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Environmental Security

Environmental Security and Ecoterrorism

Edited by
Hami Alpas
Simon M. Berkowicz
Irina Ermakova

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Environmental Security and Ecoterrorism

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Series C: Environmental Security

Environmental Security and Ecoterrorism

edited by

Hami Alpas
Middle East Technical University
Food Engineering Department
Ankara, Turkey

Simon M. Berkowicz
Hebrew University of Jerusalem
Arid Ecosystems Research Centre
Jerusalem, Israel

and

Irina Ermakova
Russian Academy of Sciences
Institute of Higher Nervous Activity and Neurophysiology of RAS
Academy of Geopolitical Problems
Moscow, Russian Federation

Springer

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Preface

During 2010, several diverse incidents or threats took place related to environmental security and ecoterrorism. In August, several hundred wildfires broke out across the Russian Federation killing several dozen people and contributing to the deaths of hundreds affected by the poisonous smog. In October a toxic reservoir collapsed in Hungary, killing a handful of people and contaminating an estimated 1 million hectares of farmland. In December, US Department of Homeland Security officials indicated that the Al Qaeda group may try to poison food supply sources such as salad bars and buffets in restaurants and hotels and Israel's largest forest fire occurred killing over 40 people. No matter whether harm to the environment and to lives is caused by deliberate actions, through negligence, or act of nature, they can serve as harbingers for future potential disasters.

It was thus timely that a NATO Advanced Research Workshop (ARW) on "Environmental Security and Ecoterrorism" was held in Moscow, Russian Federation, between April 27–29, 2010, covering a multitude of topics related to this theme. A total of 43 participants from 17 different countries and from four continents participated in this Workshop and presented their research. Folowing each keynote speaker and at the end of each Session, considerable time was set aside time for debate and discussions. In addition, the participants had the opportunity to share experiences based on national and international best practices and studies performed. The forum was very fruitful regarding the Workshop theme and the informative presentations and congenial atmosphere contributed to the success of this ARW. The Workshop brought together a diverse group of individuals and we anticipate that new collaborative links will develop between some of the participants.

Although the term "environmental security" is a rather straight-forward concept, "ecoterrorism" requires some explanation and definitions. One can divide ecoterrorism into two separate components. The first is where individuals or groups are environmental "activists", carrying out actions against industries, companies or even governments that they believe are harming the environment, as a means to attract attention to their cause. For the large part, damage is caused to property although some deaths have been reported. The second is where the environment is used as a weapon to harm an opponent. Here the intended outcome is usually large-scale deaths, severe damage to the environment, and generating fear into the populace.

Perhaps we can add a third definition of ecoterrorism as harm caused by companies, industry, or governments through negligence. Here, lack of either environmental regulations or enforcement by regulatory agencies can allow for hazardous sites to be established and/or become potential sites for natural disasters or that could attract the attention of terrorists. Insufficient forest fire outbreak monitoring capabilities, low standards for the construction of mining waste dams, and inadequate infrastructure are all examples that can provide inadvertent support of catastrophes.

This book begins with a paper by Shearer & Liotta on how the environment is a security matter for a state. This is followed by Berkowicz who provided a background to definitions of ecoterrorism and a discussion on countermeasures. Kharlamova proposed modeling ecologic-economic complex systems to calculate the possible negative impacts of ecoterrorism. Issues related to food security weaknesses are covered by Veiga, Komar & Dvorak, and Bozoglu. Omelchenko focused on lead contamination buildup in the environment as a kind of latent ecoterrorism. Gnatko et al. looked at the application of electrolyzed aqueous solutions for water disinfection. Khaydarov et al. investigated intriguing questions related to environmental and health issues involving nanoparticles. Kharytonov & Kroik examined the environmental safety of mine wastes that are exposed during storage on the surface. Nochvai et al. dealt with air quality management and emergency response systems, while Popov et al. explored the application of hyperspectral imagery to detect contaminated soils. Winkler examined environmental security issues related to water resources crossing international boundaries. Ermakova completes this book with problems related to genetically modified organisms.

The main outcomes of this ARW were:

(i) Environment quality management systems should be developed for integrated assessment of environmental risks for the population, no matter if the threat is from terrorism or negligence, and for attaining optimal strategies to reduce such risks.
(ii) Rapid detection, response, and coordination efforts must be developed for emergencies, accidents and terrorist attacks. Countermeasures must be prepared to cover most-likely contingencies.
(iii) Reducing environmental risks requires public awareness of hazards and environmental education on possible threats.
(iv) Technological developments may provide the needed tools for detecting, preventing, or monitoring of given threats to the environment and people.

