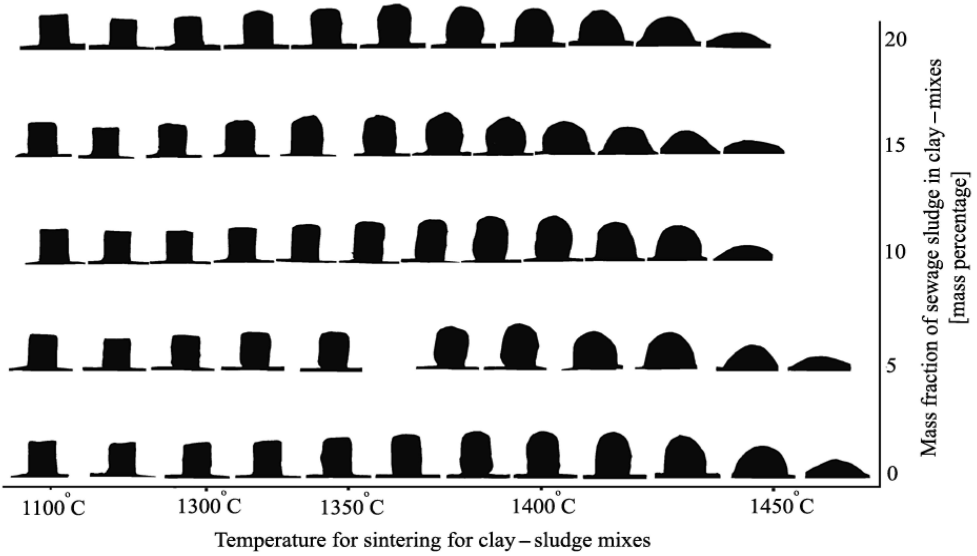

Figure 5. The susceptibility of mixes (clay + sewage sludge) to sintering temperature. obtained by high temperature microscopy. The scale is not at regular intervals as the time parameter was not taken into account.

the raw material is prepared and exposed to heat treatment are different. In the ceramic plant "Keramzyt", LECA is produced from clay of low expanding capacity. In order to improve the porosity of the aggregate, various additives are added to the raw material. The permissible addition of different admixtures to ceramic mass, was restricted, by internal provisions, to maximum 26%. The "Keramzyt" plant produces about 100 thousand tons of lightweight aggregate per year. The aggregate is burnt in the rotary coal-fired kiln which is in constant movement. Hence, the conditions of sintering are quite different.

For the industrial test 120 tons of ceramic material and 21 tons of moist sewage sludge collected from sewage treatment plant were used. During one shift 75 tons of lightweight aggregate was produced from raw material containing sewage sludge.

Technological parameters of LECA production in PKL "Keramzyt" are presented in Table 1.

The raw material of 18.9% moisture content in the natural state was obtained from the Budy Mszczonowskie deposit.

The sludge had the consistence of humid soil, the water content was 80.3% and the content of organic matter in dry mass was 65.2%. The high water content was the result of heavy snowfall on the day preceding removal of the sludge from storage.

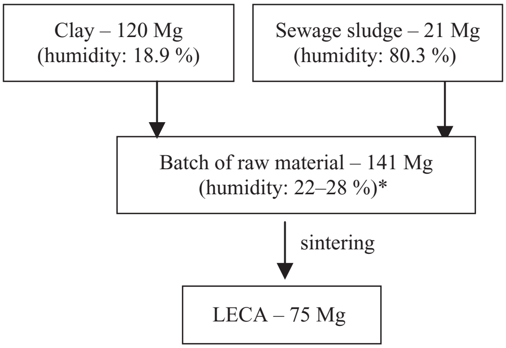

Figure 6. Mass balance of raw materials and products. *data taken from process line.

In the industrial studies the mixture of clay and 15% of wet sludge – equal to 4% dry matter, after working reached the average humidity of 25.3%. The amount of the sludge added was limited by the humidity of the mixture which if exceeded obstructed the process line (sticky feeder box).

By dosing the sewage sludge from the feeder, the raw material mixture in the raw material store was averaged. The raw material mixture was worked in the crusher, moulded into granules (a train of perforated rollers) and placed in the rotary kiln. The supply of raw material was 7 m^3/h. The raw material was sintered in the kiln for 45 minutes including 10 minutes in the maximum temperature zone (1170°C). Other operating parameters in the manufacture of sintered aggregate in the ceramic plant PKL "Keramzyt" are presented in Table 1. Next, the sinter was moved to the cooler and to the storage bins. The mass balance of raw materials and products is illustrated in Figure 6. The block flow diagram of the process line is presented in Figure 7. The characteristics of the aggregate obtained in the industrial trial is presented in Tables 2–3 and Figure 8.

During the industrial test the emission of pollutants into the atmosphere was also measured. The samples were collected behind cloth filters in the chimney.

To determine the emission level of gas pollution in exhaust gases (dust, SO_2, NOx, CO) the microprocessor exhaust gas analyser "SEMIDUR-700" fitted with an exhaust gas dryer"GA-10" was used.

The emission levels of metal in the emitted dust were identified by means of dust samples collected

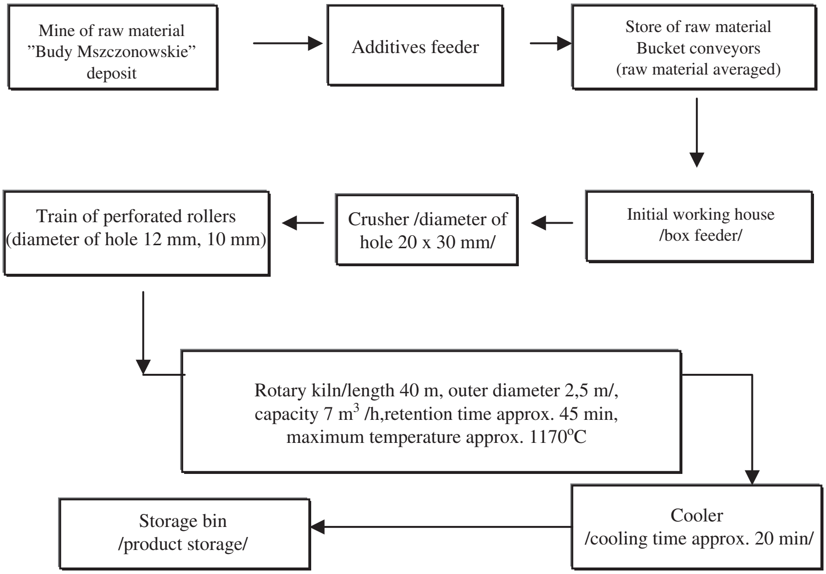

Figure 7. Block flow diagram of the LECA process in ceramic plant PKL "Keramzyt" Mszczonów.

Table 2. Results of standard qualification tests conducted on clay and sewage sludge – based LECA according to Polish standard PN-86/B-23006.

Parameter [%]	Industrail test LECA fraction [mm]			Values admissible for a brand	
	0–4	4–8	8–16	1	2
Mineral dust	1,21	0.46	0.24	4.0	6.0
Impure particles	none	none	none	0.5	1.0
Irregular grains	–	4.63	3.23	–	–
Decomposition of calcium	–	0.61	0.4	–	–
Sulfur content		0.0077		1.5	2.5

on quartz filters. Afterwards, the metal content was determined by atomic absorption spectrophotometry using a "SHIMADZU AA-660".

To determine hydrocarbon concentrations the method of active carbon adsorption was applied. The chromatographic analysis of adsorbed hydrocarbons was carried out by means of gas chromatography (VARIAN-STAR 3400; "SHIMADZU GC-14A"). The results are shown in Table 4.

3 RESULTS AND DISCUSSION

The laboratory experiments showed the positive effect of sewage sludge upon the structure of ceramic sinter.

Table 3. Class of lightweight concrete obtained from LECA in industrial studies.

Specification	Unit	Denotation	Batch				
			I	II	III	IV	V
Concrete class of the samples	MPa	RGb	B-10	B-10	B-15	B-10	B-10
Number of samples	Piece	N	6	6	6	6	6
Average strength obtained	MPa	$R_{śr}$	13.78	16.7 4	21.52	12.74	13.74
Coefficient dependent upon number of samples		A	1.1	1.1	1.1	1.1	1.1
Minimal strength	MPa	R_{min}	12.00	14.67	20.67	11.56	13.33
Verification of concrete class:	Rmin ≥	αRGb	yes	yes	yes	yes	yes

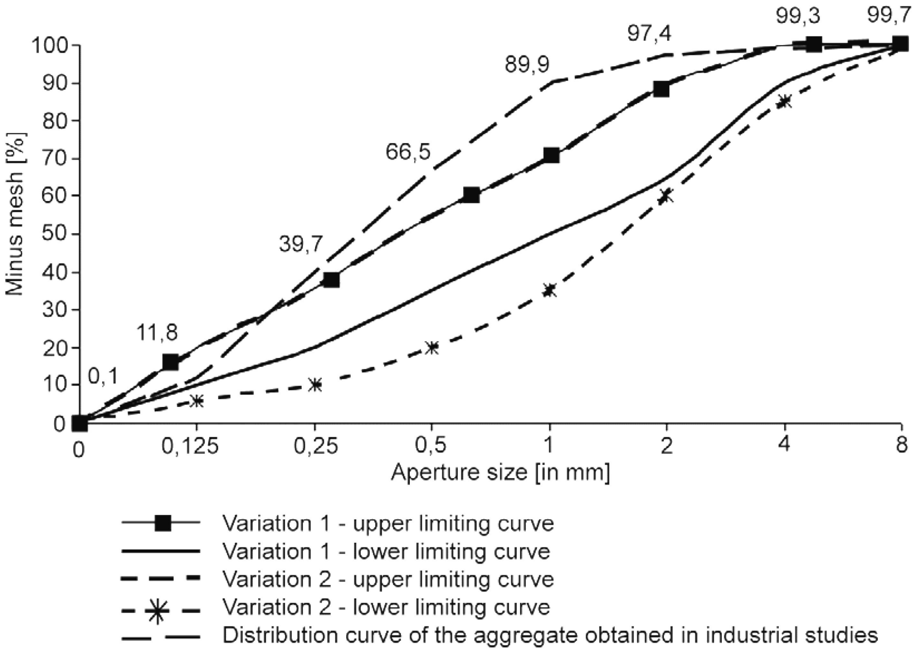

Figure 8. Grain size of lightweight expanded clay aggregate and limiting curves (according to the Polish standard, industrial studies).

The aggregate obtained from a raw material containing sewage sludge had higher porosity and lower bulk density.

In the photographs of micro sections showing samples magnified 100 times the effect of sewage sludge upon composite texture can be easily observed (Photographs 1–3). The sample of sinter with no sludge added had a texture with only a few small size pores (Fig. 1); the one containing 10% of the sludge in mass (Fig. 2) showed visibly porous texture and the texture of the granule containing 20% of the sludge in mass (Fig. 3) was very porous with macro pores forming cavities. The cavities and inhomogenities in the texture appeared as a result of degassing caused by thermal decomposition of organic material present in the sludge added to the mixture of raw material.

The results of bulk density and total porosity investigation (Fig. 4), show that the greatest influence of sludge addition was between 5 to 10% of sludge content (as dry mass). It is also seen in Figure 5, showing that the observed samples profiles were mostly affected by sludge addition in this range.

The optimum content of sewage sludge determined in the laboratory experiments could not be applied in the industrial test because the humidity of the sewage sludge was too high. Thus, the content of sewage sludge in raw material used in the industrial test was reduced from 5% to 4% (calculated for dry mass). This, however, did not cause significant deterioration of the aggregate's parameters.

On the basis of these results it may be concluded that the aggregate produced with the addition of sewage sludge has properties similar to those possessed by commercial sludge and hence can be used in the production of lightweight concretes. The high porosity of the aggregate makes it useful in environment protection, especially in sewage treatment and the elimination of odours and ammonia from gaseous emissions.

The ceramic plant uses, in compliance with relevant acts of law, a lot of waste matter of considerable heating value including waste coal-tar, waste oils and others which enables the elimination of waste, the recovery of energy and an increased expansion factor influencing the insulating properties of the aggregate. The additives in raw material cannot exceed the permissible values specified in the order of Mazowiecki Voivode (the state regulation).

No production disturbances causing production stoppage were observed when the test was being performed. The average bulk density of the aggregate at a loose state was 787.73 kg/m^3.

The increased level of SO_2 emission observed when the raw material containing sewage sludge was burnt (Table 4) was caused by the increased content of sulphur in the fuel used for the industrial test. The higher emission of ash was the result of the increased fuel consumption caused by higher humidity of raw material mixture and slightly smaller heating value of the fuel used during the industrial test (Table 5). The higher fuel consumption resulted in the higher emission of heavy metals (in trace amount). The emission levels were, however, much below the permissible values specified in the order of Mazowiecki Voivode. For nitric oxide, carbon monoxide, lead oxide, toluene and benzene they were even lower than those determined during the production of commercial aggregate.

Table 4. Emission levels of gaseous pollutants identified during industrial test and in the production process of the commercial aggregate.

Parameter kg/h	Average measurement: Industrial test with sewage sludge content	Average measurement: Production of commercial aggregate	Permissible value*
Dust	1.289	0.574	21.206
SO_2	9.455	7.278	20.48
NO_x	5.472	6.572	16.568
CO	3.116	5.956	32.994
Zn	0.0018	0.0001	0.018
Pb	0.0009	0.0012	0.011
Cd	0.00007	0.00007	0.002
Ni	0.0005	0.0001	0.047
Cr	0.0009	0.0002	0.127
Cu	0.0004	0.0001	0.141
Mn	0.0015	0.0001	0.004
Co	0.0002	0.0001	0.005
Fe	0.1311	0.0128	7.056
Toluene	0.0098	0.0132	0.122
Benzene	0.0084	0.0108	0.017
Xylene	0.0247	0.0133	0.182
Ethylbe-nzene	0.006	0.0028	0.053
Acetone	0.0239	0.0147	0.843
Styrene	0.0032	0.0026	0.016
n-butyl alcohol	0.0138	0.0018	0.673

* according to the guideline set out by the Mazowiecki Voivode (20 August 2001); currently the standards applied in "Keramzyt"are being adjusted so as to comply with the UE directives.

Table 5. Parameters of fuel used in the industrial kiln at the ceramic plant PKL "Keramzyt".

Parameter	Hard coal dust (fraction <1 mm): Industrial test	Hard coal dust (fraction <1 mm): Production of commercial aggregate
Heating value	22 MJ/kg	23.5 MJ/kg
Ash content	15%	15%
Sulphur content	0.8%	0.7%

Our work has shown that, by adding 5% (dry mass) of sewage sludge to LECA, five thousand tons of dry sewage sludge can be utilized in "Keramzyt" plant per year.

4 CONCLUSIONS

This work has proved that sewage sludge can be added to the mixture of raw materials used in the production of lightweight aggregate thus providing an extra source of energy by way of combustion of the organic substance contained therein. The organic material decomposes into gaseous products in the high temperature of the kiln thus increasing the porosity and insulating power of the aggregate.

The images of sinter micro sections from the scanning electron microscope confirm the beneficial impact of the sewage sludge upon porosity of LECA's granules.

Based on laboratory tests it was shown that the optimum content of sludge in ceramic mass was in the range 5–10% (dry mass). However, the high humidity of sludge used in the industrial test limited the sludge content to 4% of dry mass (equivalent to 15% of wet mass).

The high humidity of sewage sludge caused higher coal consumption which, in turn, resulted in higher emissions of some gaseous pollutants.

Excessive humidity of the raw mass after the sludge had been added negatively effected the grain size distribution of the aggregate. The implementation of this technology requires reduction of the sludge moisture content to 50–60%. To dry the sludge the heat generated by combustion gases released in the rotary kiln can be used. The emission levels of the measured pollutants did not exceed the permissible values.

The obtained light aggregate satisfies the Polish standard PN-86/B-23006, so that the aggregate based on sludge can be used as a standard component of light concrete.

The high porosity of the aggregate additionally makes it useful in environment protection, especially in sewage treatment and for the elimination of odours and ammonia from gaseous emissions.

The research has revealed a positive ecological aspect of sewage sludge utilization. The use of the sewage sludge as the additive to raw material will reduce the environmental nuisance caused by waste disposal sites and will prolong their operation. On the basis of our work a new trend of waste utilisation has been proposed. The waste is recovered as the raw material (the component of ceramic sinter) and, owing to its content of combustible organic materials is also useful as an energy carrier.

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Management of Pollutant Emission from Landfills and Sludge – Pawłowska & Pawłowski (eds)

Environmental results of application of city refuse compost "DANO"

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ABSTRACT: In this work, the main goal was to evaluate the effects of long-term application of "Dano" compost on farmlands. The experimental parameter was the number of years required to exceed the I° of soil contamination when applying compost every three years. The content of analyzed heavy metals in the compost was lower than the permissible critical levels for agriculture utilization of wastes. Applied in a single application in three–year crop rotation, the compost increased the content of total and HCl-soluble forms of the studied metals. Under these conditions the admissible standards of heavy metals content in soil were not exceeded. Application of compost "Dano" resulted in increased total heavy metal content in the soil. The time period over which the heavy metal content in soil will attain the I° of soil pollution resulting from "Dano" application is as follows: Ni > Zn > Cu > Cd > Pb.

Keywords: City refuse compost Dano, heavy metals, soil

1 INTRODUCTION

Recently, attempts have been made to apply organic waste materials derived from public utilities to agriculture. City refuse compost produced with "Dano" technology is one such material. It is an organic substance of high yield and humus-forming value (El Nadi et al. 1995, Hartl et al. 2003, Sharma et al. 1997). However, the high content of heavy metals in these composts may be an obstacle to their use on farmlands (Baldwin, Shelton 1999, Jordao et al. 2006). A similar situation occurs in other European countries. Approximately 15% (9 million tonnes) of the recoverable organic fraction is currently recovered through home composting or source separation and centralised composting throughout the EU (Slater, Frederickson 2001). Among the reasons for the low use of composts for farmland manuring, the most important are: inadequate quality of these composts, societal disapproval vis-à-vis the use of wastes for manuring, and insufficient marketing activity (Slater, Frederickson 2001). In recent years, decisions on the construction of new urban waste composting plants have been made and are being realized in Poland, resulting in the increased production of compost. Hence, it is advisable to consider different aspects of applying the compost.