We take this opportunity to thank the Academy of Geopolitical Problems (AGP) for providing personnel and logistical support during the Workshop. Special thanks go to the NATO Emerging Security Challenges Division, Science for Peace and Security Section (SPS), for their unfailing support throughout all phases of this Workshop, in particular Dr. Deniz Beten, Programme Director Environmental Security, and to Lynne Campbell-Nolan, SPS Programme Assistant. The editors also greatly appreciate the valuable support of our distinguished colleagues Allan Shearer (University of Texas at Austin, Texas, USA), Alexandra Veiga (Universidade

Nova de Lisboa, Portugal), and Alex Omelchenko (University of Manitoba, Manitoba, Canada) for additional editing assistance.

Last, we find it most appropriate to dedicate this book to the memory of our distinguished colleague, Dr. Tatiana Parshikova, Russian Federation, who tragically passed away during the ARW.

Hami Alpas
Simon M. Berkowicz
Irina Ermakova

Participants of the NATO-ARW ”Environmental Security and Ecoterrorism”, Moscow, Russian Federation, April 27–29, 2010

Contents

Contributors

Hami Alpas
Food Engineering Department, Middle East Technical University,
Ankara 06531, Turkey
imah@metu.edu.tr

Simon M. Berkowicz
Arid Ecosystems Research Center, Hebrew University of Jerusalem,
Jerusalem, Israel
berkowi@vms.huji.ac.il

Faruk Bozoglu
Department of Food Engineering, Middle East Technical University,
Ankara, Turkey
Bozoglu@metu.edu.tr

Seung Y. Cho
Department of Environmental Engineering, Yonsei University,
Wonju, South Korea

Jiri Dvorak
University of Defence, 65 Kounicova, Brno, The Czech Republic
jiri.dvorak@unob.cz

Irina Ermakova
Institution of Russian Academy of Sciences, Institute of Higher Nervous
Activity and Neurophysiology of RAS, Academy of Geopolitical Problems,
Moscow, Russian Federation
Ermak_i@mail.ru

Svetlana Evgrafova
V.N. Sukachev Institute of Forest SB RAS, Krasnoyarsk, Russia

Elena N. Gnatko
Ukrainian State University for Chemical Engineering, Dnepropetrovsk, Ukraine
gelnik2011@mail.ru

Ganna Kharlamova
Kiev National Taras Shevchenko University, Kiev, Ukraine
akharlamova@ukr.net

Mykola M. Kharytonov
Dnipropetrovsk State Agrarian University, Voroshilova St.,
25, Dnipropetrovsk 49027, Ukraine
mykola_kh@yahoo.com

Renat R. Khaydarov
Institute of Nuclear Physics, Tashkent, Uzbekistan
renat2@gmail.com

Rashid A. Khaydarov
Institute of Nuclear Physics, Tashkent, Uzbekistan

Ales Komar
University of Defence, 65 Kounicova, Brno, The Czech Republic
ales.komar@unob.cz

Anna A. Kroik
Dnipropetrovsk National University, Gagarina Av.,
44, Dnipropetrovsk 49600, Ukraine

Vasilij I. Kravets
Ukrainian State University for Chemical Engineering, Dnepropetrovsk, Ukraine

Elena V. Leschenko
Ukrainian State University for Chemical Engineering, Dnepropetrovsk, Ukraine

P.H. Liotta
Salve Regina University, Newport, RI, USA

Ludmila P. Lischenko
Scientific Centre for Aerospace Research of the Earth, Kiev, Ukraine

Vladimir V. Lukin
National Aerospace University, Kharkov, Ukraine

Volodmyr I. Nochvai
Pukhov Institute for Modeling in Energy Engineering, National Academy
of Science Ukraine, Kiev, Ukraine
volivn@ukr.net

Alexander Omelchenko
Department of Physiology, Institute of Cardiovascular Sciences, St. Boniface
General Hospital Research Centre, University of Manitoba,
Winnipeg, MB, Canada
omelca@sbrc.ca

Nikolay N. Ponomarenko
National Aerospace University, Kharkov, Ukraine

Mikhail A. Popov
Scientific Centre for Aerospace Research of the Earth, Kiev, Ukraine

Angelina V. Shavrina
Main Astronomical Observatory, National Academy of Sciences of Ukraine, Kyiv, Ukraine

Allan W. Shearer
School of Architecture, The University of Texas, Austin, TX, USA
ashearer@austin.utexas.edu

Sergey A. Stankevich
Scientific Centre for Aerospace Research of the Earth, Kiev, Ukraine
st@casre.kiev.ua

Alexandra Veiga
Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. da República, Oeiras 2780-157, Portugal
aveiga@itqb.unl.pt

Oleksandr A. Veles
Main Astronomical Observatory, National Academy of Sciences of Ukraine, Kyiv, Ukraine