The aim of the present studies was to evaluate the hazard of soil pollution with heavy metals (Zn, Cu, Pb, Cd, Ni) as a result of applying increasing doses of city refuse compost "Dano".

2 MATERIALS AND METHODS

In the paper, the effects of long-term application of "Dano" compost on farmlands is evaluated by estimating the period required to exceed the I grade of soil contamination according to Kabata–Pendias et al. (1993), with application of compost every three years. This prediction was made on the basis of a long-term field fertilizer experiment located at the Warsaw Agricultural University Experimental Station in Skierniewice. The soil of Skierniewice Experimental Station is mainly stagnic luvisol (according to the FAO classification). The texture of the ploughing layer (0–25 cm) is of loamy sands, containing 14–17% of silt and clay (diameter < 0.02 mm), and 5–8% of clay (<0.002 mm of diameter). Before the beginning of the experiment, the plough horizon of soil was slightly acid (according to pH_{KCl}) and the natural content of heavy metals (Zn – 23.4, Cu – 11.5, Pb – 16.4, Cd – 0.34, Ni – 9.0 $mg\,kg^{-1}$ of soil). The compost applied in this experiment was produced by a method using bio-reactors known as DANO (Sharma et al. 1997). The compost applied (every 3 years) in the experiment was characterized by the heavy metals content shown in Table 1) in accordance with the Polish standard BN-89/9103-09. The experiment was carried out for four increasing doses of fresh "Dano" compost ($7\,t\,ha^{-1}$, $14\,t\,ha^{-1}$, $21\,t\,ha^{-1}$ and $28\,t\,ha^{-1}$,), which satisfied respectively 25%, 50%, 75% and 100% of forage beets nitrogen requirements. In the experiment, three test

Table 1. Total content of some heavy metals in compost "Dano".

	Zn	Cu	Pb	Cd	Ni
Content	mg kg^{-1}				
maximum	1978.1	665.6	686.0	13.9	58.6
minimum	1010.7	113.5	251.0	3.3	21.1
mean	1443.9	304.0	448.0	7.4	36.9
W*	18.9	48.3	19.2	31.7	27.8

* W – variability coefficient.

crops were grown in following sequence: forage beets, spring barley and Italian ryegrass. Soil samples were collected three years after application of compost. The heavy metal (Zn, Cu, Pb, Cd, Ni) content of the samples was determined after dissolution in aqua regia and 1 M HCl. Zn and Cu determinations were performed using atomic absorption spectroscopy (AAS). Pb, Zn and Ni were determined with atomic emission spectroscopy (ICP). The analyses were carried out using the reference material 7001. The results obtained were subjected to statistical treatment with one- and multifactorial variance and regression analysis methods. The significance of differences between the means characterizing the factors studied was estimated by Tuckey's test with $\alpha = 0.05$.

3 RESULTS AND DISCUSSION

The content of heavy metals in city refuse compost is one of the most important parameters, characterizing the usefulness of these materials as fertilizers. In the "Dano" compost analyzed, zinc had the highest and cadmium, the lowest content of all heavy metals studied. The heavy metals content in compost increased in the following sequence: Cd < Ni < Cu < Pb < Zn. All studied elements showed a greater variability in content than macroelements. During the study period, the copper content had the greatest variability coefficient, while Zn and Pb had the most stable contents (Table 1, Figures 1–5).

Similar trends in the changes of heavy metals content in "Dano" compost from Warsaw were also reported by Chwastowska et al. (1993).

The content of all heavy metals studied was, as a rule, greater in the winter and spring months compared with the last two quarters of the year (Table 2). The results of studies reported here, are in partial agreement with other work by Rosik-Dulewska and Karwaczyńska (1999). These authors analyzed the heavy metal content in compost from Katowice and noted similar relationships regarding Zn and Cd. Cu, Pb and Ni however, showed a contrary trend. These differences may be caused by the differing sources of the wastes used for composting and their different morphological composition. This, according to some authors (Pascual et al. 1997, Jordao et al. 2006, Sharma et al. 1997) is the main factor affecting the chemical composition of the product.

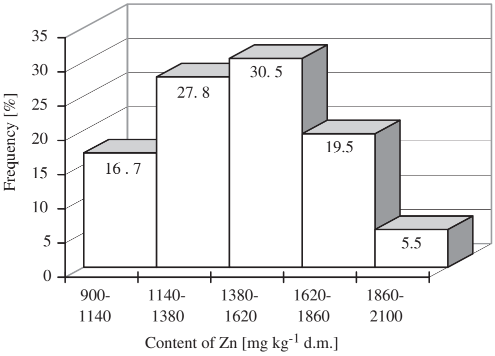

Figure 1. Frequency of compost samples with different content of zinc.

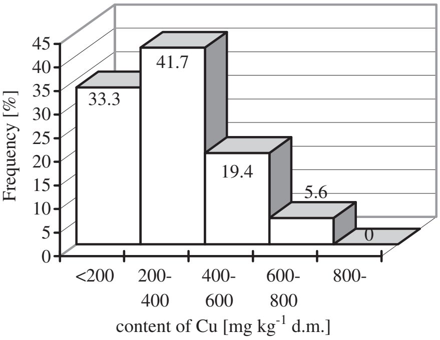

Figure 2. Frequency of compost samples with different content of copper.

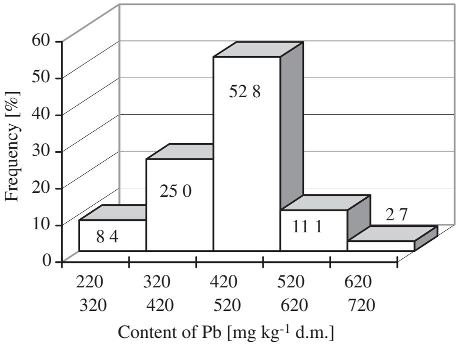

Figure 3. Frequency of compost samples with different content of lead.

On the basis of the strict relationship between the dose of compost and the total content of heavy metals

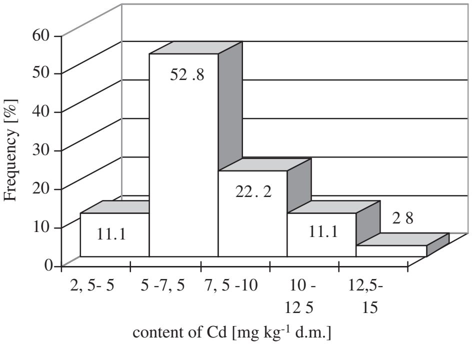

Figure 4. Frequency of compost samples with different content of cadmium.

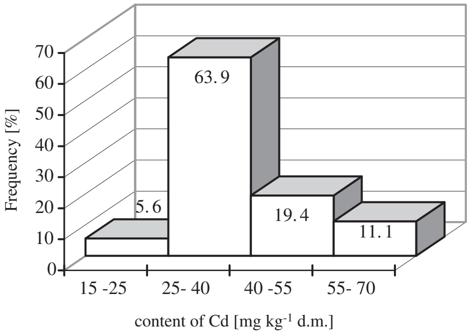

Figure 5. Frequency of compost samples with different content of nickel.

Table 2. Total content of heavy metals in compost "Dano" in dependence on terms of taking of compost samples.

Quarter of year	Zn	Cu	Pb	Cd	Ni
	mg kg^{-1}				
I	1600.0	381.6	436.5	9.07	46.5
II	1615.3	353.5	496.6	7.21	31.2
III	1403.5	239.4	432.6	6.71	31.8
IV	1156.5	241.4	426.2	5.93	32.6

in soil (Table 3), the range of their uptake by plants, and also the soil and climatic conditions of the experiment, it is possible to present an approximate prediction of the consequences of long- term compost application on farmlands.

Both, the total content and the HCl (1 mol dm^{-3}) soluble form content, of heavy metals in soil plough layer increased with increasing "Dano" compost dose. However it should be emphasized, that even the highest dose of compost did not cause exceeding of the I grade of soil contamination with heavy metals.

Table 3. Correlation coefficients between doses of compost "Dano" and total content of heavy metals in soil.

Metal	Dose of compost
Zn – zinc	0.89**
Cu – copper	0.91**
Pb – lead	0.94**
Cd – cadmium	0.92**
Ni – nickel	0.92**

** significant relation for $p = 0.01$

Table 4. Relationship between content of heavy metals soluble in 1 mol dm^{-3} HCl (Mr) in soil and total heavy metals content in soil (Mc) after three years application of compost "Dano".

Fertilization t f.m. ha^{-1}	Mr/Mc			
	%			
	Zn	Cu	Pb	Cd
0	51.7	34.0	61.3	58.8
Dano 20	50.2	36.7	58.2	54.3
Dano 40	55.8	37.2	59.7	57.1
Dano 60	62.4	47.2	61.7	56.5
Mean	55.0	23.8	60.2	56.7

From the point of view of assimilability of heavy metals by plants, the proportion of 1 mol dm^{-3} HCl soluble forms to the total forms of heavy metals is essential. Lead was characterized by the highest solubility (60% in relation to the total content of this element in soil), and copper had the lowest solubility (33%) of all heavy metals studied. The range of solubility of heavy metals can be presented, as follows: Pb > Cd > Zn > Cu (Table 4). Jordao et al. (2006) found that the content of heavy metals in soil after addition of urban waste compost from Rio de Janeiro increased as follows: Zn > Pb > Ni > Cu > Mn. The results obtained indicate that a single application of "Dano" compost in agricultural doses does not cause unfavorable changes in the soil environment.

Our calculations allow us to conclude that in conditions of long- term compost application, the safe level of heavy metals would be exceeded most quickly by nickel (in 12 years, while applying 28 t f.m. ha^{-1} of compost every 3 years) (Table 5). For zinc, for all dose ranges used, the time period needed to achieve the first grade of soil contamination is three times longer, than in the case of nickel. The first grade of soil contamination would be attained after 37 years of "Dano" compost application at a dose of 28 t f.m. ha^{-1}. For the remaining elements this period is still longer, and, in comparison with nickel is four times longer for copper and six times longer for cadmium. The least threat, from the point of view of soil contamination, appears

Table 5. Period (in years) when heavy metals content in soil will obtain the first degree of soil pollution as a results of compost "Dano" application single in three-year crop rotation.

Doses of compost t d.m. per ha	Zn	Cu	Pb	Cd	Ni
7.0	190	213	423	330	50
14.0	79	99	206	141	21
21.0	50	64	136	90	15
28.0	37	48	101	66	12

in relation to lead. The first grade of soil contamination would be achieved after 101 years of compost application at a dose of 28 t f.m. ha^{-1}, and even after 423 years of application of 7 t f.m. ha^{-1} of compost (Table 5). According to the time period, after which the safe (I° grade of soil contamination according to Kabata–Pendias et al. (1993) level of heavy metals in soil would be surpassed , the sequence of the elements is as follows: Ni > Zn > Cu > Cd > Pb (Table 5).

These studies on the heavy metal contents in city refuse composts produced according to "Dano" technology indicate that introducing them to soil will firstly cause the liberation of those elements which are predominantly bound in exchangeable and carbonate fractions, i. e. chromium, cadmium, zinc and nickel. However, lead is the element which is found mostly in slightly soluble form (mainly bound with iron and manganese oxides) in composts. This situation causes the liberation of lead to soil to be much slower (Evans 1989).

On the basis of calculations it can be concluded that the relatively high heavy metal content in "Dano" compost may be an obstacle to its repeated application on farmlands, even if the regulations concerning the use of city refuse composts were observed. McGrath et al. (1994) obtained similar results, while applying sewage sludge. Even twenty five years after the last application of sewage sludge, they found that 71–96% of heavy metals introduced to soil still remained in the upper layer. Both sewage sludge and city refuse composts contain significant quantities of heavy metals which are chelated with organic matter. During decomposition of organic matter, the heavy metals are liberated and then bound by soil components (Woodbury 1992). During this time the uptake of heavy metals with crop yields is inconsiderable. As Gorlach (1996) reports, the share of heavy metals removed with crop yields during one year, with the quantities assumed in soil and plants, is low and amounts to between 0.02% for lead and 0.33% for cadmium and zinc, of their total content in the plough layer of soil. It should be emphasized that the increase of heavy metals in soil after consecutive three-year periods of compost application will not be equal for particular metals. This is caused by the different intensity of leaching and absorption of heavy metals by plants. The solubility of heavy metals in soil, and thus their susceptibility to leaching and uptake by crops depends both on soil properties and metal (Evans 1989). For example, the binding ability of lead is much greater even at $pH = 4.0$; than of cadmium at $pH = 6.0$. Considering the greater mobility of zinc and cadmium in the soil environment and their high coefficients of bioaccumulation in plants (Deportes et al. 1995), it can be concluded that the time period needed to exceed the I grade of soil contamination with these elements will be long. In the case of lead, the element is strongly bound by soil, and thus absorbed by plants in small quantities (Woodbury 1992), the opposite tendency will occur. The time period needed to exceed the I grade of soil contamination with lead, will be shortened after consecutive three-year periods after application of compost.

4 CONCLUSIONS

1. Application of "Dano" compost over several dozens of years in reasonable doses, satisfying 25–50%, of the plant nutritional requirements leads to the exceeding of I° grade of soil contamination with heavy metals.
2. After long-term application of "Dano" compost in agricultural doses, the safe level of heavy metals in soil will be exceeded most rapidly by nickel. The ranking of the elements arranged according to the time period needed to exceed the safe content of heavy metals in the ploughing layer of soil, is as follows: Ni > Zn > Cu > Cd > Pb.
3. The "Dano" compost, although containing significant quantities of heavy metals, if only used in three-year crop rotation in agricultural doses (20, 40, 60 t f.m. ha^{-1}) on coarse soil, increases the total and HCl (1 mol dm^{-3}) soluble forms of heavy metals in the soil plough layer. However, the admissible standards of the content of these metals in soil are not exceeded.

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The possibilities of natural management of the ashes from the Bełchatów power plant

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ABSTRACT: The site used for the dumping of ashes and slags coming from the Bełchatów power station is the biggest "wet" site with landfill of this type in Poland. The cup of the dump embraces about 150 ha. In this paper we present data on the chemical properties of ashes stored at the dump. For the purpose of assessing these, samples of ashes were taken from the slopes surrounding the dump. The reaction and contents of micro- and macroelements were determined. The results indicate that the ashes are characterized by a basic reaction and high contents of macro- and microelements. At the same time, the content of heavy metals in ashes does not exceed the permissible value at natural sites using waste. The ashes derived from brown coal combustion may be applied in sewage sludge treatment. The addition of brown coal ash to sewage sludge caused a decrease in the heavy metal content compared to the sewage sludge itself.

Keywords: Ashes; macro- and microelemnts content; Bełchatów power plant; sewage sludge.

1 INTRODUCTION

In 2004, 6.3 million tons of ashes originating from combustion of brown coal were produced in Poland. Unfortunately, 70% of this remained on disposal sites. Only the gesso (gypsum) originating from fuel desulphurization is fully used in production of construction materials. In the Polish energy sector, ashes high in calcium are derived mainly from brown coal combustion or coal combustion in fluid boilers. These ashes are least managed because of lack of experience and the necessary technology. Up to now hundreds of millions of tons of such wastes have been stored at Polish disposal sites. The wastes from Bełchatów power plant have been gathered in the Bełchatów mine for a considerable time. This power plant produces annually 3.3 million tons of furnace wastes (ashes and slags). In the years 1981–1992, the all these wastes was located at the "Lubień" disposal site, out of the reach of Bełchatów exposure. This site occupies an area of 4.4 km^2 and contains 65 millions m^3 of wastes. In 1993 storing ashes at the "Lubień" site was ceased, and the practice of depositing all furnace wastes, after mixing with overlayer material, on the internal waste tip of the Bełchatów exposure, was begun. However, it soon became clear that, also at this dumping site, storage of ashes was exerting an unfavorable effect on the zone above the subterranean water table. The contamination derived from wastes are displaced to this zone by way of infiltrating rainwaters.

The purpose of this paper is the assessment of the possibility of environmental use of ashes from brown coal. We also attempted to limit the activity of heavy metals in sewage sludge using the addition of ash from brown coal.

2 MATERIALS AND METHODS

2.1 *Characteristics of the "Bełchatów" S.A. Power plant disposal site*

The "Lubień" ashes and slags disposal site, at which the brown coal ashes are being deposited is situated in the macroregion of Nizina Południowowielkopolska in the west of Poland. The area of the disposal site is a natural basin surrounded by knolls and sand-dunes. The basin is open to the southeast. It is located at a distance of 4 km north of the Widawka river valley about 0.5 km from the Struga Żłobnicka valley (Mastalski et al 1998).

The furnace wastes disposal site "Lubień" is a "wet" dump. Ash and slag from the "Bełchatów" power plant, after mixing with water in dredge pumping stations, is pumped, as a pulp, to the dumping sites in pipelines. The dumped wastes are sedimented and the excess water is intercepted by overflow wells and sent to recirculation. During operation the dump is constructed in pyramidal form. The embankment is constructed of deposited material. It is the largest disposal site for such wastes in Poland. It occupies an area of about

4.4 km^2; the cap of the dump comprises 150 ha. There is about 65 millions m^3 of waste at the disposal site.

Currently, the "Lubień" site is gradually closing down. The quantity of wastes arriving at the site bas been considerably reduced from 4.1 million tons in 1988 to 0.9 million tons in 2000. The slope of the dump has been partially reclaimed, and now it is covered by many plant species, such as red fescue, perennial rye-grass, privet, sea buckthorn, eleagnus oleaster, downy mountain willow, maple, birch and false acacia. However, the problem of the cap of the dump remains without a solution.

2.2 *Collection of samples for analysis*

Ashes have been deposited at the "Lubień" site for more than 20 years. The collected samples include ashes of approximate age 2–25 years. In order to collect samples from the dump, the plants growing on the slopes of the disposal site were removed, and eighteen samples were collected from a depth of 0.5 m. The individual samples were taken from different parts of the tip and differed in their duration of storing. The effect of addition of brown coal ash on the reduction of heavy metal content in sewage sludge was also studied by preparation of mixture of ash with sewage sludge in proportion 2/3 sewage sludge and 1/3 brown coal ash.

2.3 *Chemical analysis*

In the samples of ashes collected from the dump, the following parameters were determined:

- reaction – pH in 1 mol dm^{-3} KCl,
- total contents of selected macro- and micronutrients and heavy metals, after hot extraction in 1 mol dm^{-3} HCl: the potassium content was determined by flame photometry, the calcium, magnesium, manganese, zinc and copper content by atomic absorption spectroscopy, the cadmium and lead content by atomic absorption in a graphite cuvette.

In the samples of sewage sludge and the mixture sewage sludge and ash, the following were determined:

- total contents of chosen macro- and microelements and heavy metals, after hot extraction in 1 mol dm^{-3} HCl: the potassium content was determined by flame photometry, the calcium, magnesium, manganese, zinc and copper content by atomic absorption in flame, the cadmium, nickel and lead content by atomic absorption in a graphite cuvette. The nitrogen content was determined with the Kjeldahl method modified.

3 RESULTS AND DISCUSSION

The differences in the content of particular elements in the studied ashes, resulted rather from the chemical composition of the coal burnt, than the duration of ash storage. However, the period of storage did affect the physical properties of ashes. After only a few years of storage the ashes and slags are subject to caking and hardening. These processes occur especially with ashes stored with the "wet" method. For that reason, the disposal sites are constructed with plane, leveled and consolidated surfaces. The hardening of the ash mass occurs under the influence of CO_2 fixing by calcium carbonate formed as a result of reaction of carbonic acid anhydride with calcium hydroxide (Gilewska 2004).

Table 1. Reaction and content of macro- and micronutrients at a disposal site for power plant ashes.

Storage time	pH	Ca	Mg	K	Mn	Zn	Cu	Cd	Pb
		g kg^{-1}			mg kg^{-1}				
25	7.2	98.4	7.2	4.4	279.6	187.5	1.57	0.62	3.78
24	7.4	92.8	4.5	4.6	300.1	156.0	1.96	0.32	3.98
22	7.5	130.3	5.0	4.5	395.5	226.5	1.38	1.23	9.56
21	7.6	145.9	4.3	4.3	384.5	189.8	2.07	0.99	9.41
19	7.7	67.9	5.7	3.4	329.4	185.3	2.05	0.89	4.65
18	7.8	68.9	5.8	3.3	340.6	227.3	1.78	1.01	4.75
17	7.8	95.7	5.8	4.8	314.4	146.3	3.15	1.09	7.21
16	7.8	92.5	5.9	4.8	322.6	188.3	3.20	1.14	7.44
13	7.7	84.1	4.8	4.1	272.9	120.0	2.32	1.42	5.74
12	7.7	81.8	5.0	4.0	291.3	128.3	2.65	1.35	5.65
10	7.9	126.9	6.4	3.8	347.1	147.0	1.30	0.72	5.02
9	7.9	141.3	6.6	2.7	241.6	136.5	1.14	0.69	4.93
7	7.8	44.6	4.4	2.7	179.6	236.3	0.94	0.65	3.20
6	7.8	44.9	4.5	2.8	180.3	222.0	0.98	0.42	2.81
4	7.9	169.2	8.2	2.5	291.3	129.0	1.27	1.01	3.21
3	8.0	168.1	8.0	2.4	282.5	126.0	1.11	0.85	3.32
2	7.8	125.2	5.2	2.7	193.6	148.5	2.72	1.10	4.01
1	7.9	129.3	4.9	2.7	189.9	150.8	2.61	0.96	4.23

The studies concerning the chemical composition of brown coal ashes indicate that these ashes are multicomponent mixtures. Their main components are aluminum (determined as Al_2O_3) and silicon (determined as SiO_2), which are present, globally in 70–75% of the wastes analysed (Kalembasa, Tengler 1992, Kovács, Mang 2002, Ural 2005).

The ashes derived from brown coal burning in the "Bełchatów" S. A. power plant are characterized by a very constant chemical composition, which is not subject to changes under influence of storage time (tab. 1).

The ashes studied are alkaline – the pH values determined in 1 mol dm^{-3} KCl are in the range 7.2–8.0. This appears to result from the high content of alkaline metals, such as calcium, magnesium and potassium. The total calcium content is between 45 and about 170 g kg^{-1}, magnesium –4.0–8.0 g kg^{-1}, and potassium –2.4–4.8 g kg^{-1} (tab. 1). Similar contents of

Table 2. The heavy metals content in hard and brown coal ashes, average for EU countries (for more than 300 samples).

	Hard coal	Brown coal	Admissible content*
Element		mg kg^{-1}	
As	6–117	16–144	
Cd	0.1–5.1	0.6–1.5	20–40
Cr	20–330	33–305	
Cu	52–264	18–131	1000–1750
Hg	0.0–1.7	0.0–0.9	16–25
Ni	28–249	41–280	300–400
Pb	9–660	7–64	750–1200
Zn	28–533	34–320	2500–4000

* according to EU directive 86/278/EEC.

Table 3. The content of heavy metals in sewage sludge and sludge treated with brown coal ash.

	Mn	Fe	Cd	Ni	Zn	Cu	Pb
Fertilizer	mg kg^{-1}						
Sewage sludge	759.0	3316.6	2.49	430.1	1443.8	324.5	15.8
Sewage sludge with ash	427.1	3734.2	2.44	32.5	746.5	149.5	11.2

these elements were also observed in dry ashes from "Konin" and "Adamów" power plants in studies by Gilewska (2004), Kovács, Mang (2002), Jala, Goyal (2006), Ural (2005).

Low quantities of heavy metals (manganese, zinc, copper, cadmium and lead) were also found in the analysed ashes. The content of manganese varied between about 180 and 400 mg kg^{-1}, the zinc content-between 120 and 140 mg kg^{-1}, the copper content –0.98–3.20 mg kg^{-1}, the lead content –2.81–10.41 mg kg^{-1} and the cadmium content 0.32–1.42 mg kg^{-1}. These are lower than the values observed by Gilewska (2004). The heavy metal contents in ashes from Bełchatów power plant, which were observed in our study, were relatively low and did not exceed the values determined in ashes derived from burning of brown coals in the European Union (Kyte et al. 2000). Neither did they exceed the admissible heavy metal contents in sewage sludge destined for fertilization, according to European Union directive (86/278/EEC) (tab. 2).

In spite of the fact, that the lower slopes are partly reclaimed, and are covered by many plant species, the problem of reclaiming the cap of the dump still remains, because it is indispensable in limiting dust emissions to the atmosphere. Unfavourable physical properties (quick hardening of ash mass) makes proper plant rooting difficult, resulting in dwarfed and dried-out plants. The development of plant cover is also made more difficult by the alkaline reaction. Water deficiency is another factor limiting plant growth. The optimal humidity of ashes is between 29 and 32%, but a considerable portion of water in them is unavailable, as for example hygroscopic water (Gilewska 2004). The low amount of nitrogeneous compounds available to plants is also a peculiarity of the ash rock. This element is present in ashes mainly in the residues of unburnt coal. A wide C/N ratio renders decomposition of organic substances present in ash difficult. For this reason, plants introduced to disposal sites, suffer nitrogen deficiencies (Gilewska 2004). Phosphorus is another nutrient limiting plant development, because it occurs mainly in compounds unavailable for plants, as for example aluminum and iron phosphates, according to Łączny (1983).

In addition to the worsening of landscape amenities, the "Lubień" disposal site contributes to pollution of the atmosphere by emission of dust containing heavy metals. In view of the difficulties involved in reclaiming disposal sites, a more active programme to limit the storage of ashes should be pursued. The ashes derived from brown coal combustion may be applied in, among other things, the production of building ceramics, concrete, cement, hydraulic binders, and also in fertilizing, sewage sludge treatment and compost production (Kovács, Mang 2002, Manz 1997, Jala, Goyal 2006). Moreover, as studies carried out in the EU indicate, the grassing of ash disposals is not the only method for their reclamation. Considering similar properties of ash mass and soil, these areas may be used for agricultural purposes (Kyte et al. 2000).

The addition of brown coal ash to sewage sludge caused a decrease in the heavy metals content in comparison with the sewage sludge itself (tab. 3).

The brown coal was mostly effective in reducing the Ni content, which was diminished by 92% in comparison to sewage sludge. Other metal concentrations were reduced as follows: Cu by 54%, Zn by 48%, Mn by 44%, Pb by 29% and Cd by 2%. Increases in the iron and magnesium contents by 13% and 5%, respectively compared to sewage sludge alone were found, as well as decreases in nitrogen (by 50%) and potassium (by 77%).

The reduction of content of heavy metals in the studied mixture is caused by the alkaline reaction of the added ash (pH = 7.2–8.0). As other authors have pointed out, the content of calcium oxides, which determine the reaction of the ash, may reach 50% d.m. of the ash (Ural 2005). However, the reduction of nitrogen content is caused by the low content of this element in the ashes (from ca. 0.1 g kg^{-1} when stored as pulp to 2.0 g kg^{-1} when stored in the dry state) (tab. 4).

Moreover, this element is found mostly in the remains of unburnt coal, which is decomposed only

Table 4. The content of heavy metals in sewage sludge and sludge treated with brown coal ash.

	N	K	Mg
Fertilizer	g kg^{-1}	mg kg^{-1}	
Sewage sludge	37.5	3706.2	2068.7
Sewage sludge with ash	18.6	868.3	2176.2

with difficulty because of the broad C/N ratio noted in ashes (Gilewska 2004).

4 CONCLUSIONS

1. Tested ashes from brown coal combusted in the Bełchatów power plant are not a risk to the natural environment. The heavy metal contents of ashes from the Bełchatów power plant were relatively low and did not exceed the values typically determined in ashes derived from burning of brown coals elsewhere in the European Union. Furthermore, these concentrations did not exceed the admissible heavy metals contents in sewage sludge allowed for fertilization, according to a European Union directive.
2. The ashes derived from brown coal combustion may be applied in sewage sludge treatment. The addition of brown coal ash to sewage sludge caused a decrease in the heavy metal content in comparison with the sewage sludge itself.

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Methane fermentation as a pro-ecological method of biogas generation and of sewage sludge and vinasse utilisation

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ABSTRACT: The comparison of a quasi-continuous methane fermentation process, on two kinds of organic waste: sewage sludge and vinasse is presented in the work. The quantity of biogas generated from every kind of the examined matrixes has been determined. For both matrixes the quality of the generated biogas, determined by the contents of methane and carbon dioxide, have been investigated. The degree of reduction of dry organic mass as well as the yield and material efficiency of the process have been determined for the examined substances. It is determined by the quantity of the biogas generated in between the dosing of the fresh portion of the examined organic matrix into the digestive chamber.

Keywords: Biogas, methane fermentation, methane, sewage sludge, vinasse.

1 INTRODUCTION

Methane fermentation is the microbiological and biochemical process of anaerobic digestion of complicated organic compounds into simple, stable forms. The final product of the process is biogas containing, in addition to a variety of volatile organic compounds, mainly methane and carbon dioxide.

The process of methane fermentation is a very complex phenomenon. For convenience it is usually divided into four stages. The criteria for this division are based on the variety of microorganisms taking part in each of the following stages (Denac 1988, Al-Masri 2001, Kashyap 2003, Sreekrishnan 2004):

- stage I – *hydrolysis* of water insoluble components of the fermentating matrix;
- stage II – *acidogenesis* – conversion of the products from stage I into volatile fatty acids, mainly into acetic and propionic acids;
- stage III – *acetategenesis* – transformation of volatile fatty acids into acetates;
- stage IV – *methanegenesis* – the methane and carbon dioxide synthesis from the products obtained in the stage III.

For technological reasons, the aforementioned division has been reduced to two stages, the first of which includes the stages of hydrolysis, acidogenesis, and acetategenesis and is called in short, acid fermentation.

In a reactive environment, all four stages of fermentation take place in parallel, and the effectiveness of each depends on the operating conditions process and the composition of the fermenting waste. The final efficiency of the process is determined by the slowest of the stages, which is the methanegenesis stage (Denac 1988, Al-Masri 2001, Kashyap 2003, Sreekrishnan 2004).

Methane fermentation is an effective method of generating biogas, reduction, and stabilization of organic material resulting from many biological waste products. The utilization of these is often impossible due to their characteristic features. The waste products are the following: sewage sludge, floral biomass, animals fecal matter, manure, municipal and industrial waste, for example, vinasse derived from spirit production (Viswanath 1992, Sarada 1994, Nallathambi-Gunaseelan 1997, Murphy 2004).

Sewage sludge is a complicated mixture of organic compounds, comprised mostly of amylum, cellulose, carbonates, fats, and proteins. All these ingredients are susceptible to the reaction of enzymes of methane bacteria. Depending on the partition of each substrate in the sewage sludge, the amount and composition of generated biogas may vary (Nallathambi-Gunaseelan 1997, Górski 2002).

Apart from organic compounds, the sewage sludge contains many ingredients, like: water, sulphur and phosphorus compounds, carbonates, ammonia, ammonium salts, and metals, including the heavy ones (Cimochowicz-Rybicka 2001). The presence of inorganic compounds may have enormous influence on the course of processes taking place during fermentation. Depending on the quantity of inorganic compounds, their presence in sewage sludge can be required or disturbing for the proper course of the process (Hansen 1998, Mandal 1998, Maćkowiak 2000, Zayed 2000, Sterling 2001).

Vinasse is the waste product obtained from the alcoholic fermentation of beetroot molasses. Molasses is a dense and adhesive liquid, containing high quantities of sugars, mainly glucose, fructose, and sucrose and large amounts of iron, calcium, potassium, and copper. The individual chemical composition of molasses strongly depend on the conditions of beetroot growth, the method of fertilization, and technology of sugar production.

Apart from alcohol production, molasses is used as an additive to fodder and also in baker's yeast production.

The current work describes the process of quasi-continuous methane fermentation, involving two troublesome organic wastes: sewage sludge and vinasse. The process has been implemented, adopting fermenting microflora grown in the industrial tanks of a mechanico-biological sewage treatment plant, during anaerobic decomposition of vinasse organic material.

The process has been described by the quantity and composition of biogas obtained during fermentation. The analysis of obtained biogas has been performed. It was carried out for each of the examined matrixes, and for the intermediate stage of the experiment, in which fermentation of the mixture of sewage sludge and vinasse has taken place.

A comparison of the efficiency of each examined matrix has been performed and it has been determined as the proportion of the amount of obtained biogas to decomposition stage of dry organic mass.

2 EXPERIMENTAL PART

2.1 *Apparatus*

The process of sewage sludge and vinasse methane fermentation, has been carried out in the glass reactor with capacity of about 42 dm^3, equipped with an electric motor, mechanical stirrer and heating water jacket. The reactor was thermstatted to ±1°C. A scheme of the reactor is presented in Figure 1.

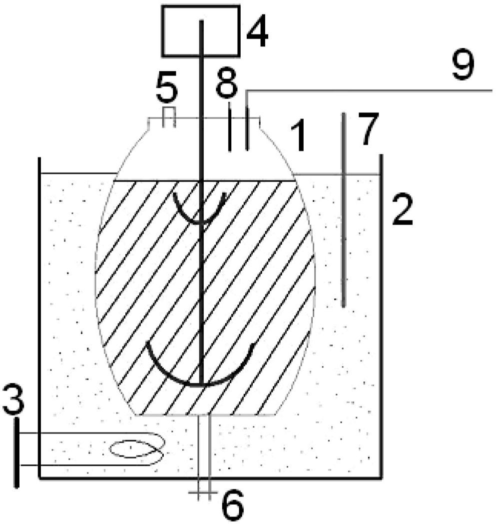


Figure 1. Scheme of experimental reactor, 1. Fermentation chamber 2. Water jacket 3. Heater with a thermostat 4. Electric engine with a mixer 5. Supply of fresh molasses 6. Disposal of post fermented molasses 7. Temperature measurement 8. Biogas disposal 9. Excess biogas disposal.

2.2 *Comparison of specific physico-chemical parameters of matrixes used during fermentation process*

Table 1 shows a basic physico-chemical parameters of the wastes used during the experiment.

Table 1. Physicochemical properties of examined matrices before fermentation.

		Matrix	
Parameter	Units	Sewage sludge	Vinasse
pH		6.85 ± 0.05	6.92 ± 0.05
Dry matter	[%]	5.54 ± 0.02	9.46 ± 0.02
Dry inorganic matter	[%]	3.15 ± 0.8	6.58 ± 0.6

The experiment was designed in such a way that the dry mass contents of vinasse were double that of the contents of dry mass of sewage sludge. The aim of such proceedings was to ascertain the possibility of adapting fermenting bacteria, in relation to altering the operating conditions of the process.

2.3 *Procedures*

The synthesis of biogas from vinasse was carried out by means of mezophile methane fermentation, conducted in a quasi-continuous form of isothermal reactor. Sewage sludge was applied as a source of bacterial flora (mainly: *Methanobacterium bryanti, Methanobacterium formicium, Methanobrevibacter arboriphilus, Methanobrevibacter ruminantium, Methanosphaera stadtmaniae, Methanococcus vanieli, Methanomicrobium mobile, methanospirillum hungatei, Methanosarcina vacuolata, Methanothrix soehungenii* (Zinder 1979, Ollivier 1984, Zinder 1984,

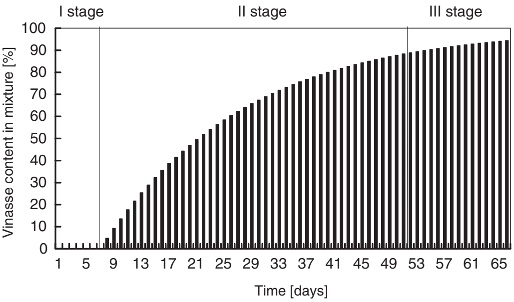


Figure 2. Changes in vinasse concentration during experiment time.