Stefanie Wagner
Institute of Technical Chemistry, Gottfried-Wilhelm-Leibniz University, Hanover, Germany

Igor Winkler
Yu. Fedkovych Chernivtsi National University, Kotsiubynsky St., 2
Chernivtsi 58012, Ukraine
igorw@ukrpost.ua

Chapter 1
Environmental Security and Its Meaning for the State

Allan W. Shearer and P.H. Liotta

Allan W. Shearer is faculty member of the University of Texas School of Architecture, where he first served as a Harrington Fellow there. As a member of the IPCC Working Group II, P. H. Liotta shared in the award of the 2007 Nobel Peace Prize. Liotta and Shearer are authors most recently of *Gaia's Revenge: Climate Change and Humanity's Loss.*

Abstract Underscoring the critical tension between environmental security and ecoterrorism, the authors present two essential propositions linking environments, states and security. The first is that the praxis of security should be understood as extreme efforts within a state's larger management of uncertainty about the future. By focusing on a motivation for government action – rather than as a locus of bureaucratic activity – we open the possibility for more nuanced discussions and decisions on security. As such, recognizing the critical relationship between environmental security and ecoterrorism, it becomes possible to consider greater sources of uncertainty and alternative responses. The second proposition suggests that the planning, design, and use of the environment are fundamental aspects of a state's response to uncertainty and vulnerability. By examining uncertainty, recognizing vulnerabilities, and designing adaptive response measures, will fundamentally improve security.

Keywords Uncertainty • Vulnerability • Environmental security • Police powers • Operational environments

A.W. Shearer (✉)
School of Architecture, The University of Texas, Austin, TX, USA
e-mail: ashearer@austin.utexas.edu

P.H. Liotta
Salve Regina University, Newport, RI, USA

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1.1 Introduction

The term *security* stems from the Latin *securitas*, which translates as 'lack of care' [33]. This basic definition seems unproblematic and it is a truism to say that security is a critical matter for individuals and societies. The concept becomes contested through its application, when several referents must be specified. Specifically, security is a derivative term in that it presupposes something to be secured [58, p. ix]. Defining just what that something is raises questions about how values – or in a more limited way, interests – are established, shared, and maintained. Security also presupposes some *other* that poses a danger. Here, the hazard must be qualified: How is it manifest? From where does it come? When might it strike? [5, 55, p. 229]. Further complicating the understanding of the word is the context of its use. Because security risks are, in common practice, associated with matters of survival, security trumps other political activities and it can allow for extraordinary measures. It must therefore be asked who within a society has the authority to declare something a security issue, who has the responsibility to respond, and what (if any) are the limits of action? [16] The dynamics of operations also present problems: Increasing security in one way may lessen it in others [28], and providing security for one group may render other groups less secure [50, 51].

Theorizing society's relationship to the environment as matter of security can be traced (at least) to the eighteenth century economist Thomas Robert Malthus. He projected that the growth of human population would outpace the growth of resource production, and thus bring about a societal catastrophe [63]. Much more recent archaeological evidence has shown that in the past, shortfalls in the ecological base led to conflict among tribes, bands, and chiefdoms [59]. These findings are significant because these units of social organization are still operative in parts of the world today where state authority is weak. Arguments that the environment is a security concern at the social unit of the state became a concern among environmentalists in the 1970s [12], a subject of academic debate in the 1980s [88], an espoused factor in national strategy in the 1990s [13, 23, 77], and an increasing source of public anxiety through the 2000s [74].

But, just how is the environment a security matter for a state? Attempts to provide a state-environment-security nexus can result in extreme positions that thwart nuanced thinking and stifle productive dialogue. On the one hand, because the environment provides an ecological context to all human activity (providing the material base for individual sustenance and spatial setting for social interactions), it seems intuitive that the environment contributes to the construction of risk and to the limitation of available courses of action. As such, one can argue that the environment should be considered a security referent or issue. Following from this position, environmental degradation has been called 'the ultimate security issue,' because it permeates all aspects of society [25, p. 85]. But, on the other hand, (precisely) because the environment provides an ecological context to all human activity, it can overwhelm, or at least obfuscate, the conventionally thematic focus of security studies on potential or real violence among definable actors. As such, considering the environment as a security issue can result in analysis that is ambiguous, if not meaningless [30, 31].