Touzel 1985, Clarens 1990, Shcherbakova 1991, Strevett 1995, Ilyin 2004)), indispensable for the initiation of a microbiological process in the reactor. The sewage sludge and was taken from separate fermentation tanks of a mechanico-biological water sewage treatment. The experiment was carried out for 66 days, and was divided into three significant stages. The first stage was aimed at modification of the microbiological balance existing in the fermenting mass of sewage precipitate taken from fermentation tanks, into a balance suitable for technological conditions, imposed in the reasearch reactor. The establishment of new balance was done seven days after the beginning of the experiment. In this period, vinasse was not added, and life in the digestion chamber was sustained by adding fresh portions of sewage sludge.

The next stage of the experiment was the modification of the fermentating composition of organic deposit, by means of gradual substitution of the former reactor charge. Modification of the reactor charge was carried out with a daily dosage of fresh vinasse in a rate suitable for sustaining the specified retention time of the reactor batch, and receiving the specific volume from the chamber. This part of the experiment has lasted for forty four successive days and led to total displacement of organic deposit, together with modification of bacterial flora suitable for vinasse materia fermentation process. The scheme of vinasse concentration changes in the reactor during the experiment is shown in Figure 2.

The proper synthesis of biogas from organic material of vinasse took place in stage III of the experiment, after 51 days of fermentation. After this period total stabilization of the process was noted. Stage III lasted 15 days and was focused on carrying out indispensable measurements. They were necessary to draw out the description of vinasse decomposition and defining its effectiveness (Figure 2).

The operational parameters of the laboratory experiment in the reactor were specially selected, so as to allow the execution of a high-fidelity simulation of the process taking place on the industrial scale. The conditions held in the fermentation cell were as follows:

- Temperature of the process: 38 ± 0,3°C;
- Retention time of vinasse in reactor: 21 days;
- Frequency of vinasse dosage to reactor: once per day.

In order to achieve the correct description of the examined phenomenon, and define the effectiveness of fermentation, the following parameters of the process have been analysed:

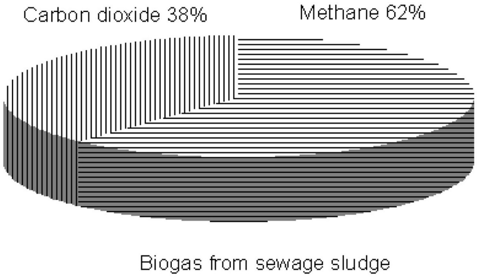
- Temperature – constant measurement. The measurement was carried out by means of electronical thermometer of DT 1 type with the scope of measurement ranging from −30°C to 120°C;
- The amount of obtained biogas – one measurement per day was carried out three hours after the last dosage of fresh vinasse, one measurement per one hour was done additionally for the period of two days. The amount of gas was determined on the basis of time measured during filling the calibrated glass vessel of capacity 200 cm^3.
- The average daily amount of the obtained biogas was determined by measuring the surface area under the curve showing the dynamics of daily biogas generation.
- The amount of basic components of the obtained biogas (CH_4, CO_2) – altogether five measurements, were carried out just before the dosage of fresh vinasse. The measurement was carried out by means of portable gas analyzer type Gas Data LMSx, calibrated by means of a gas chromatograph with mass spectrometer and katharometer;
- Reaction, dry, organic and mineral mass – the measurements were done for sewage precipitate and vinasse. In case of both matrixes, the analysis was carried out from reactor batch and samples obtained from fermentation;
- Contents of alkaline and heavy metals – these measurements were done for products obtained from fermentation.

3 RESULTS

3.1 *The quantity and quality of obtained biogas*

The contents of basic components of biogas, obtained in the first and third stages of the experiment, conducted at a temperature 38 ± 0,3°C, are presented in Figure 3.

The above diagram shows how the content of generated biogas changes, depending on the composition of organic mass it contains. The difference in biogas composition may prove the activeness of other stirps of fermentation microorganisms taking part in processing of specific organic material. The amount of



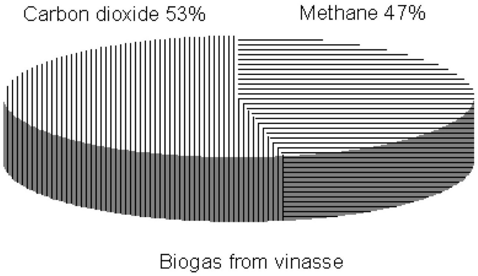


Figure 3. Comparison of biogas content between different sources of fermentation.

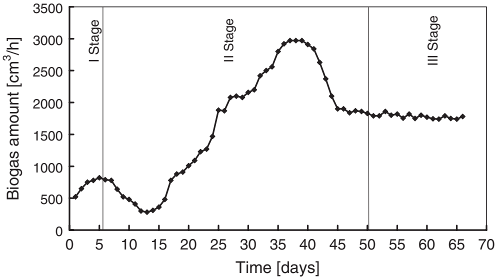


Figure 4. Changes in biogas content during experiment time.

carbon dioxide formed may be multiplied by high susceptibility of vinasse ingredients to bacteria, which take part in acidgenesis process, and at the same time decrease the activity of autotrophic methane bacteria.

The relation of the quantity of the obtained biogas to the duration of the experiment is presented in Figure 4.

The above diagram, clearly outlines the borderlines between the three stages of the experiment. In the first stage, the microbiology of the system has well suited to new conditions existing in the experimental fermentation cell. It has also regenerated after the thermal shock appearing during filling the reactor with sewage sludge. The growth of amount of generated biogas in the period from the first to the fifth day, and late stabilization in the period from the fifth to the seventh day reflects the high abilities of the bacterial flora to acclimatise to the sewage precipitate. This has enabled the further modification of the conditions existing in the fermentation cell through the gradual enrichment of the reactor contents in vinasse.

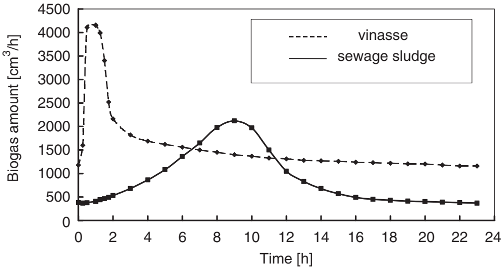


Figure 5. Twenty-four hours distribution of biogas content.

The period of the experiment from the eighth to fifty-first day revealed very changeable effectiveness of biogas production, ranging from 280 to 3 000 cm^3/h. It may reflect high transformation of the biological system of fermentation. After a preliminary decrease in the efficiency of the process, which is typical of sudden change of conditions existing inside the cell; there was a remarkable improvement of biogas synthesis, starting with the thirteenth day of the experiment. After short-term stabilization of the efficiency, ranging about 3 000 cm^3/24 h within the period from the forty-first to forty-fifth day of the experiment, there was a sudden decrease of biogas production to the level, in which the constant stability of methane fermentation process took place. In this period of time, the dynamic biogas production reached the level of 1800 cm^3/h. The fifty-first day was taken as the beginning of the third stage, in which vinasse was the sole component of the fermentation chamber.

The dependence presented above has been outlined on the basis of quantity of biogas, measured each time with a three-hour interval, after applying the fresh vinasse dosage.

Figure 5 displays the scheme of daily intensiveness of biogas production in the first and third stage of the experiment.

The intensity of the fermentation also changed daily. This effect was the consequence of the method of dosing into the chamber fresh portions of fermenting matrix. This dosage took place with frequency once per day, what caused the high amplitude of age of the fermenting mass, in the period of one day. Adding to the system in the first stage of the experiment, the fresh dosage of sewage sludge, caused a small increase in the intensity of biogas production. Its maximum reached 2100 cm^3/h and took place in the ninth hour after dosage. After seven following hours, the efficiency of the reactor diminished to not higher than 400 cm^3/h. The described effect can be explained by the fast growth of the concentration of nutritious substances, available to microorganisms, dosed with the

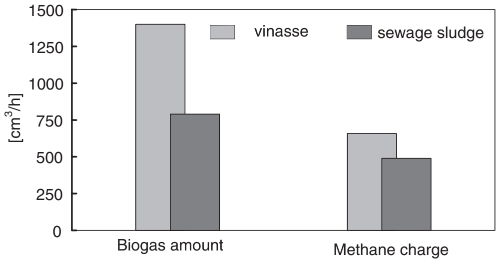


Figure 6. Comparison of biogas and methane content.

new portion of reactant. After dosing the fresh portion of vinasse in the third part of the experiment, there was a sudden increase in biogas synthesis. Its maximum reached 4100 cm^3/h and took place in the first hour after dosage. As the time went by, As the reaction time increased, the process stabilized, and the effectiveness oscillated at about 1200 cm^3/h. Differences in the shape of the curves can be explained by the differing bioavailability of dosed matrix in each of the described stage. In case of sewage sludge, most of nutritious substances were trapped in dead microorganisms of the active sewage sludge. This makes the material, inaccessible for the enzymes of fermented bacteria. In case of vinasse, the whole dosed organic matrix is situated within the vinasse, hence fermentative bacteria may have easier access to it. The consequence is fast growth of biogas synthesis. The average daily quantity of obtained biogas has been established on the basis of surface under the curves (Figure 5). Taking into account the defined density of methane in generating biogas, the average daily dosage of processed methane has been specified. A comparison of the quantity of obtained biogas and methane is presented in Figure 6.

The amount of biogas obtained in the third stage of the experiment, when vinasse was added to the process of fermentation, amounted to 1400 ± 100 cm^3/h. This makes almost double the amount than the case of sewage sludge, where the maximum amount reached 790 ± 60 cm^3/h of biogas. This difference may be explained by the much higher concentration of the dry mass in the vinasse.

In the case of methane, due to depletion of its contents in biogas obtained from vinasse, the of CH_4 processed from the vinasse is slightly higher and comprises 660 ± 50 cm^3/h, in relation to 490 ± 40 cm^3/h of sewage sludge.

3.2 *Comparison of physico-chemical properties of matrixes after fermentation*

The physico-chemical properties of sewage sludge and vinasse are shown in Table 2.

Examining the data from the above table, it can be seen that both matrixes subjected to the process are quite different, mostly in relation to their of contents of metals. The vinasse shows a higher concentration of alkaline metals, this is particularly clear in the case of potassium ions, whose contents are 45 times higher in vinasse, than in sewage sludge. The reverse is the case for heavy metals, the content of which is much higher in sewage sludge. This tendency is the most outstanding for copper ions (ca. twentyfold decrease of vinasse density) and nickel ions (sixfold decrease of contents).

Table 2. Physicochemical properties of examined matrices after fermentation.

		Matrix	
Parameter	Units	Sewage sludge	Vinasse
pH		7.41 ± 0.05	7.72 ± 0.05
Dry matter	[%]	3.90 ± 0.02	5.87 ± 0.02
Dry inorganic matter	[%]	2.01 ± 0.01	3.11 ± 0.02
Sodium	[mg/dm^3]	n. d.	2080 ± 30
Potassium	[mg/dm^3]	250 ± 4	11170 ± 59
Magnesium	[mg/dm^3]	5.0 ± 0.1	41.70 ± 0.90
Calcium	[mg/dm^3]	85.1 ± 0.3	923.2 ± 1.3
Cadmium	[mg/dm^3]	0.08 ± 0.01	0.10 ± 0.01
Lead	[mg/dm^3]	1.92 ± 0.43	0.40 ± 0.01
Nickel	[mg/dm^3]	10.1 ± 1.2	1.68 ± 0.30
Copper	[mg/dm^3]	10.3 ± 0.3	0.49 ± 0.04
Chromium	[mg/dm^3]	6.48 ± 0.02	0.12 ± 0.01

This imbalance, apart from the dry mass content, may significantly influence the change of mechanism of the process and its different course for each examined matrix. Contrary to the dry mass contents, in the case of metal ions, there was no way of selecting an optimum of concentration and consequently, we were unable to estimate the impact of their content on the course of the process.

Figure 7 shows the stages of reduction of dry mass and dry organic mass in the process of fermentation of the examined matrixes. The dependences are displayed as the proportional decrease of dry and organic mass content in relation to the raw material input of the each of examined matrixes.

As shown in Figure 7, the reduction of dry mass and dry organic mass was in both cases higher in vinasse, and amounted to 38% for the dry mass and 48.3% for dry organic mass. In case of sewage sludge, the results were 28,3% for dry mass and 36.of 2% for dry organic mass. The observed differences may be explained by the enlarged amount of biogas generated from vinasse, which is caused by higher contents of dry mass in this matrix and increased bioavailability of vinasse ingredients for fermentative microorganisms.

Figure 8 displays the efficiency of the process for the examined matrixes determined in m^3 of the

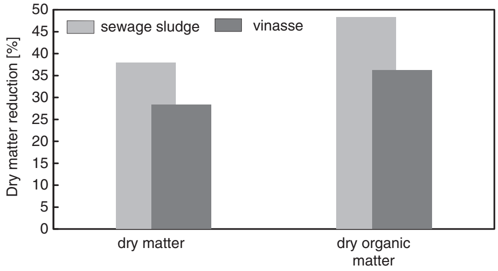


Figure 7. Reduction of total dry matter and total organic matter for sewage sludge and molasses.

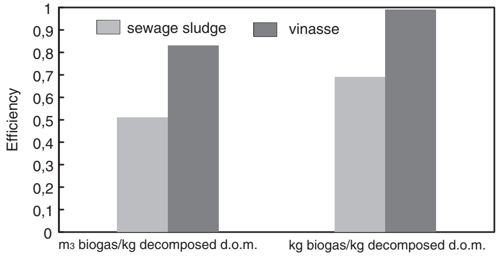


Figure 8. Efficiency of biogas production from sewage sludge and molasses.

obtained biogas per 1 kg of decomposed dry organic mass, for each of the examined matrixes.

As can be seen from Figure 8, the effectiveness of fermentation process is much higher for sewage sludge, in comparison to vinasse. In the case of sewage sludge, this parameter reached the value of 0.83 m^3 gas/kg decomposed dry organic mass, which resulted in 0.99 kg of biogas per kg of decomposed biomass. The process of fermentation based on vinasse resulted in 0.51 m^3/kg, which, converted into biogas mass resulted in 0.69 kg of gas per kg of decomposed dry organic mass.

The above values are caused by the differing mechanisms taking place in each matrix fermentation process. In the case of vinasse, biological conversion taking place in the reactor may be directed towards not only the biogas synthesis, but also the process of complete mineralization of organic material, the final products of which are carbon dioxide and water. Such a mechanism is also indicated by the increased contents of carbon dioxide in the biogas obtained from vinasse, and the higher relation of dry mass reduction to vinasse, caused by enrichment of the system in water produced during process of mineralization.

Methane fermentation of sewage sludge proceeded with an efficiency of almost 100%, which indicates the total decomposition of biomass of sewage sludge by means of methane fermentation, and consequently, potential utilization of this otherwise troublesome production waste. This technological process can be truly counted to those procedures carried out in accordance with the so-called green chemistry principles.

4 CONCLUSIONS

The following conclusions can be made based on the results of our experiment:

– anaerobic methane fermentation is an efficient method of obtaining biogas from both sewage sludge and vinasse – a waste product in alcoholic spirits production.
– due to the specific properties of vinasse compared to sewage sludge, caused by conditions of obtaining the former, the actual biogas production must be preceeded by a preliminary stage of obtaining the bacterial flora indispensable for starting biological processes. Fermenting sewage sludge, generated in typical mechanico-biological water sewage treatments, may be employed to this process. The growth of effective biological deposit, appropriate to the waste, may entail a couple of months. This period is determined by the hydraulic burden of the biological reactor, and for a retention period of twenty one days, has been determined to be about fifty days.
– the period, in which the enrichment of the system in vinasse took place, stood for high instability of work, observed by changeable amount of biogas, produced by the system, and different contents of methane in biogas. These changes have been caused by modification of bacterial stirps, indispensable to decomposition of organic deposit of changeable features.
– after homogenising the reactor contents caused by dislodgment of the whole sewage sludge by vinasse, the process of fermentation stabilized, the biogas production and its quality were stable, typical of new organic matrix, subjected to fermentation.
– in comparison to methane fermentation of sewage sludge, the process of obtaining biogas from vinasse, proceeded with a higher efficiency. Biogas production from vinasse increased by about 88% in relation to the total biogas production of sewage sludge.
– The ethane content in biogas processed during vinasse fermentation decreased in relation to sewage sludge fermentation from 62% to 47%. However, the remarkable growth in the amount of biogas caused by methane processed from vinasse increased in relation to methane from sewage sludge by about 75%.
– the shape of the curve of the daily amount of produced biogas from vinasse, in relation to that based on sewage sludge, reflects the high variability of efficiency, depending on the time passed

after the dosage of fresh vinasse. This is caused by higher bioavailability of organic ingredients of vinasse. This effect is observed only in cases of one-time dosage of major part of the fresh batch into the fermentation chamber, which must be semi-continuous, due to technical restrictions of the experiment. In industrial conditions, the efficiency of the process is constant, as a result of continuous exchange of vinasse.

- the efficiency of the process, determined by the amount of biogas calculated as the unit value of decomposed dry organic mass, attains different values for each of the fermenting matrixes. This reflects the various mechanisms proceeding in both matrixes.

ACKNOWLEDGEMENTS

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Miscellanea

Management of Pollutant Emission from Landfills and Sludge – Pawłowska & Pawłowski (eds)

Effect of hydrolysis of municipal sludge on biogas production in the digestion process

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ABSTRACT: One method of increasing the degree of fermentation and biogas production from sludge is to use two stage digestion, with prior hydrolysis.

The main purpose of this study was to find the effect of separation of hydrolysis phase on the degree of mineralization and biogas production.

The experiments were carried out on sludge samples taken from three Polish WWTP. Two series are reported for each sludge: one phase digestion with 21 days retention time and two phase digestion with 48 hours of hydrolysis and 21 days of methanogenesis.

Two-phase digestion of a mixture of primary and excess sludge resulted in volatile solid (VS) reduction from 56.2 to 65.2%, compared to 43.5–47.5% during one phase digestion. The one phase digester generated 0.28–0.40 m^3 of biogas per kg of VS, whereas, in the two phase digestion, the total biogas production was 0.46 to 0.63 m^3/kg VS.

Keywords: Two-phase sludge digestion, biogas production.

1 INTRODUCTION

Methane fermentation is the most popular method used by Wastewater Treatment Plant (WWTP) for anaerobic decomposition of organic matter in sludge. The processes of decomposition reduce the proportion of organic matter in the dry mass of the sludge down to about 50% and make it more stable. With a properly functioning sludge digester, it also produces:

- biogas composed of 70% of methane and 30% carbon dioxide,
- over-sludge liquor.

The process of digestion allows part of energy to be recovered, via the high energetic value of biogas (ca. 20 MJ/Nm^3) and, by reducing the number of bacteria, improves the hygienic quality of the sludge.

The process of methane fermentation is theoretically divided into four phases:

- hydrolysis phase,
- acidogenic phase,
- acetogenic phase,
- methanogenic phase.

During the hydrolysis phase the organic matter is most frequently decomposed by hydrolytic bacteria into simpler, water-soluble substances. Hydrolytic cellular enzymes are produced by such bacteria as: *Clostridium, Peptococcus, Vibrio, Micrococcus and Bacillus*.

In the acidogenic phase, the products of the hydrolysis are decomposed into simpler organic acids. For this reason, the acidogenic phase is characterised by a significant decrease in sludge reaction, even to pH about 5, which makes the development of methanogenic bacteria difficult or even impossible.

In the acetogenic phase, the acids created in the previous phase are decomposed into lower fatty acids, represented by acetic acid CH_3COOH, as well as into hydrogen and carbon dioxide. The acids produced are known collectively as total volatile acids (TVA), as their boiling points are lower than that of water. Two groups of bacteria take part in this phase. They are: obligate hydrogen producers, also referred to as proton reducers, which are able to develop only at a low concentration of hydrogen atoms. This group includes *Syntraphomonas volfei* and *Syntrophbacter wolinie*. They can live in symbiosis with methanogenic bacteria, which absorb hydrogen. Another reason for the symbiosis between these two groups of bacteria is balancing the reaction energy. Metabolic reactions are endogenous, and the energy required for their realisation has to be delivered from exogenous reactions, i.e., the production of methane.

The second group of bacteria taking part in the production of acetates includes homoacetogenes, which are purely anaerobic organisms. They catalyse the production of the acetic acid from hydrogen and carbon dioxide. This group includes: *Acetobacterium, Acetoanaerobium, Acetogenium, Butribacterium, Clostridium and Pelobacter* (Goel, 2002).

In the fourth phase, the methanogenic phase, methane is produced by methanogenic bacteria from the acetic acid, hydrogen and CO_2. During this phase, part of the organic matter is mineralised, and the volume of methane is proportional to the degree of mineralisation.

The methanogenic bacteria are absolute anaerobes. Since particular groups of those bacteria can decompose only selected well-defined groups of compounds, complete stabilisation of the sludge requires the action of many groups of these bacteria, such as: *Methanococcus, Methanobacterium, Methanobacillus, Methanosarcina*, etc. Two basic ways of bacteria-based methane production are: biological decomposition of the acetic acid and microbiological reduction of carbon dioxide.

From the practical point of view, two phases are important: the first three mentioned above, treated as the first one, occurring at low pH, and the fourth one, treated as the second, occurring by $\mathrm{pH} > 7$.

In most Polish WWTP the sludge is stabilized in a one-phase digestion process. The main goal of this process is to decrease the contents of organic matter in the sludge and its side effect is the biogas, produced by methanogenic bacteria. Theoretically, depending on the digestion temperature, the volume of biogas production can reach as much as 500 liters per kilogram of organic matter in the sludge. In practice, however, Polish waste water treatment plants yield much lower volumes of biogas, ranging from 0.139 Nm^3 in Pulawy to 0.254 Nm^3 in Zamosc. In this context all attempts to intensify the production of biogas are of considerable economical importance.

A promising method is two-phase digestion, with the primary hydrolysis phase carried out in a separate tank with short retention time. The preliminary acid hydrolysis, carried out in a separate tank, was examined in pilot and full technical scale at the Woodridge waste water treatment plant, DuPage County by Ghosh,1995. Before changing to the two-phase system, the Woodridge WWTP used a conventional two stage digestion facility consisting of a mesophilic high-rate digestion and an unheated secondary digestion. The digestion feed was mixed activated sludge plus septic tank sludge with 1% of clarifier scum. The high rate digester operated at a loading rate of 1.91 to 2.16 kg $\mathrm{VS/m^3 \cdot d}$ and HRT of 20 days. In the first stage, the methane digester exhibited a methane yield of 0.25 $\mathrm{m^3/kg}$ VS added.

During the experiments with two-phase digestion the HRT of the acid digester was changed from 44 to 96 hours, and the loading rate from 25.5 to 12.2 kg $\mathrm{VS/m^3 \cdot d}$. Based on this experience, an acid digester loading rate of at least 16 kg $\mathrm{VS/m^3 \cdot d}$ and a corresponding minimum feed VS concentration of 48 g/l and an HRT of 3 days were selected for operation of the two-phase system.

In the full scale two-phase system performance at a mesophilic temperature of 36°C the feed concentration was about 5% VS, HRT in acid phase – 2 days, and in the methane phase – 16.4 days.

The corresponding loading rate was 27.4 and 3.3 kg $\mathrm{VS/m^3 \cdot d}$ and a maximum gas yield in the system was 0.60 $\mathrm{m^3/kg}$ VS added.

The total gas production was twice as high as that formerly obtained in the one-phase mesophilic reactor.

However, it is not always the case that the gas yield and volatile solids reduction during two-phase digestion increased. Schmidt, 2001 found in his experiments that the total biogas production 0.30–0.42 $\mathrm{m^3/kg}$ VS and VS reduction 47.6 to 71.6% compared to 0.28–0.33 $\mathrm{m^3/kg}$ VS and VS reduction 39.6–69.3% in a single-phase digestion.

2 MATERIALS AND METHODS

Material for the study was the sludge from three Polish waste water treatment plants: "Czajka" plant in Warsaw, the Ciechanow plant, and the "Warta S.A." plant in Czestochowa. From each plant two types of sludge were collected; the primary sludge, from the preliminary sedimentation tank and the excess sludge, taken from the thickener. A mixture of primary and excess sludge was used in the experiments carried out by Bhattacharya,1996.

The raw sludge directed to digestion was a mixture of the preliminary sludge and the excess sludge.

The separate acid phase of the fermentation was carried out in a reactor built in our laboratories. It consisted of a thermostatted water heating bath and two or three static reactors (0.75 $\mathrm{dm^3}$ each, depending on the volume of the processed sludge (fig. 1).

The methane fermentation chamber was a bioreactor of the type LabFermenter L 1523 (BIOENGINEERING, CH-8636 Wald, Switzerland) (fig. 2).

During the technological investigations, the sludge samples from each waste water treatment plant were the object of a classical one-stage methane fermentation (with the retention time of 21 days), thus producing the reference material, and of the fermentation preceded by the preliminary biological hydrolysis (21 days + 2 days of acid phase). The duration of the acid phase was determined during

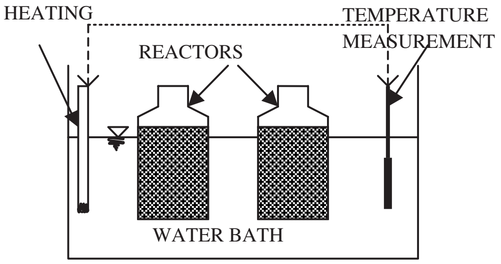

Figure 1. Scheme of the device for acid sludge hydrolysis.

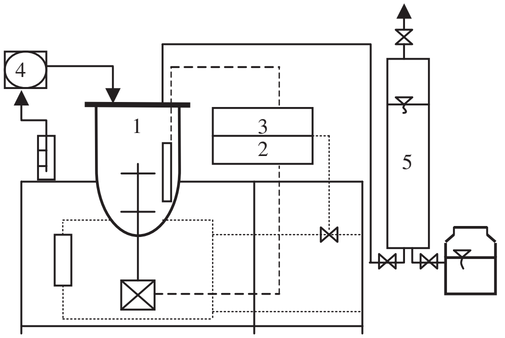

Figure 2. Scheme of the research rig: 1-reaction chamber, 2-mixing system, 3-temperature control, 4-small peristaltic pump, 5-biogas tank.

the experiment. All experiments were carried out at 36°C (mesophilic digestion). The volume of biogas was measured under standard conditions (atmospheric pressure, temperature 200°C). Total volatile acids and total and volatile solids were determined according to standard methods [5].

3 RESULTS AND DISCUSSION

In order to determine the optimal duration for the biological hydrolysis, the pH level and the contents of volatile fat acids in the raw sludge were measured after 24 and 48 hours of retention in the acid phase. For the sludge collected in the Ciechanow plant the following results were obtained:

- Raw sludge: pH = 6.33, TVA = 900 mg CH_3COOH/dm^3,
- After 24 hours: pH = 6.11, TVA = 1470 mg CH_3COOH/dm^3,
- After 48 hours: pH = 5.86, TVA = 2100 mg CH_3COOH/dm^3.

For the sludge collected in the "Warta" plant in Czestochowa, the following results were obtained:

- Raw sludge: pH = 6.57, TVA = 252 mg CH_3COOH/dm^3,
- After 24 hours: pH = 6.58, TVA = 330 mg CH_3COOH/dm^3,
- After 48 hours: pH = 6.56, TVA = 840 mg CH_3COOH/dm^3.

The sludge from the "Warta" plant revealed a lower TVA content, as compared to that collected from the Ciechanow plant, and the increase in TVA content recorded after 24 hours was not very high, therefore it was decided to prolong the examination of the sludge to 48 hours. After this time, a more than three-fold increase of the TVA content in the sludge was recorded. It was decided that the time duration of the acid phase for the "Warta" plant ought to be increased to 2 days (48 hours).

The sludge from the "Czajka" plant in Warszaw yielded the following results:

- Raw sludge: pH = 6.71, TVA = 438 mg CH_3COOH/dm^3,
- After 24 hours: pH = 6.70, TVA = 1140 mg CH_3COOH/dm^3,
- After 48 hours: pH = 6.68, TVA = 1446 mg CH_3COOH/dm^3.

Because, after 48 hours, the TVA content in the sludge was lower than that recorded in the first sludge, it was decided that the time duration for the acid phase would be extended to 48 hours in all cases.

The first result of the hydrolysis phase separation is an increased concentration of total volatile acids (TVA) in the sludge pumped to the second, methanogenic phase.

The feed VS concentration during all experiments was varied in the range from 2.15 to 3.12% and was about half that used by Ghosh,1995. Because of the lower feed concentration, the loading rate – 1.32 kg $VS/m^3 \cdot d$ was correspondingly lower.

The investigations aimed at determining the effectiveness of the methane fermentation preceded by the preliminary biological hydrolysis, as compared to the classical one-stage mesophilic fermentation. The biological hydrolysis was introduced as the first stage to intensify the entire fermentation process.

The reported investigations have revealed that the optimal retention time in the acid phase ranges between one and two days, depending on the plant and waste water treatment technology used there.

In experiments carried out by Ghosh, 1995 the time of acid-phase digestion was changed in the range from 44 to 96 hours and the corresponding loading rate was 12 to 26 kg $VS/m^3 \cdot d$. For full scale performance an HRT of 2 days in the acid phase was chosen, by loading rate about 30 kg $VS/m^3 \cdot d$. The loading rate for both phases was about 3 kg $VS/m^3 \cdot d$. The same time of two-days acid phase digestion is recommended by US Patent 4 022 665.

In our experiments 2 days HRT of acid-phase was kept in all series, and the loading rate of acid-phase

Table 1. Production of biogas: one-phase mesophilic digestion carried out in 36°C, 21-day retention time.

Day	Biogas production [m^3/kg VSa] Ciechanow	Biogas production [m^3/kg VSa] "Warta"	Biogas production [m^3/kgVSa] "Czajka"
1	0.44	0.28	0.35
2	0.38	0.21	0.42
3	0.43	0.23	0.37
4	0.40	0.32	0.36
5	0.43	0.36	0.35
6	0.38	0.35	0.38
7	0.36	0.29	0.43
8	0.40	0.23	0.35
9	0.42	0.23	0.42
10	0.38	0.29	0.35
11	0.38	0.24	0.34
12	0.40	0.33	0.38
13	0.36	0.25	0.36
14	0.38	0.29	0.38
Ave	0.40	0.28	0.37

VSa – Volatile solids added.

Table 2. Production of biogas: mesophilic digestion carried out at 36°C with preliminary biological hydrolysis with 2 days HRT and 21-day HRT in methane phase.

Day	Biogas production [m^3/kgVSa] Ciechanow	Biogas production [m^3/kgVSa] "Warta"	Biogas production [m^3/kgVSa] "Czajka"
1	0.52	0.65	0.41
2	0.50	0.69	0.48
3	0.50	0.71	0.42
4	0.50	0.69	0.40
5	0.60	0.60	0.40
6	0.62	0.58	0.38
7	0.61	0.55	0.55
8	0.60	0.58	0.41
9	0.62	0.56	0.42
10	0.62	0.49	0.50
11	0.60	0.68	0.51
12	0.60	0.58	0.50
13	0.61	0.73	0.53
14	0.62	0.68	0.50
Ave	0.58	0.63	0.46

was 12 kg VS/m$^3 \cdot$ d, and total – 1.4 kg VS/m$^3 \cdot$ d (due to lower feed concentration).

It was observed that plants making full use of gravitational preliminary sludge thickeners require shorter retention time of the preliminary and excess sludge mixture in the acid phase. For the Ciechanow and "Czajka", Warsaw, plants, a retention time as short as 24 hours in the acid-phase was sufficient to observe a significant increase in the TVA content. This was evidence that the hydrolysis of high molecular weight polymers to simpler compounds took place, and that the hydrolysed substances were decomposed into organic acids (expressed as TVA).

During the two-stage fermentation with 21-day HRT in the methane phase, an increase in biogas production similar to that recorded by Ghosh, 1995 was obtained.

The results obtained in particular test series are as follows:

- For the Ciechanow plant, 0.40 m^3/kg VS and 0.58 m^3/kg VS were obtained, respectively,
- For the "Warta" plant in Czestochowa 0.28 m^3/kg VS and 0.63 m^3/kg VS were obtained, respectively,
- For the "Czajka" plant in Warsaw 0.37 m^3/kg VS and 0.46 m^3/kg VS were obtained, respectively (compare the results in tables 1 and 2).

The highest increase in biogas production was obtained for the "Warta" plant while the lowest was obtained for the "Czajka" plant. Theoretically, it would be expected that the results for these plants would be comparable to each other, as they are both large plants of over 100 000 PE capacity, with a similar composition of collected sewage, similar sewage treatment technology, and the same proportion of the sludge directed to fermentation.

Among other goals, the reported investigations aimed at determining whether the preliminary biological hydrolysis positively affects the methane fermentation, expressed as the level of volatile matter reduction, and the degree of fermentation. During the investigations the operation of the fermentation chamber was also controlled, among other methods, by measuring pH, alkalinity and TVA content in the sludge after fermentation.

Examination of the methane fermentation process of the sludge taken from the Ciechanow plant has revealed a remarkable increase in the organic matter reduction level, from 43.5% during the mesophilic fermentation to 58.3% during the two-stage fermentation, accompanied by the improved fermentation degree, from 44.0 to 58.3%. The content of volatile fatty acids in the sludge after digestion was slightly lower in the stage without the hydrolysis than with it, but in both cases the recorded values were very low. In the series with the hydrolysis and 21-day retention time a more than two-fold increase in the volume of the produced biogas was obtained, compared to the classical mesophilic digestion.

Examination of sludge samples from the "Warta" plant has also shown that the preliminary biological hydrolysis positively affects the methane fermentation. A significant increase was observed in the organic matter reduction level, from 46.7% in the stage without the hydrolysis to 56.2% with the hydrolysis. It was accompanied by a similar improvement in the fermentation degree, from 38.6 to 48.4%. The content of total volatile acids in the sludge after fermentation was slightly higher in the stage without the hydrolysis than with it, but in both cases these values were very low, testifying to a good performance of the digester. In the experiment with the hydrolysis and 21-day retention time an over 30% increase in biogas production was obtained, compared to that observed in classical mesophilic fermentation.

As in the two previous cases, for the sludge samples taken from the "Czajka" waste water treatment plant in Warsaw, the increase in biogas production in the stage with hydrolysis was accompanied by an increase in fermentation degree and by higher reduction of the organic matter. A remarkable increase of average organic matter reduction level was recorded, from 49.2% in the stage without hydrolysis to 59.5% with hydrolysis. This increase was accompanied by an improvement in fermentation degree from 47.5 to 65.2%. The content of volatile fatty acids in the sludge after fermentation was lower in the single-phase, than in the two-phase with hydrolysis, but low values recorded in both cases testified to good performance of the fermentation chamber. In the experiment with hydrolysis and 21-day retention time a 30% increase in biogas production was obtained, compared to that observed in the classical mesophilic digestion.

4 CONCLUSIONS

Bearing in mind that the main goals of the methane fermentation process are the stabilisation of the sludge, expressed as the reduction of the VS and the production of methane, we can draw the following conclusions from our study:

1. When preceded by biological hydrolysis, methane fermentation assures a higher production of biogas than that obtainable during a classical one-stage mesophilic fermentation, thanks to optimal conditions for bacteria development, kept in each fermentation phase. The increase in biogas production can vary depending on the size of the waste water treatment plant and type of sludge produced. The maximum reported increase in biogas production was more than 100% from 0.28 to 0.63 m^3/kg of VS added. The average was 60%.
2. The investigations have revealed that the fermentation with prior hydrolysis of the sludge results in better stabilisation, in terms of the fermentation degree and organic matter reduction, compared to the classical one-stage methane fermentation. The increase of the fermentation degree may exceed 10%.
3. The duration of the preliminary biological hydrolysis depends on the rate of increment of volatile fatty acids in the sludge and ranges between 24–48 hours. The loading rate of the first phase, due to the short retention time, can be roughly ten times higher than in the second phase.
4. Following common practice in Polish waste water treatment plants, the methanogenic phase of each series examined lasted 21 days, Attempts to shorten the HRT in the second phase led to much worse results.