To move the discussion beyond these polarized positions, this paper views the praxis of security as, foremost, part of a state's larger management of uncertainty about the future. States face imaginable possibilities that range from immanent existential threats to seemingly mundane, but cumulatively significant, contingencies. Focusing on uncertainty as a primary motivation for government action rather than focusing on any locus of bureaucratic activity provides several advantages. Broadly, it avoids the pitfalls of overstated analytic distinctions that have been common in political theory. Notably, the strict dichotomy between 'high politics' (that is, action related to sovereignty and international alliance) and 'low-politics' (such as action related to social and economic relationships) is recognized increasingly as having limitations [75, 92]. Similarly, different arguments have been put forth about how the once academically separated spheres of domestic politics and international affairs are intertwined [39]. More narrowly, a focus on conditions of uncertainty and a recognition that different attitudes toward it are possible can allow issues to be re-examined as a society's understanding of its situation within the world changes. Extraordinary measures in the face of great uncertainty may be necessary; however, routine practices can be developed and institutionalized as sources of uncertainty become better recognized and understood. It can also be suggested that without the flexibility to escalate and deescalate a posture toward uncertainty, a society may fail to properly address emerging dangers or misallocate limited resources. Perhaps above all, considering security within a larger discourse of uncertainty can contribute to the goal of making acts of security better integrated with larger political processes [90].

We argue that the state remains an organizing entity for many kinds of actions that are locally, regionally, and globally meaningful. Some of these actions directly alter or regulate the environment at spatial scales that are ecologically significant for the support of individuals, communities, and the states themselves. While the two considerations mentioned above present limitations and may leave some analyses incomplete, the state's relationship to the environment cannot be dismissed easily at this time and it, therefore, warrants continued attention.

As Berkowicz [9] clearly articulates, understanding and grappling with current and future challenges, ecoterrorism can be defined as: (1) Terrorism intended to hinder activities considered harmful to the environment and (2) Terrorism intended to damage the "environment" of the enemy. Thus, nature itself can and is used as weapon to further political and/or ideological goals. Within the context of ecoterrorism, therefore, a state's responsibility to addressing environmental vulnerability is both fundamental and absolute requirement to move toward enhanced security.

1.2 Uncertainty, Vulnerability and the Environment

Uncertainty may become apparent in any or all of three instances [66]. First, uncertainty may be related to future conditions, such as the state or position of identified elements, the way elements will behave and interact, the rate at which elements will change, or the timing of future events. (For example, will the hurricane strike the coastal town and will it gain or lose strength as it approaches?) Second, uncertainty may be related to the magnitude or timing of effects related to some (certain or uncertain) future condition. (If the hurricane strikes as a category-3 storm, how many buildings will be damaged or destroyed?) Third, uncertainty may be related to the appropriate response to (certain or uncertain) future conditions that have (certain or uncertain) impacts. (If the hurricane strikes as a category-3 storm and it will severely damage but not destroy all of the buildings on Main Street, should the structures be fortified or evacuated?). The first two instances of uncertainty (those of conditions and effects) raise questions of ontology – if we can know the world with certainty – and of epistemology – how we can know the world with certainty. The third instance of uncertainty (that of action) carries questions about the limits of agency (what options are available) and of morals and ethics (what should be done) [85].

Uncertainty becomes a potential problem when it is connected with vulnerability. A vulnerability can be understood as a weakness, often one that is made apparent in times of change, such as when elements within a system are, in some way, reconfigured [11]. The opposite of vulnerability – the ability to adapt or overcome change – is resilience [19, 41]. More comprehensively, vulnerability is manifest in the lack of an ability to anticipate, avoid or resist, cope, and/or recover from the impact of a harm [65, 71]. This conceptualization of vulnerability foregrounds awareness of internal limits relative to context. An evocative characterization of how marginal changes to vulnerable systems can produce devastating effects is provided by R.H. Tawney: He describes the rural population in China during the 1920s as, 'that of a man standing permanently up to the neck in water, so that even a ripple is sufficient to drown him' [86, p. 77]. As with some kinds of uncertainty, some societal vulnerability related to the environment is constructed though the acts of meeting societal needs and achieving aspirations [68, 71].

The latter part of the twentieth century saw recognition of the limits of scientific knowledge and technological know-how. In particular, attention was given to 'manufactured uncertainties' that are produced through the increasing interconnectivity and complexity of social systems [7, 44, 45]. In this era, the new watchword 'precaution' called for the proof of safety before the taking of action. While still only in the beginning of the twenty-first century, the formalized precautionary principle has been criticized for embodying a paradox: on the one hand, there is the acknowledgement that scientific evidence is not decisive; on the other hand, there is the call by decision-makers to science for analysis that is conclusive [89]. More strongly, the precautionary principle has been criticized on the grounds that it 'replaces the balancing of risks and benefits with what might be described as pure pessimism,' and, as such, may be excessively conservative [72]. In reading across these changes in perspective it becomes evident that greater knowledge and technical ability shifts the focus of uncertainty, but it does not remove uncertainty. Instead, new advances make us aware of what we were previously unaware. That is, to use a common truism, 'the more we know, the less we know.' Therefore, what is needed to move forward in any decision making process is an explicit articulation of assumptions about the kinds of uncertainty that are recognized and the corresponding means that are available to address them.