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Management of Pollutant Emission from Landfills and Sludge – Pawłowska & Pawłowski (eds)
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Separation of fats from wastewaters and processing wastes using flotation for the needs of efficient sludge management

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ABSTRACT: The paper presents results of research on the separation of animal fats from post-production effluents and after-centrifugal silts from lard rendering which is performed in the meat industry. Two flotation techniques were used to separate fats: induced air flotation (IAF) and dissolved air flotation (DAF). These methods were enhanced by adding by hydrogen peroxide, giving two new oxyflotation methods named OxDAF and OxIAF. In carrying out the research, the following appliances were used to remove impurities from the effluents and after-centrifugal silts: a mechanical aerated separator with a preliminary biological chamber, a storage-equalizing ground basin and a flotation station supported by pressure saturation. The efficiencies of the appliances eliminating fats from the processing wastewaters were compared.

Keywords: Fat separation, induced air flotation (IAF), dissolved air flotation (DAF), oxyflotation.

1 INTRODUCTION

The use of fat separators is not sufficient to solve the problem of eliminating these compounds from the processing wastewaters in meat plants (Bull et al., 1982; Martinez et al., 1995; Cammarota et al., 2006; Mittal, 2006). Conventional methods for the reduction of fats in slaughterhouse wastewaters by using mechanical or aerated separators and dissolved air flotation (DAF) are characterized by a relatively high efficiency (>70–85%) (Courtial, 1975; Köhler, 1975; Hopwood, 1977; Rüffer and Rosenwinkel, 1991). Highly efficient separation of those substances is necessary to correctly conduct the processes of biological wastewater treatment (Angelidaki et al., 1990; Martinez et al., 1995; Masse et al., 2001; Masse et al., 2003). Fats, especially in high concentrations (above 50 mg/l), may become a limiting factor reducing the effectiveness of aerobic and anaerobic biological processes of pollutant load decomposition (Bull et al., 1982; Gariépy et al., 1989; Cammarota et al., 2006). As regards aerobic methods, they result in colmatation of activated sludge microorganisms and in disturbances in oxygen management (Krause, 1982), whereas anaerobic methods reduce the efficiency of organic waste biotransformation, i.e., hydrolysis, acidolysis, methanogenesis, and decrease biogas yield (Hanaki et al., 1981; Koster, 1987; Koster and Cramer, 1987; Angelidaki and Ahring, 1992; Batstone et al., 1997). The processes of biological treatment are blocked particularly due to long-chain fatty acids formed during enzymatic hydrolysis of fats (Hanaki et al., 1981; Angelidaki and Ahring, 1992; Cammarota et al., 2006). After being adequately isolated and refined, fats may become a valuable raw material for power production or in the oleochemical industry (Żak and Pawlak, 2006a). However, they ought to be characterized by high purity and favorable parameters, i.e. trace protein contents, the lack of microbiological infections – particularly no pathogenic microorganisms, low acid and peroxide values (AV and PV), etc. (Regulation (EC) No 1774/2002; Commission Regulation (EC) No 92/2005).

The aim of the study was to assess the usability of different types of separators applied to eliminate fats from the processing wastewaters and the AC-silts formed during wet lard rendering. The goal was to elaborate methods of minimizing fatty substances in effluents and processing wastes and to separate them from flotates in order to obtain parameters reliable enough to use fats for the production of methyl or ethyl esters, or to transform them into fuel oil additives or technical greases, e.g. to produce fatty acids, soaps, detergents, animal glycerol, etc. (Tashtoush et al., 2004).

2 MATERIALS AND METHODS

The methods for separating fats suspended in processing effluents were tested in a full-scale technological plant. The separation was made in the appliances as integral parts of the processing wastewater treatment plant. The separating appliances were installed at a section of a sewage system that directs the processing effluents into the anaerobic-aerobic biological treatment plant with the flow capacity of $750.0 \pm 50.0\,m^3$/day. The processing effluents were taken from slaughtering, cutting swine carcasses and animal raw material processing, and from cleaning the processing appliances (routine washing using alkaline agents; washing with acidic reagents used once a week). In order to achieve the aims of the research, two flotation techniques were tested: IAF (induced air flotation) and DAF (dissolved air flotation). These methods were also enhanced by using hydrogen peroxide, forming the modifications named: OxIAF (oxidizer enhanced induced air flotation) and OxDAF (oxidizer enhanced dissolved air flotation). These enabled us to estimate the effectiveness of the applied separation and recovery methods in practice. The research was conducted in the spring season when the mean-monthly temperatures were: 14, 19, 25°C in April, May and June, respectively.

2.1 *Technical part*

The studies were carried out on the following separation devices.

2.1.1 *Aerated mechanical separator (AMS)*

A two-chamber earth tank of rectangular cross-section ($2.0 \times 5.0\,m$) and filling height 2.0 m, with the volumes: aeration chamber – $16.0\,m^3$; flotate thickening chamber – $4.0\,m^3$ was applied. The separator was equipped with a frame surface skimmer and a fine bubble aeration system (including 8 Pfleiderer Water System Co. bottom disc diffusers of diameter $\varphi = 240$ mm, with a membrane duct diameter $d = 120\,\mu m$). The flow capacity through the separator during the work was $500.0 \pm 50.0\,m^3$/day. The separator set was additionally equipped with a station dosing the 30% aqueous solution of hydrogen peroxide directed into a pipe mixer installed at the inlet of the raw effluents into the separation chamber.

2.1.2 *Aerated separator with a preliminary biological chamber (ASPBC)*

A three-chamber earth tank of rectangular cross-section ($2.0 \times 6.0\,m$) and filling height 2.0 m with a biological chamber, vol. $10.0\,m^3$, an aeration chamber $10.0\,m^3$ (with 10 Pfleiderer Water System Co. disc diffusers of diameter $\varphi = 240$ mm, with a membrane duct diameter $d = 120\,\mu m$) and the flotate thickening chamber $4.0\,m^3$ was applied. The tank was equipped with a surface flotate skimmer (installed over the aeration zone) and a bottom skimmer (installed in two zones: biological and aeration) to remove sediment silts directed into a hopper part of volume $1.0\,m^3$, located in the aeration chamber. A cyclically thickened anaerobic sludge was introduced into the biological chamber from the methane fermentation chamber of the biological treatment plant ($1.0\,m^3$/day with the content of dry mass ca. 20.0–30.0 g/l). After mixing with raw effluents, the sludge was mechanically discharged into a thickening hopper. Then, it was pressed by a sludge pump into a silt thickening chamber and directed for repeated fat rendering or into anaerobic hydrolyzing tanks together with a flotate separated in the aeration zone. After the preliminary 14-day anaerobic hydrolysis, it was transported into the methane fermentation chamber of the biological wastewater treatment plant when its hydraulic loads were at their lowest. The flow capacity through the separator during the test was $500.0 \pm 50.0\,m^3$/day.

Aerated mechanical separators (AMS) and a preliminary biological chamber (ASPBC) were installed in a parallel system so that they could be used together or separately.

The effectiveness of the ASET (aerated storing-equalizing tank) and the DAFS (dissolved air flotation station) were tested after mechanical treatment of wastewaters on screens, mesh 3 mm.

2.1.3 *Aerated storing-equalizing tank (ASET)*

Earth cylindrical tank of volume: $50.0\,m^3$, equipped with a bottom fine bubble aeration system (with 20 Pfleiderer Water System Co. disc type diffusers of diameter $\varphi = 240$ mm, with a membrane duct diameter $d = 120\,\mu m$) and a surface frame flotate skimmer was applied. The tank flow capacity while conducting the tests was $500.0 \pm 50.0\,m^3$/day. The tank system was equipped with a station dosing a 30% aqueous solution of hydrogen peroxide into the pipeline in front of an inlet to the tank. Raw effluents were directed by the pipeline into a central position of the tank bottom zone and discharged to an outlet, located at the wastewater level.

2.1.4 *Dissolved air flotation station (DAFS)*

The flotation set was equipped with a pretreated wastewater saturation station – two pressure tanks, vol. $6.0\,m^3$ (the process was conducted under saturation pressure of 400–500 kPa, recirculation level of saturated wastewater: 15–20% and time of saturation: 10.0 min.) and a flotation chamber, vol. $25.0\,m^3$ equipped with a surface frame flotate skimmer and flocculent preparation, a dosing station (0.5% aqueous solution of Praestol 859 BC Stockhausen), and also with a station dosing the 30% aqueous solution of hydrogen peroxide. The tank flow capacity while conducting the tests was $600.0 \pm 50.0\,m^3$/day ($500.0 \pm 50.0\,m^3$/day of raw effluents and 15–20% of re-circulated saturated wastewaters).

The research on minimizing fats in the after-centrifugal silts (AC-silts) from wet rendering was carried out on a system characterized by the parameters given below.

2.1.5 *Two-chamber flotation station for fat separation from after-centrifugal silts (TCFSFS)*

A plant set for fat recovery has been constructed to process maximum amounts of AC-silts with the capacity of $10.0\,\mathrm{m}^3$/day. The set consisted of three tanks: a storing-equalizing tank, vol. $5.0\,\mathrm{m}^3$, where $5.0\,\mathrm{m}^3$ of the AC-silts were introduced flown in, and a pressure tank with saturated water, vol. $1.0\,\mathrm{m}^3$. The storing-equalizing tank was equipped with a system of inner circulation, a sludge pump, a gate mixer and a heating coil which maintained the temperature at 70–80°C. When silts were stored longer than 24 hours, the 30% aqueous solution of hydrogen peroxide ($\rho = 1.11\,\mathrm{mg/m}^3$) was dosed in the amount of 8.0–10.0 kg H_2O_2/m^3 to stop putrefaction processes. The flotation chamber was equipped with: a circulation mixer with a sludge pump, a vertical gate mechanical mixer, a system of aeration with 6 disc diffusers (of diameter $\varphi = 240\,\mathrm{mm}$, with a membrane duct diameter $d = 120\,\mu\mathrm{m}$) and a system of flotate discharging. After heating and mixing with saturated wastewater in the pressure pipeline, the AC-silts were pumped by means of the sludge pump into the flotation chamber.

2.2 *Analytical part*

To assess the efficiency of the separators used to eliminate fats from processing effluents and AC-silts from lard rendering, the ether extract (EE) (Polish Standard PN-74/C04573/02 and 03 and 10) was determined at the inlet and outlet of the individual appliances. Fat concentrations in raw effluents at the inlets of particular separators and numbers of measurement series are presented in the footnotes of the individual tables. In order to assess the quality of fats separated from the flotates by wet rendering, the following parameters were determined according to Polish Standards: contents of fatty substances (PN-87/C-04288.04), and peroxide value (PV) (PN-88/C-04288.10) and (PN-ISO:3960:1996); acid value (AV) (PN-88/C-04288.06) and (PN-ISO 660:1998). In order to check the fatty fractions in the flotates, fatty acids were analyzed using a gas chromatograph (GC) (Hewlett Packard HP-5890 series II, capillary column HP-1: length $l = 30.0\,\mathrm{m}$, $\varphi = 0.52\,\mathrm{mm}$, phase: Hypersil ODS Shandon) with detection by AED and ECD and a mass spectrometer (MS 5972 series Mass Selective Detector – column: Pona $l = 25.0\,\mathrm{m}$, $\varphi = 0.52\,\mathrm{mm}$), extracting in the liquid–liquid system by means of chloroform and ether.

In raw flotates and in fats isolated from the flotates, the presence of *Salmonella sp.* was determined by routine procedure, in accordance with the user's operation manual RapidChek® *Salmonella sp.*, or it was confirmed by other methods given in the following (Collins et al., 1991; FSIS/USDA/MLG, 2001).

3 RESULTS AND DISCUSSION

The purpose of the research was to describe the effect of hydrogen peroxide on the efficiency of fat elimination and on the quality of fats after their separation in the processes of pre-treating the food processing effluents using the IAF and DAF methods.

The studies on minimizing the amount of fats in the after-production effluents and wastes were carried out to:

- Recover them from the effluents in aerated mechanical separators and by using hydrogen peroxide enhanced DAF;
- Recover them from the lard production AC-silts by using hydrogen peroxide enhanced IAF.

In the literature there are scant data on using hydrogen peroxide to support wastewater pretreatment, particularly to reduce COD (chemical oxygen demand), BOD (biochemical oxygen demand) and fat contents (Maennig and Scherer, 1989; Steiner and Gec, 1992; www.h2o2.com). Apart from that, hydrogen peroxide reveals bacterio- and fungistatic properties with reference to microorganisms and fungi spores that occur in wastewaters, thus increasing their biological stability (Casani et al., 2005). The efficiencies of the aerated separators: AMS and ASPBC were tested using preliminary untreated raw wastewaters. In this way, the fat elimination efficiency could be precisely determined for the individual separators. Hydrogen peroxide was introduced at the inlets to separators and was dosed into the pressure pipeline. Fats from the industrial effluents in the aerated separators: AMS, ASPBC and ASET without hydrogen peroxide were eliminated, by respectively: 16.8–48.5%, 33.9–56.2% and 9.4–37.0% (Tables 1–3). The content of fatty substances in the flotate dry mass was: 8.5–14.7%, 4.9–11.9% and 14.9–28.7%. For the DAFS station with no hydrogen peroxide, the elimination of fatty substances under conditions of 20% recirculation of saturated effluents and with saturation pressures of 400 and 500 kPa was, respectively: 45.9–83.9% and 58.7–83.2% (Table 4, No. 2 and 7). The content of fatty substances in the flotate dry mass amounted to: 18.5–36.4%, 17.0–27.0%. The above levels were used as reference values in order to define the effect of hydrogen peroxide. For the aerated separators: AMS and ASPBC, the low content of these substances in the flotate resulted from the dominating fraction of coarse impurities (mainly fragments of the unprocessed raw material, contents of stomachs and intestines, blood

Table 1. Typical parameters of the flotate isolated on the AMS.

No.[(a)]	Concentration of hydrogen peroxide ($g\,H_2O_2/m^3$)	Level of fat elimination from wastewaters (%)[(b)]	Fat content in the flotate phase (%)[(c)]	Acid value (AV)[(d)] (mg KOH/g)	Peroxide value (PV)[(d,e)] (meq/kg)
1	0.0	16.8–48.5	8.5–14.7	0.11–0.35	0.13–0.41
2	100.0	14.7–34.7	5.9–16.6	0.19–0.51	0.39–1.27
3	400.0	22.8–53.9	7.7–17.5	0.28–0.80	1.83–3.78
4	500.0	28.5–63.0	7.9–22.3	0.27–0.79	1.87–3.13

Where: (a) fat content in raw effluents at the inlet of separator No. 1–4: 320.9–888.2, 418.6–1104.8, 201.7–916.7 and 379.9–1303.0 mg/l; (b) values obtained basing on No. 1–4: 8, 9, 12 and 10 measurement runs; (c) in the flotate dry mass; (d) in refined fatty phase isolated from the obtained flotate; (e) meq/kg – PV in milliequivalents of active oxygen in 1.0 kg of fats (Polish Standard PN-ISO 3960:1996).

Table 2. Typical parameters of the flotate isolated on the ASPBC.

No.[(a)]	Concentration of hydrogen peroxide ($g\,H_2O_2/m^3$)	Level of fat elimination from wastewaters (%)[(b)]	Fat content in the flotate phase (%)[(c)]	Acid value (AV)[(d)] (mg KOH/g)	Peroxide value (PV)[(d,e)] (meq/kg)
1	0.0	33.9–56.2	4.9–11.9	0.20–0.47	0.30–0.63
2	100.0	24.7–59.7	5.4–16.6	0.28–0.78	0.46–1.40
3	400.0	30.8–67.9	5.7–15.5	0.30–0.87	1.61–2.69
4	500.0	33.9–61.2	5.9–12.3	0.36–0.96	2.23–3.37

Where: (a) fat content in raw effluents at the inlet of separator No. 1–4: 312.9–840.3, 230.7–831.7, 380.3–920.5 and 289.6–1017.8 mg/l; (b) values obtained basing on No. 1–4: 9, 9, 10 and 11 measurement runs; (c) in the flotate dry mass; (d) in refined fatty phase isolated from the obtained flotate; (e) meq/kg – PV in milliequivalents of active oxygen in 1.0 kg of fats (Polish Standard PN-ISO 3960:1996).

Table 3. Typical parameters of the flotate isolated on the separating set of the ASET.

No.[(a)]	Concentration of hydrogen peroxide ($g\,H_2O_2/m^3$)	Level of fat elimination from wastewaters (%)[(b)]	Fat content in the flotate phase (%)[(c)]	Acid value (AV)[(d)] (mg KOH/g)	Peroxide value (PV)[(d,e)] (meq/kg)
1	0.0	9.4–37.0	14.9–28.7	0.24–0.50	0.32–0.67
2	100.0	7.9–38.9	8.7–25.1	0.32–0.79	0.38–0.80
3	400.0	11.6–40.4	9.4–25.7	0.39–1.10	1.89–3.18
4	500.0	24.7–48.8	7.7–14.2	0.43–1.39	2.57–4.94

Where: (a) fat content in raw effluents at the inlet of separator No. 1–4: 420.8–950.2, 438.6–1205.8, 330.7–1007.3 and 305.8–1105.8 mg/l; (b) values obtained basing on No. 1–4: 8, 8, 11 and 10 measurement runs; (c) in the flotate dry mass; (d) in refined fatty phase isolated from the obtained flotate; (e) meq/kg – PV in milliequivalents of active oxygen in 1.0 kg of fats (Polish Standard PN-ISO 3960:1996).

clots, bristles, etc.), making up a considerable part of the pollution mass. These separators were installed on the sewage system in front of the mechanical screen. Fats obtained from the separated flotates were characterized by favorable final parameters: low levels of AV (<0.5 mgKOH/g) and PV (<1.0 meq/kg). When the separators were supported with hydrogen peroxide in doses of 100.0–500.0 gH_2O_2/m^3 of raw effluents, a small increase in the fat elimination efficiency (ca. 10–20% with hydrogen peroxide doses of 400.0 and 500.0 g/m^3) was observed in AMS. However, no effect of hydrogen peroxide and its differing doses was observed on the level of eliminating fatty substances as far as the ASPBC system was concerned (Table 2). As this result shows, this technical solution will not be useful for separating fats which are to be

Table 4. Typical parameters of the flotate separated from the effluents by using OxDAF method.