A focus on vulnerabilities differs analytically and operationally from a focus on threats (hazards posed by some *other*), which has been the traditional topic of security studies [62]. A threat analysis examines how a harm (whether from an armed opposing force or force of nature) might disrupt, degrade, or destroy different objects or systems. That is, this task considers a range of possible effects given a potential cause. By contrast, a vulnerability analysis examines how disruption, degradation, or destruction might arise by a set of different potential harms. That is, this task considers a range of possible causes given a potential effect. In this light, threat analysis and vulnerability analysis might be viewed as complementary activities. A parallel might be drawn to the relationship in systems theory between 'event tree' analysis, which charts what might follow if an event (usually a failure) takes place, and 'fault tree' analysis, which charts how an event might arise through different means.

Perhaps the most challenging – and the most promising – aspect of applying vulnerability analysis within security studies stems from its shift of attention. Because threat analysis focuses on external agents who may cause potential damage, it allows – if not depends upon – a friend-foe dichotomy of political relationships, such as was advanced by theorist Carl Schmitt [80]. Because vulnerability analysis focuses on internal conditions of damage, it allows that harm may be the by-product of otherwise beneficial intentions undertaken by neutral neighbors, friends, allies, or even by oneself. Recognizing that significant environmental damage is often the result of local efforts of improvement or development, is tempting to cite Walt Kelly's satirical transformation of Commodore Oliver Hazard Perry's, 'We have met the enemy, and they are ours' declaration of victory [42, p. 186] into, 'We have met the enemy and he is us' statement of resigned incrimination [57]. But to do so risks confusing the total consequences of meeting a perceived need with motivation for meeting that need. That is, no one intentionally produces toxic pollution, spoils renewable resources, or otherwise seeks to make themselves more vulnerable to environmental disaster; these are unfortunate byproducts of trying to achieve other goals. More significantly, while unintended harm must, inevitably, be addressed, the motivations that prompted the initial action may persist and demonization may be counterproductive to achieving goals. To the degree that a foe must be identified, we suggest that a more apt quotation comes from George H.W. Bush: 'The enemy is uncertainty. The enemy is unpredictability' [14].

Put into practice within a decision making process, the results of threat and vulnerability analyses demand different sorts of thinking. Threats are readily identifiable, immanent, and prompt an understandable response. Within a security-as-defense framework, the sizing of military force and the acquisition of matériel are examples of typical threat response. Presumably, if the threat is removed or can be neutralized, then subsequent effects (whatever they might be) cannot happen. But, even if a vulnerability is conceptually recognized, it is not always clear how best to make processes and functions less susceptible to damage. Further, harm to vulnerable elements is signaled often only by indicators that may not suggest which of the potential causes needs to be addressed. There is also the possibility that the cause or source of the damage is not understood – like, at one time, the salization process associated with irrigation was not understood. This situation makes responding to vulnerabilities 'differently difficult' than responding to threats. Nevertheless, failure to recognize and address vulnerability can result in dire, in not catastrophic, consequences as evidenced by the previous collapse of complex societies [32, 84].

1.3 The State, Uncertainty, and the Environment

The state, the environment, and uncertainty are bound together in two related ways. The first is by a set of social practices. The expansion of the kinds of uncertainty addressed by government that began in the eighteenth century has continued; as has the extension of means to manage uncertainty through police power that started in the nineteenth century. Because of the many ways states now manage routine and extreme uncertainty related to coupled socio-ecological systems, it can be argued, minimally, that the shaping and management of the environment is *potentially* a security issue. It might also be argued, maximally, that the scope of these government activities is so great that the environment is *de facto* a security issue.

The second binding agent is geography. Social practices play-out over space, and the shaping of the built environment has always been fundamental to the state's provision of both Thomas Hobbes-like security related to violence [52] and Jeremy Bentham-like security related to economic well-being [8]. Here, it can be said, minimally, that the growth of cities and the spread of suburbs demand increasing coordination of efforts to manage different kinds of uncertainty; maximally, that given continued extensive and intensive transformation of the landscape (that is, further imbrication of social systems and natural processes, not necessarily ecological degradation), the built environment may become, indeed, the ultimate source of uncertainty and, therefore, the fundamental security objective for the state.

Beginning with social practices, how do those acting on behalf of the state conceptualize sources of uncertainty? And, more significantly, how do these conceptualizations inform responses to manage that uncertainty and thereby further the broadly defined goal of security? Insight on these questions is offered by Brian Rathbun's typology of how ideas of uncertainty contribute to the study and practice of international relations [73]. Although it was developed to consider uncertainty between states and matters of high politics, it can be extended to consider uncertainty within a state and matters of low politics. He identifies four schools of thought that each focus on a different cause of uncertainty. At any given moment, it is likely that each notion of uncertainty will be recognized; however, it is not likely that each will be recognized equally and the emphasis of expectation will result in different prioritizations of effort and expenditure.

The first school identified by Rathbun is that of 'realism.' Its adherents locate uncertainty in a lack of information, and more pointedly, in a fundamental inability to know what others might do. Motivated by fear, the realist response is to prepare for conflict by acquiring increased power, be it through bigger armies or larger infrastructure projects (such as walls, dams, flood control structures).

The second school, 'rationalism,' also emphasizes a lack of information, but the assumption is that motivations and capabilities *could* be known. Motivated by an interest in overcoming ignorance, the response is to provide the means to learn, and assess the actions, of others through increased transparency, monitoring, and the signaling of interests. Security relationships among states in the European Union is predicated on such thinking [27] as are requirements to provide environmental impact statements.

The third school, 'cognitism,' locates uncertainty in ambiguity that results from complexity that is too difficult to resolve. Motivated by an interest in removing sources of confusion, the response calls for increased technical know-how that is shared among stakeholders. Between states, the development and sharing of such knowledge is accomplished through international organizations [46, 47]. Responses under the school of cognitivism include the various forms of zoning: Euclidean zoning (named after the town of Euclid, Ohio, USA) that segregates land uses within a municipal area, form-based zoning that regulates the size and shape of buildings irrespective of their use, and performance zoning that prescribes criteria for how a building or landscape functions vis-à-vis established goals [38]. In each case, the goal is to manage spatial, volumetric, and/or operational aspects of the built landscape while recognizing that not all possible arrangements or patterns can be predicted.

Finally, the fourth school, 'constructivism,' locates uncertainty in ambiguity that results from indeterminacy that is rooted in the lack of conventions. Motivated by an interest in removing ambiguity, the response is to prescribe normative behavior and to ascribe agreed upon meaning to terms and actions. It assumes that identity is socially constructed and that behavior is socially enabled (or correspondingly constrained). Here, multinational and non-governmental organizations shape relationships by identifying and advancing new problems that are to be addressed by states. Providing solutions, in turn, requires states to redefine their own interests and responsibilities [40, 54]. An equivalent concern in environmental management is finding a common and practicable definition of sustainability [6, 17, 53, 70].

As with matters of high politics, routine procedures to manage uncertainty in low politics may be overwhelmed by exogenous factors. Although these factors may come in the form of a jolt, they often appear when thresholds to manage uncertainty within systems are reached. These situations can call for temporary extraordinary actions until new procedures can be implemented. Examples related to development of coupled socio-ecological systems include the suspension of building permits (a regulatory mechanism to manage uncertainties associated with development) due to drought [18] or lack of adequate infrastructure planning [35]. Here, short-term emergency measures are undertaken to provide the broad sense of security that was articulated by Bentham and others. However, it must be emphasized that in taking these actions, normal political processes are suspended in favor of administrative or executive authority.

While concerns about “rogue” cities and failed states continue to warrant significant attention within security studies, the relationship between Bentham-like security and Hobbes-like security is not simply a projective narrative about the reversal of history to an earlier and more limited management of uncertainty. Separating environmental aspects activities related to the state’s authorized monopoly of violence with other activities is difficult since defense-related efforts have been central to the organizing and shaping of the environment since the earliest settlements. In other words, the contingencies of geography matter for understanding the means and ends of security . Given the mutual evolution of military and civilian activities, it must be recognized that efforts to provide Hobbes-like security result in sometimes positive and sometimes negative contributions to Bentham-like security goals.

The most obvious military-civilian synthesis is the layout of towns – a topic that includes the fortification of cities to provide defense against enemy attack [3, 43], the placement of garrisons in support of frontier settlement and imperial ambitions [24, 26], and distributions of industries in support of military needs [64, 91]. After their military use, abandoned forts and battlefields have become significant cultural referents and objects for historic preservation efforts [61, 79]. The construction of road and highway networks has been seemingly always as much about moving troops as it has been about moving goods for trade [67, 76], and more pervasively, military trained engineers and military techniques of problem solving have significantly contributed to the planning and design of civilian infrastructure projects [60, 83]. Not often mentioned in discussions of high politics, there have been jointly supportive military and civilian activities, such as the making of victory gardens in times of war [49] and the US Army’s role in protecting that nation’s first national parks [48]. A topic that has emerged in recent years is the ecological consequences of war [4, 87].