No.[a]	Level of wastewater recirculation (%)	Saturation pressure (kPa)	Concentration of hydrogen peroxide (g H_2O_2/m^3)	Level of fat elimination from wastewaters (%)[b]	Fat content in the flotate phase (%)[c]	Acid value (AV)[d] (mg KOH/g)	Peroxide value (PV)[d,e] (meq/kg)
1	15	400	0.0	60.9–79.5	16.6–31.8	0.20–0.46	0.24–0.67
2	20	400	0.0	45.9–83.9	18.5–34.6	0.36–0.78	0.28–0.53
3	15	400	200.0	68.9–88.0	21.8–39.6	0.29–0.69	0.92–1.85
4	15	450	400.0	70.6–92.6	10.0–23.6	0.33–0.84	1.38–2.83
5	20	450	450.0	78.9–97.8	12.3–23.9	0.47–1.11	2.07–4.27
6	15	500	450.0	83.8–93.2	13.9–22.1	0.43–1.49	1.86–4.38
7	20	500	0.0	58.7–83.2	17.0–27.0	0.33–0.41	0.37–0.89
8	15	500	500.0	86.4–94.1	14.7–20.8	0.56–1.60	2.53–4.79
9	20	500	500.0	90.9–98.7	11.5–17.9	0.74–1.57	2.74–5.37

Where: [a] fat content in raw effluents at the inlet of separator No. 1–9: 270.5–707.0, 302.8–840.2, 424.7–1049.9, 328.4–890.4, 207.3–1050.4, 377.9.4–805.0, 278.4–1170.4, 337.0.4–1001.5 and 339.8–713.7 mg/l; [b] values obtained basing on No. 1–9: 12, 9, 10, 11, 10, 12, 11, 8 and 9 measurement runs; [c] in the flotate dry mass; [d] in refined fatty phase isolated from the obtained flotate; [e] meq/kg – PV in milliequivalents of active oxygen in 1.0 kg of fats (Polish Standard PN-ISO 3960:1996).

further isolated from the obtained flotates. However, it may be effectively used to separate waste suspensions from wastewaters to produce biogas. For the ASET system, a significant increase in fat elimination by ca. 10–20% was only found for a dose of 500.0 g/m^3. However, the content of fats in the flotate was relatively low compared to the method without hydrogen peroxide (Table 3). Introducing hydrogen peroxide in this dose resulted in worsening quality parameters of fats separated from the flotate by rendering, especially in the increase in PV which exceeded 2.5 meq/kg. For pressure flotation supported by hydrogen peroxide in a dose of 500.0 g H_2O_2 per m^3 of processing effluents (with saturation pressure 500 kPa, raw effluent recirculation: 15% and 20%, and with the flocculent Praestol 859 BC Stockhausen in a dose of 35.0 g per m^3 of the effluents), the fat reduction exceeded 85% (Table 4, No. 8 and 9). The quality of the obtained fats was low – the PV was more than 2.5 meq/kg. Since there is no literature data concerning the effect of hydrogen peroxide on fatty substances separated from technological effluents using flotation processes, it is difficult to compare the results obtained with those of other authors. However, the effectiveness of the hydrogen peroxide-enhanced DAF in the applied doses turned out to be comparable with literature data (Maennig and Scherer, 1989; Steiner and Gec, 1992). The increase in hydrogen peroxide concentration by more than 600.0–800.0 g/m^3 caused no measurable increase in the flotate volume on the tested separating appliances. A further increase in hydrogen peroxide concentrations is unreasonable because it would considerably increase the costs of wastewater treatment. An increase in the hydrogen peroxide was more important in reactions connected with decoloring and coagulation of blood which precipitated and flotated as light creamy suspensions and colloids. This resulted in a higher mass of the flotates and lower content of fatty substances, which considerably limited the possibility of their recovery by rendering. At higher wastewater temperatures (above 25°C), the fixation of fatty protein emulsions was observed, which limited the effective separation of fatty flotate. This phenomenon was also observed for higher concentrations of protein in the processing effluents. The chromatographic analysis of fatty phase contents showed the existence of saturated fatty acids: 12:0 (0.06–0.09%), 14:0 (0.56–0.59%), 16:0 (22.49–22.81%), 18:0 (13.06–13.13%), monoenic acids: 16:1 (2.30–2.36%), 18:1 (50.34–50.41%), 20:1 (1.98–2.03%) and polyenic ones: 18:2 (5.27–5.33%), 18:3 (1.10–1.18%). The ratio of polyenic to saturated acids was 0.18. *Salmonella sp.* was found in neither separated flotates nor re-rendered fats.

In order to manage fats isolated from the separated flotates it is necessary to obtain a material of favorable utility parameters (among others: low AV and PV, protein content lower than 0.15% wt., free of *Salmonella sp.*). In practice, this is difficult to achieve on an industrial scale, as it is connected with a relatively long time of storing wastewaters in the pretreatment appliances and in the sewage system. The problem is illustrated by the results of the PV and AV (though to a smaller degree) for fats isolated from the flotates trapped on the individual separators (Tables 1–4). The influence of storage time is significant: the longer the time, the higher PV in the obtained fat. This problem is augmented in the summer when the temperatures are higher. At that time the fractions of soluble COD and BOD grow rapidly with reference to the total COD_T and $BOD_{5(T)}$ as the storage time and spontaneous biochemical changes develop. It results in, e.g.,

Table 5. Typical parameters of flotate phase separated from AC-wastewaters by using OxIAF method.

No.[(a)]	Concentration of hydrogen peroxide ($g\,H_2O_2/m^3$)	Level of fat elimination from wastewaters (%)[(b)]	Fat content in the flotate phase (%)[(c)]	Acid value (AV)[(d)] (mg KOH/g)	Peroxide value (PV)[(d,e)] (meq/kg)
1[(f)]	0.0	74.1–82.8	66.7–74.6	0.29–0.48	0.29–0.49
2[(g)]	0.0	71.7–84.3	62.7–71.6	0.35–0.47	0.32–0.49
3[(h)]	0.0	71.8–77.4	60.8–68.2	1.18–3.27	0.87–2.45
4	750.0	80.2–87.3	75.2–80.2	0.38–0.63	2.84–4.64
5	1000.0	83.8–90.2	76.0–82.1	0.28–0.87	3.17–8.97
6	1500.0	80.4–92.4	77.4–80.3	0.29–1.06	4.32–12.93
7	2000.0	85.5–96.6	76.5–81.6	0.40–0.70	5.92–13.40

Where: [(a)] values obtained basing on: No. 1–7: 9, 8, 11, 10, 9, 8 and 10 measurement runs; [(b)] the content of fats in total mass of mixed after-centrifugal wastes: 4.1–10.2%; [(c)] in dry mass of the flotates; [(d)] in the phase of refined fats isolated from the flotate; [(e)] meq/kg – PV in milliequivalents of active oxygen per 1.0 kg of fats (Polish Standard PN-ISO 3960:1996); for No. 1–3, the waste storage time: [(f)] less than 5.0 hour, [(g)] 3 and [(h)] 7 days.

spontaneous hydrolysis of fats that induce an increase in AV. The investigation revealed that hydrogen peroxide added to processing wastewaters which had been stored for a long time caused fermentation processes and biological hydrolysis of fatty compounds to be inhibited to some degree (Żak and Pawlak, 2006b). However, the obtained fats were characterised by lower quality, i.e., by lower PV, which means they can be used as fuel material only.

In order to recover fats from AC-silts produced during lard rendering, a highly efficient separation of the individual phases, i.e., of fatty phase and water-protein phase, is necessary. During lard production in the factory under investigation, AC-wastewaters containing water from the raw material and the processing water amounted to 20–45%, and the amount of AC-silts was ca. 5–10% with reference to the dry mass of the animal raw material. The quality content of the pollutants showed homogeneity: fats and proteins dominated. The content of fats in the AC-silts ranged from 32.6 to 57.9%, and, in the after-centrifugal wastewaters – from 0.21 to 0.36%. The tests showed that the recirculation of the AC-silts for fat re-rendering reduced the total silt content by ca. 50% and the content of fats by 60–80%. In this way, the loss of fats and the amounts of the AC-silts can be considerably reduced below 2% with reference to the dry mass of animal raw material. The fats in the tested wastes were thickened by flotation and, after re-rendering, they were refined in vertical centrifuges (6000 rpm, Alfa Laval 140E). Comparing the two flotation techniques: IAF and OxIAF, it is possible to estimate the usability of these methods for fat recovery. The tested wastes (mixed silts: shootings and after-centrifugal effluents) were flotated in the separating system TCFSFS after heating to 70–80°C and after mixing with saturated water (under pressure 500 kPa for 10.0 minutes) in volume ratio 4:1. When IAF was applied by using air evolved from saturated water and diffused by six supporting disc diffusers, fats were eliminated with an efficiency exceeding 70%, and the fat content was more than 60% (Table 5, No. 1–3). In the method with hydrogen peroxide dosed in the amount of 750.0-2000.0 gH_2O_2/m^3 of silts, the elimination of fats exceeded 80%, and the fat content in flotates exceeded 75% (Table 5, No. 4–7). However, the use of hydrogen peroxide to support the flotation increased peroxides in the fats rendered from the flotates. Owing to the more favorable usability parameters (lower PV), the variant with IAF without dosing the oxidizer permits the recovery of fats which are characterized by more advantageous usability parameters.

4 CONCLUSIONS

Separation of fatty substances from after-processing wastes in meat factories is a complex problem. This issue has to be discussed as regards its economical use, particularly for plants of high production where the amounts of the produced effluents and fat losses are considerable. Isolation of fatty compounds by using aerated mechanical separators and hydrogen peroxide enhanced DAF results in the increased elimination of fats from AC-wastewaters. Owing to more favorable fat usability parameters (PV <1.0 meq/kg), the variant with separators in which IAF and DAF are not enhanced with hydrogen peroxide is more advantageous for recovering fats intended for technical application, whereas the use of the hydrogen peroxide enhanced DAF and IAF variants may be applied to a limited degree, e.g., for wastes stored for a long time, for separating fats intended for heat production, or for separating flotates intended for biogas production.

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Biotests in solid waste quality assessment and its management

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ABSTRACT: This paper presents the results of projects dealing with the assessment of the threats to the environment posed by old, unsealed municipal waste landfills, industrial landfills and polluted lake sediments. Acute and chronic toxicity studies were conducted on ground water samples collected from beneath municipal waste landfills, samples of waste from a post-metallurgical dumping site and sediment samples taken from the retention reservoir bottom. Simultaneously typical chemical analyses were conducted within the range required by the proper Decree of the Minister of the Environment of Poland (2002), as well as analyses of samples for organic chemicals content, the presence of which in the environment is not regulated by law. The results of studies presented here show new areas of possible application of biotests, where ecotoxicological results can efficiently support quality assessment of solid waste and further decisions about its management including their disposal in the environment.

Keywords: Waste quality assessment, municipal waste, industrial waste, excavation material, biotests.

1 INTRODUCTION

One of the most characteristic features of the economic growth that could be observed after World War II was the increase in the production of plastic materials and massive production of consumption goods. During last decades the situation has led to rapid growth of the amount of wastes – both of municipal and industrial origin.

The lack of solid knowledge about disposal and usage of these wastes became a problem to competent authorities of cities and communes which could not solve this problem. Solid wastes, very often mixed with semi-fluid wastes, were most often chaotically collected in accidental places. In many cases the areas targeted for use as waste disposal sites were previously not checked from a geological, hydrogeological or geochemical point of view. These places were mostly post-exploitation excavation lands (e.g., of gravel, sand) or agricultural lands. Most of them are still functioning albeit without the required safety measures that would minimize their noxiousness to the environment, and lacking a control-measurement system that mostly makes it almost impossible to assess the influence of such disposal sites on the surroundings. The view of the environment was distorted and the recreational areas' value was decreased as well. Severe damage was also done to surface and ground waters.

This more and more dangerous state of affairs has finally mobilised communes, cities and countries to take specific actions. Scientific research began in the 1970s and found reflection in numerous sets of regulations obligatory in different countries as well as in communes' dispositions. The aim of these actions was to prepare a pathway for rational waste management that will support environmental protection.

Actually, concepts of modern, properly placed and designed landfills are being implemented. They protect surroundings from their own destructive influence. Although more and more secure actions are undertaken, waste disposal is still noxious to the environment and will always require controlling.

One of the ways by which the wastes negatively influence the environment during their disposal is by water leaching. For this reason, during waste disposal, special attention is given to restricting pollution of ground waters. Substances, especially those difficult to degrade, spread in the underground waters and finally reach the food chain. For this reason the main responsibility of each landfill manager is to monitor the content of the ground waters, surface flows, air, soil and flora (in and around the disposal site) as well as control eventual emissions of pollutants.

However, rational waste management requires first of all knowledge about its content. Based on such information it is possible to classify the waste material according to specific quality classes, which shows the scale of their noxiousness and threat to the environment.

The assessment of the real threat resulting from the presence of a variable mixture of pollutants (due to the wide spectrum of compounds, their concentration levels and speciation forms) in the environment, is an extremely complex task. To a great extent, such an assessment is based on the results of monitoring the chemical indices of environmental pollution.

Chemical analysis enables the detection, quantitative determination and identification of organic and inorganic pollutants, but does not provide information about the potential negative impact of environmental compounds on particular components of ecosystems. Such an underestimation is a result of not taking into account the following factors (Zabetoglou et al., 2002; Baun et al., 2004; Mantis et al., 2005):

– all the compounds present in the environment,
– the bioavailability of their different forms,
– their different biological activities.

A complementary approach, taking into account the above-mentioned facts, can include the application of biotests. Moreover, usage of biotests enables the detection of toxic effects of the combination of many different pollutants in a sample. Synergistic as well as antagonistic effects can be observed (Salizzato et al., 1998; Pérez et al., 2001; Boluda et al., 2002).

Bioassays provide data about the effect, without pinpointing the substances and the potential source. Therefore, a tool is necessary for providing toxicity data as well as an identification of the compounds causing the effects. An integrated approach based on parallel application of bioassays and chemical analysis is the most powerful tool for the assessment of environmental pollution (Brack et al., 1999; Reineke et al., 2002).

The main purpose of this paper is to demonstrate that biotests can be effective and efficient tools that enable additional information to be obtained about the influence of the old, unsealed municipal landfills, post-production materials from the metallurgical industry and dangerous wastes from lake dredged material on aqueous ecosystems. Biotests were used, together with chemical methods, to assess the threat posed by particular kinds of wastes to which specific bioindicating organisms were exposed.

2 MATERIALS AND METHODS

2.1 *Origin of samples*

Research about the impact of municipal wastes on the ecotoxicity of ground waters was conducted for seven large municipal waste dumps open before 1990. None of them is watertight. Overall, more than 10,000 mg of waste are stored at these sites. More detailed information on the characteristics of each of these dumps (underground water sampling and sampling treatment) are presented elsewhere (Wolska et al., 2006).

The sediment samples were collected from Turawa Impoundment Lake – an artificial reservoir built on the Mała Panew River, located in SW Poland within the Opole voivodship. This region was selected for a pilot project among fourteen other objects from the Odra river catchment within the large-scale program called "The ecological state of barrier lakes in the Odra river basin and conducted works towards its improvement". The major drilling campaign in the bottom of the lake was carried out in the period between June and September 2004. In total 260 sediment samples were collected from 34 sediment cores (from 0.07 to 8.00 m in length).

Waste samples from a post-production dumping site (used by the metallurgical industry) were collected from the old industrial waste lagoon, which is located close to the bank of the Mała Panew river, near its mouth to Lake Turawskie. Material disposed there contains moulding sands, metallurgical gravels and gravels from electrothermal power plants. Toxic substances present in the slags are eluted by rain water and then transported by river water, either dissolved or adsorbed on suspended matter, directly into Lake Turawskie, located 2 km away.

2.2 *Ecotoxicity testing*

Acute toxicity was determined using the *ToxAlert 100*® (ToxAlert 100 Operating Manual, 1999) and the *Microtox*® *Model 500* (Microtox Analyzer Manual, 2006). As bioindicator organisms the bioluminescent bacteria from the comma bacillus group (*Vibrio fischeri* class) were applied. Toxicity measurements of water samples and aqueous elutriates obtained from sediments were conducted in accordance with the requirements of ISO standards (PN-EN ISO, 1998; PN-EN ISO, 2002). Additionally, the determination of the toxicity of water samples included (i) a microbiotest performed by application of *Daphnia magna* crustacean in order to determine the acute toxicity (*Daphtoxkit F*^{TM} *magna*) according to the ISO standard (PN-EN ISO, 2002) and (ii) also the chronic toxicity tested in accordance with the ISO standard (ISO, 2000). Sediment samples were also tested for toxicity using the *Ostracodtoxkit F*^{TM} *chronic* aimed at the determination of chronic toxicity in the presence of *Heterocypris incongruens* crustacean. This test was performed according to the recommendation of Prof. Dr. Guido Persoone (*MicroBioTests Inc*., Nazareth, Belgium) (Standard operational procedure).

2.3 *Chemical analyses*

The organic compounds present in the ground water samples from beneath communal landfills were extracted with dichloromethane and determined using the GC-MS technique.

The sediment samples, collected from Turawa Impoundment Lake, were tested using: gas chromatography coupled to mass spectrometry (PCB congeners, organochlorine pesticides, PAH), inductively coupled plasma – atomic emission spectrometry (Cr, Zn, Cu, Ni, V, Fe, Mn, Al, Li), electrothermal atomic absorption spectrometry (Cd, Pb), hydrid generation atomic absorption spectrometry (As), cold vapour atomic absorption spectrometry (Hg), the trueness of which was examined by analyses of appropriate reference materials, i.e., SRM 1941a (Organics in Marine Sediment, NIST) in the case of PCBs and PAHs, and MESS-2 (Marine Sediment, NRCC) in the case of heavy metals.

The organic compounds present in the samples from the post-production waste of the metallurgical industry were determined using the GC-MS, HPLC-MS and HPLC-DAD techniques.