The amount of land dedicated strictly to military use in times of peace was relatively very small for most of recorded history [21]. The footprint of fortifications was rarely significant and billeting troops was accomplished in closer quarters than civilian housing. Most significantly, the instruction of martial skills was accomplished in minimal space: the drilling of infantry could be accommodated on grounds smaller than 5 ha, and cavalry units could ride over nearby hills that had marginal agricultural value. However, in the mid- to late-nineteenth century, the amount of land needed to maintain a proficient military began to expand. The introduction of cannon with rifled bores and explosive shells extended the range of firepower and called for new tactics. Training new and large conscript armies with the advanced weaponry required large tracts of land which could be used constantly throughout the year. The introduction of aircraft to warfare in the early years of the twentieth century also added to the demand for target ranges. These requirements, combined with the improved transportation offered by better roads and railroads which shortened the time needed respond to a potential call for defense, prompted units to relocate to new rural installations where they would have room to maneuver. Continuing advances in technology that offer greater ranges of strike capability and the coordination of larger forces have further expanded and intensified demands on and for training areas. For example, during World War II the battlespace for a mechanized battalion was an area of approximately 1,600 ha [20]. By 1990, increases in the range of weapons and the speed of troop mobility expanded the amount of area covered by a battalion to 32,000 ha. The US Army Training and Doctrine Command Analysis Center predicts a figure upwards of 97,000 ha by the year 2025 [78]. From this vantage, the quantity of the environment in which units can prepare for battle is at issue as national defense and, by extension, a national security concern.

The quality of the environment is also a national security concern to the degree that it allows forces, 'train the way you fight, fight the way you train.' In the United States, the expansion and intensified use of training and testing lands since World War II has resulted in split set of environmental conditions. On the one hand, United States Department of Defense has produced some of the country's most toxic sites. Until the 1970s, regulation of dangerous wastes that are associated with the manufacture and use of weapons systems was limited and the result was contaminated soils, groundwater, and buildings [34, 36]. Clean-up that started in 1990s has been significant [15], but problems persist [22]. While use of these materials contributed to providing Hobbes-like security to the state and to its citizens, they also increase health risks to service personnel on the installations and to members of the general public who are exposed to pollution through transmission via the atmosphere or hydrologic systems [81].

On the other hand, DoD has maintained some of the country's most valuable ecosystems. Since the 1940s DoD has taken increasing steps to conserve maneuver areas on which training depends [2]. And because these large areas are restricted from public use, they provided havens of high quality habitat for many plant and animal species that have been negatively impacted by urban and suburban civilian growth. These factors, coupled with the distribution of installations across the country, have contributed to the situation that no federal agency harbors more endangered species than DoD. Further, although DoD manages only 12.1 million ha out of a total of 272 million ha managed by the federal government, it provides habitat for the more endangered species per unit of area than any other agency [82].

1.4 In Lieu of Closure: Issues for Further Research

In this paper, we emphasized vulnerabilities of coupled socio-ecological systems and to the protection of ecosystem services, which enable societies to develop and be sustained through a process of intentional political ecology [29, 69] – benefits that include provisioning services (such as the supply of food and water), regulating services (such as ameliorating the effects of storms and floods), supporting services (as, for example, nutrient cycling for agriculture), and cultural services (which includes spiritual inspiration and recreational opportunities) [37]. Given the connections between military and civilian uses of the land – and the environments in which military forces operate – political and warfare ecology offer focused focal points for those concerned with security studies and with sustainable development to begin a conversation. More broadly, placing the practice of security within a larger concern for uncertainty may reveal (and perhaps, re-establish) how multiple aspects of society are interconnected. Moreover, focusing on vulnerabilities can allow decision makers to better recognize how agent-context relationships change over time.

That states undertake a wide variety of activities is not to claim that every concern is a security matter or that no concern at all is a security matter. Rather, to consider all of them as part of a larger effort to address uncertainty can yield fruitful responses that can forestall (or prevent further) disruption, degradation, or destruction. Fundamentally, we must call attention to uncertainty as the fundamental interest of government.

Pragmatically, modern states have, up until this point in time, generally managed uncertainty under two separate approaches, those of security and those of police powers. But, this distinction may be increasingly inflexible – and perhaps even irrelevant – in our progressively interconnected world. Lines that previously separated military and civilian activities are becoming blurred [1, 10, 56]. This situation may be symptomatic of two different situations. At best, it may reflect recognition that managing for uncertainty requires an integrated response. At worst, it may reflect increasing vulnerability (resulting from manufactured uncertainties) and decreasing ability to address them through routine political processes.