3 RESULTS AND DISCUSSION

The problems of waste management, both municipal and industrial, and remediation or water basins dredging processes, are usually solved in Eastern Europe *via* their disposal in the environment. There is a range of local and European Community laws regulating such disposal based on various chemical factors of the waste pollution. These factors are used to classify the wastes' quality. Similarly the condition of the environment (mostly of the ground waters) around landfills is monitored and assessed.

The drawback of the system of assessing the quality of the environment based on chemical monitoring is the difficulty in directly estimating biological effects rising in the controlled ecosystem by the complex composition of pollutants already present in the environment or introduced with the wastes disposed. The difficulty of such assessment increases greatly with introducing the phenomenon of bioavailability and realising the fact that only the compounds set as environmental pollution factors are estimated. In this system the wide range of compounds of known, as well as of the unidentified structure (and *ergo* of unspecified toxicity), continues to be out of control.

Traditional chemical approaches to assessing environmental pollution levels have been supplemented with ecotoxicological research for a few years (Kristensen and Krogsgaard, 1997; Bispo et al., 1999; Galassi and Benfenati, 2000; Benfenati et al., 2003; Eilersen et al., 2004).

Not only the content of contaminants in the wastes, but also their form of existence, mobility and bioavailability or eventual presence of other than appointed compounds mentioned in regulations (the toxic action of which may pose significant problems in the environment) determine the level of threat to the environment.

Ecotoxicological research, the results of which reflect specific effects toward the tested indicating organisms exposed to the complex mixture of compounds eluted from wastes, may supply an additional source of information about the environmental threats that are rising with the tested material disposal.

In the next section results of projects dealing with the assessment of the threats to the environment posed by old, unsealed municipal waste landfills, industrial landfills and polluted lake sediments, are presented.

3.1 *Municipal wastes landfills*

Detailed information on research conducted within the framework of the project to assess effects of the municipal waste disposal toward the ground water quality, based on large unsealed municipal landfills, are presented elsewhere (Wolska et al., 2006; Kuczyńska et al., 2006).

The results obtained from these studies identify considerable discrepancies between ecotoxicological classification (according to Helsinki Committee's recommendations (No. 23/10–12; 2002), proposed by F. Krebs (1988) and G. Persoone et al. (2003)) and chemical classification (according to the Decree of the Minister of the Environment of Poland (2004)) in the ground waters quality assessment. In every case good chemical assessment was consistent with lack of toxic effects toward selected test organisms. There were certain instances where a low (bad) chemical assessment (resulting e.g., from elevated content of such components as Cl^- and Fe) found no proof of a real threat toward living organisms (no toxic effects). In such a case ecotoxicological classification supports the process of assessing the actual existing threats.

Cases of low ecotoxicological quality classification (V and VI class) for ground water were paralleled by equally low chemical quality classification. Detailed analyses aimed at identification of the toxic compounds present in water samples revealed the presence of substances, monitoring of which is not required due to relevant regulations, such as aniline, chlorobenzene, dibutyl phthalate.

The analysis of water samples applying LE-GC-MS and PT-GC-MS techniques allowed the identification of only a small portion of the compounds responsible for the high acute toxicity toward *Vibrio fischeri*. Such a conclusion can be withdrawn based on substantial differences in values of parameters TU – Toxicity Units and TII_{50} – Toxicity Impact Index (the sum of $TU = 0.0251$; while $TII_{50} = 8.26$). Values of the TU index for particular identified compounds, were calculated with the help of the literature values of EC_{50} (Kaiser and Palabrica, 1991). The summarised value of the TU index, determining the toxicity of the examined sample based on loads introduced by specific compounds, were compared to value of TII_{50}, calculated as EC_{50} value for the sample. Most probably the difference between the TU and TII_{50} results from the presence of other chemical substances, not identifiable when applying the above mentioned analytical techniques.

Research conducted during the project did not reveal any case of waters having a high chemical quality classification and a low ecotoxicological quality classification. Taking into consideration the general tendency to limit the number of chemical parameters in ground water monitoring around landfills it should not be easy to identify such a case.

In summary, the results of the studies conducted prove that ecotoxicological research constitutes a useful tool in assessing threats to ground water posed by municipal waste disposal:

- they considerably supplement the chemical quality assessment,
- they may be a base (for low ecotoxicological classification) for further, detailed chemical analyses including toxic compound identification,
- in certain cases (high quality of chemical results) they can replace chemical studies in ground waters monitoring, thus greatly lowering the costs of landfill exploitation.

It is recommended that ecotoxicological studies be more widely applied by local authorities in the process of environmental management.

3.2 *Excavation material from polluted lakes' reclamation*

The European Union regulations as well as related local ones, consider the excavation material from water basins dredging (including harbour reservoirs) and other reservoirs and water-courses (including lakes) as waste material. They are monitored for the following parameters indicated in the regulations (heavy metals: As, Cr, Zn, Cd, Cu, Ni, Pb, Hg; PAHs: BaA, BbF, BkF, BaP, IndP, DahA and BPer, and PCBs: PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180) before their disposal in the environment.

Chemical studies conducted on Turawskie Lake sediments within the project have indicated a high pollution level. The greatest amounts of analysed substances were shown to be present in the superficial layer of the sediments. In numerous samples permissible levels of benzo(a)anthracene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo (a)pyrene, indeno(1,2,3-c,d)pyrene, arsenic, mercury, cadmium, lead, zinc and copper, were exceeded. The organic compounds and heavy metals mentioned above pose a threat to biological life within the reservoir and make the eventual excavation and transport of the sediments on land impossible (Decree of the Minister of the Environment of Poland (2002)).

Considering the number of samples in which the admissible levels of PAH's and heavy metals were exceeded, pollution levels may be ranked descending in the following manner: Cd > Zn > As > Pb > BaP > IndP > Cu and BPer > BbF > BaA > Hg and BkF. This ranking indicates that cadmium, zinc, lead, arsenic and benzo(a)pyrene are the substances mostly responsible for polluting the examined sediments. The highest exceedances, which amounted to a few ten-fold of the permissible levels, were recorded for cadmium.

None of the samples indicated exceedances of admissible levels of the seven PCB congeners, dibenzo(a,h)anthracene (DahA), benzo(k)fluoranthene (BkF), chromium and nickel.

In addition to the mentioned target substances, the presence of which in the environment is regulated (as stated previously), determinations of chlorinated organic pesticide residues were conducted; of these only mostly insoluble (in water) compounds were determined in the samples and in low concentrations levels. These insoluble forms are believed not to pose a threat to living organisms. Additionally, the content of Fe, Mn, Al, V, and Li was determined. However their concentration levels did not exceed the geochemical background levels.

In cases of almost all bottom sediments samples the effects of acute and chronic toxicity toward selected organisms were observed. The ecotoxicological battery of tests consisted of organisms of different trophic levels:

- bacteria *Vibrio fischeri*, for which it is assumed that mainly dissolved forms of substances are available (including toxic substances),
- crustaceans *Heterocypris incongruens*, (direct contact test), for which probably other than only dissolved forms of substances are bioavailable (e.g., adsorbed on solid particles' surfaces).

The classification of the sample quality based on chemical parameters (according to the Decree of the Minister of the Environment of Poland (2002)), was compared to the ecotoxicological classification according to the system developed within the Arge Elbe project (Reincke et al., 2001). Almost all samples were stated to belong to the 4th and 5th ecotoxicity class (Figure 1).

Firstly it must be noted that the chemical classification is not strictly compatible to the ecotoxicological classification. For example, samples were often collected which fulfilled all criteria for being unpolluted excavation material, based on stated highly elevated toxicity toward both indicating organisms (*Vibrio fischeri* bacteria and *Heterocypris incongruens* crustacean). These sediments were stated to belong to

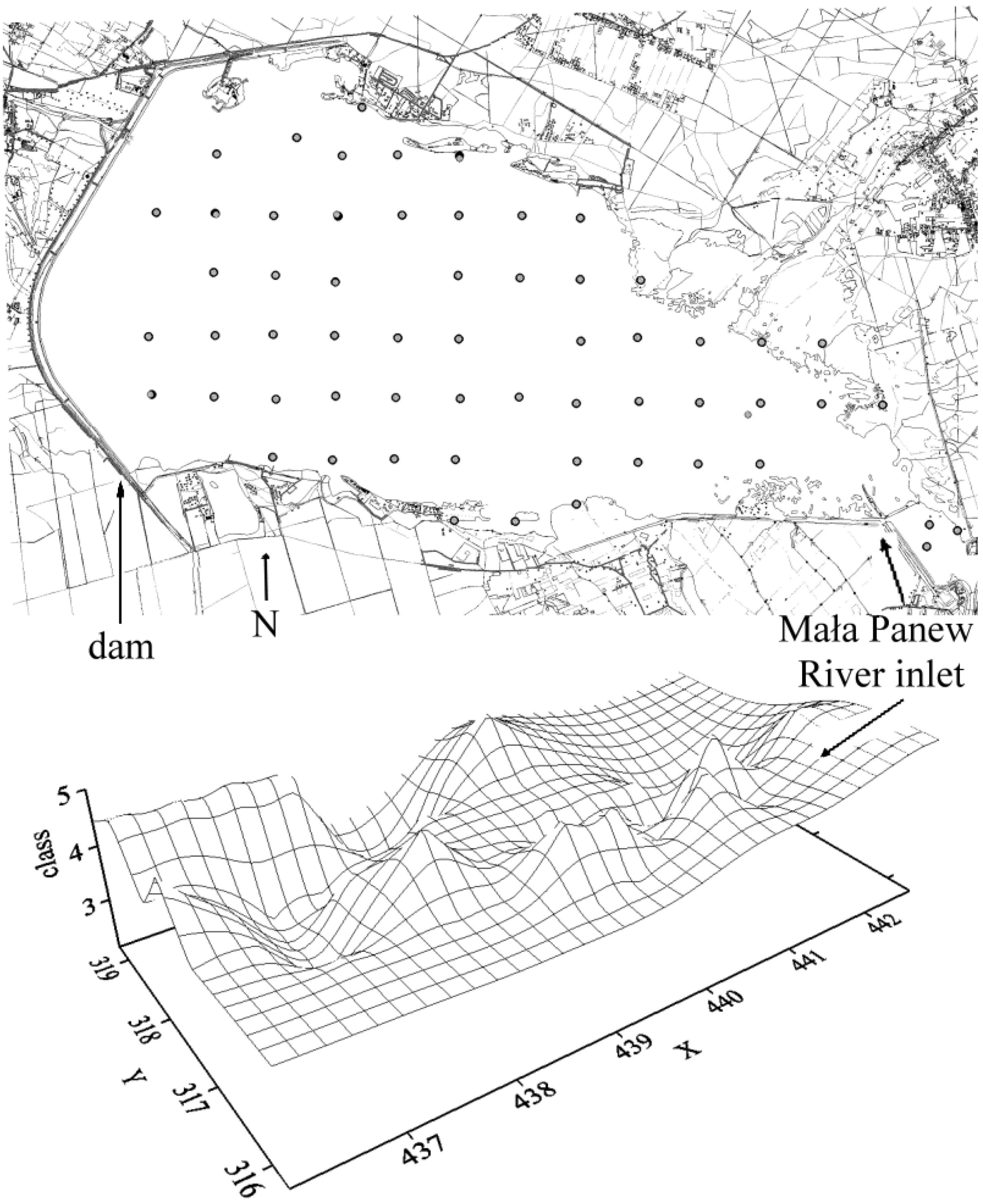

Figure 1. Sediment ecotoxicity classes (1st superficial layer) and distribution of sampling sites.

the 5th ecotoxicological class. It seems therefore that there are compounds other than those regulated (Minister of the Environment of Poland (2002)) responsible for such high toxicity levels.

The application of chemometric methods (Simeonov et al., 2007) to search for possible correlations between chemical and ecotoxicological parameters has proved the lack of such correlations. The application of the PCA has enabled the separation of four latent factors explaining nearly 70% of the total variance. The first latent factor (PC 1) explains 34% of the total variance and shows a strong correlation between the following parameters: chlorinated organic pesticides, PAH's and heavy metals. This component

Table 1. Results of acute toxicity determinations toward *Vibrio fischeri* and chronic one toward crustacean *Heterocypris incongruens* conducted on samples of postproduction wastes from "Mała Panew" metallurgical plant in Ozimek.

	Toxicity							
	Acute toward *Vibrio fischeri*				Chronic toward *Heterocypris incongruens*			
Sample number	Extract's pH	Regulated pH	Bioluminescence inhibition [%]	NOEC [%]	EC_{50} (30 min) [%]	Mean growth increment [μm]	Growth inhibition [%]	Mortality [%]
1	10,61	6,67	39	33	111	25	89,4	0
2	10,72	7,14	63	15	48	40	82,9	0
3	13,36	7,17	99	20	25	dead	dead	100
4	8,91	7,24	38	30	137	10	96	0
5	8,50	6,96	99	~0	2	dead	dead	100
6	12,92	6,44	99	~0	~0	0	100	40

unequivocally shows anthropogenic pollution, connected to the metallurgical industry, localised in the Mała Panew basin. Chlorinated organic pesticides also mark their presence in the second latent factor (PC 2), which explains 15% of the total variance. PC 3 explains 11% of the total variance and reflects the influence of compounds from the PCB group. Based on determined values of the factor loads one can conclude that in the future the cost of conducting environmental monitoring on a given area can be reduced by decreasing the number of necessary chemical parameters. The determination of PCB 51, PCB 138, α-HCH, heptachlor epoxide, arsenic content and ignition losses can be omitted. PC 4, explaining only 6.4% of the total variance, is related only to the ecotoxicological parameters. The negative values of the factor loadings determined for toxicity parameters EC_{20}, EC_{50} prove the reverse interpretation of their values in relation to other toxicity parameters (the lower the EC_{20} and EC_{50} the more toxic the sample).

Toxicological studies show how complex the influence of the pollutants toward organisms is and how greatly it depends on:

- the concentration of the bioavailable form of the toxicant, not the total concentration, because it appears that the bioavailable form is not always identical to the mobile form (knowledge about these effects is still very scarce),
- the interactions between pollutants (synergism, antagonism),
- the presence of other pollutants than those regulated to determine (including elemental sulphur, the presence of which was stated in the superficial layers of the sediments and the toxicity of which is very high toward bioluminescent bacteria of *Vibrio fischeri* $EC_{50} = 15.2 \div 35.8$ μg/L (Jacobs et al., 1992; Svenson et al., 1998a; 1998b)).

Toxicological studies are a valuable and precious supplement to the information gained from determinations of chemical parameters. They should be widely included into the excavated material's pollution level estimations, so that such estimates reflect the real threat to the location of sediment placement.

The results of the ecotoxicological studies can, moreover, constitute the basis for decisions about increasing the range of chemical research, including decisions on conducting cost studies leading to identification of the toxic compounds.

3.3 *Industrial wastes (postproduction wastes from the metallurgical industry)*

The huge problem created over many years of industrial development are the post-production wastes, disposed most often directly to the environment near factories. One example of such wastes may be the post-production wastes from the metallurgical industry disposed in the form of a dump. One such dump is localised in Poland near the Mała Panew River inlet to the Turawskie Lake artificial reservoir, directly near its banks. In the run-off waters from post-metallurgical dumps one can expect to detect the presence of a wide range of compounds, including some which are toxic. These waters influence the quality of both waters and sediments by delivering pollutants to the rivers and lakes.

Table 1 shows the results of toxicity determinations on samples collected from a post-metallurgical waste dump. Greatly elevated acute and chronic toxicities toward the test organisms are revealed. Samples numbered as 3, 5 and 6 are characterised by the highest toxicity values.

Determination of the ecotoxicological quality of the sediments tested (based on the Arge Elbe classification system developed during the Arge Elbe project (Reincke et al., 2001)) assigns all samples of the postproduction wastes to the V ecotoxicological class.

The elevated toxicity values of the materials collected from the post-metallurgical dump provided the motivation to undertake screening studies to identify the responsible pollutants. Post-metallurgical wastes possessed a very complex morphological structure. They contained fragments of slag and ashes, with large amounts of metal oxides within their structure (for this reason their extracts were of high pH, which had to be regulated to the desired range for the ecotoxicological test analyses) as well as particles containing organic components. The latter became the main subject of our interest. In the first stage chromatographic analyses were conducted on dichloromethane extracts prepared by directly treating the samples with two portions of the solvent. Chromatograms obtained in this way were very complex and the preliminary analyses of mass spectra suggested that high atomic weight compounds probably with condensed aromatic rings were present in the samples.

The highest danger to human health and life are posed by water-soluble compounds. Their bioavailability is high and thus their ability to enter organisms facile. For this reason aqueous extracts of sediment samples also underwent chemical analysis. In this case, the chromatograms contained a limited number of peaks. The GC-MS technique is most often used to analyse compounds with low atomic masses (up to 800 Da), volatile and semi-volatile, non-polar and semi polar substances. For this reason it is very probable that in the extracts tested polar compounds were present – these are not retained inside the chromatographic column of specific gas chromatograph. The high level of contamination of the precolumn during GC-MS analyses may prove the existence of these compounds.

Further analyses were conducted using the HPLC-DAD and HPLC-MS techniques. The results confirmed the information gained from GC-MS analyses. High molecular weight compounds, which gave mass or fragmentation peaks of high intensity may indicate the presence of aromatic and polyaromatic hydrocarbons. The shifts in signal maxima (even up to 280 nm) also indicate the presence of complex groups.

Results of the preliminary studies presented here show the importance of the results of the ecotoxicological studies with the application of standard biotests and of the substantial information they include.

4 CONCLUSIONS

The application of the standard test to assess the toxicity (acute and/or chronic) of the environmental samples or waste materials enables additional information to be obtained about the potential integrated influence of the material tested on living organisms. Unlike the chemical approach, the results of ecotoxicological research give a complex answer about the bioavailable portion of pollutants present in the complicated environmental matrix. Different susceptibilities against complex mixtures of toxic compounds require the test batteries to consist of organisms of different trophic levels.

The results of the studies presented here show new areas of possible application of biotests, where ecotoxicological results can efficiently support decisions about waste management including their disposal in the environment.

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