Decision makers will need to find a common base to discuss issues and options that address the fog of uncertainty as they address the political ecology of environmental security. A framework that foregrounds the causes of uncertainty and considers the spectrum of options to reduce vulnerability may offer more robust solutions. To be sure, fighting a war is not identical to combating an epidemic, a flood, or rapid urbanization, but providing security is more than just crisis control; it also involves the making of plans to avert crisis. In this light, plans made to secure borders and to assure health and well-being may be similar to the degree that uncertainties can be managed through routine political processes or, conversely, by the degree to which uncertainties call for extraordinary action. Centering discussions around the central concern of managing for uncertainty, we argue, will improve security. Within the specific context ecoterrorism – where nature is used as a weapon to further political and/or ideological goals, and, when even partially successful, narrows the policy options available to a state – these complex yet critical considerations must be taken into account.

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Chapter 2
Eco-Terrorism/Enviro-Terrorism: Background, Prospects, Countermeasures

Simon M. Berkowicz

…scholars enhance peace in the world.

Talmud berachot, 64a

Abstract The terms eco-terrorism and environmental terrorism are discussed in terms of the context in which they have been and are presently used. Their historical origins and intended targets were originally quite different but the terms are increasingly perceived as being synonymous. The ease with which the environment can be used as a weapon to facilitate an attack against civilians or armed forces is of ever-increasing concern. Forest and bush fires may become a preferred weapon of choice due to the extent of damage versus low cost and risk of the perpetrators being caught. Countermeasures will include a heavier reliance on technological developments with regard to detection, be it fixed sensors or remote sensing, as well as improved intelligence network capabilities.

Keywords Environmental security • Eco-terrorism • Environmental terrorism • Enviro-terrorism

2.1 Introduction

Eco-terrorism and environmental terrorism (or for short, enviro-terrorism) are frequently used interchangeably even though the intended targets are different. Eco-terrorism has been used to denote severe damage/destruction to property

S.M. Berkowicz (✉)
Arid Ecosystems Research Center, Hebrew University of Jerusalem,
Jerusalem, Israel
e-mail: berkowi@vms.huji.ac.il

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(farms, institutes, companies, vehicles, fences, etc.), occasional threats and/or harm against people, and/or non-violent activism caused by individuals(s) or groups protesting perceived harm/destruction to the environment and/or nature [43]. Examples include cutting cables, inserting sand into machinery or vehicle fuel tanks, hammering small metal spikes into tree trunks to damage chainsaws or mill blades, arson against housing developments and ski resorts, targeting universities or companies with animal research labs, theft, and trespassing. In France, 2004, 1,500 people destroyed a field of genetically modified corn crops. The action was led by Jose Bove, an antiglobalization activist, who was previously jailed for the destruction of company stocks of genetically modified seeds. Such individuals/groups believe that pressure can be exerted both directly and indirectly on the government, industry, or land developers through public and media exposure as a means of protecting natural resources. Here eco-terrorism is an amalgam of civil disobedience, political activism and sabotage, resulting in what can be termed radical environmentalism. With rare exception, individuals or groups labeled eco-terrorists focus their energy on harming property and not people. Eco-terrorism is commonly used in the news media in reference to environmental terrorism.

Environmental terrorism, however, can be defined as an unlawful action or set of actions leading to short or long-term harm/destruction of environmental resources and property to deprive others of its use [14]. One key difference between eco-terrorism and environmental terrorism is the aspect of scale, with the former being more localized while the latter has regional and global impacts. For environmental terrorism, nature is harnessed as a weapon for political or ideological goals to:

– target the environment (damage water supply, food chain). Harmful alien species can be deliberately introduced in order to undermine agriculture.
– harm/destroy living organisms and property (i.e. destroy a dam, nuclear plant).
– release chemical/biological weapons into the atmosphere. Lag-time between onset of an attack and awareness or detection, and difficulty in establishing the sources(s) of a release is an advantage.
– create sufficient environmental damage to induce refugee flight and cross-border spillover.

As [35] have noted, environmental terrorism relies on “weapons of green destruction”. Chemical, biological and nuclear terrorism are all threats to the Earth’s ecological functioning. For [54], a biological terror attack is greatly feared because it “requires relatively little specialized expertise and technology….and can have very large economic repercussions”. The materials and quantities needed to initiate an outbreak in plants or animals are not difficult to obtain and could be smuggled into a given territory with little risk of detection. Agricultural pathogens could be released in multiple sites so as to hasten the spread of a disease.

It is not clear to what extent environmental activism will stay within the “boundary” of environmental protection issues or shift into a more violent mode.

The ability for individuals to carry out or initiate a disastrous attack on a population has become increasingly easier, especially where religious or philosophical motivations are supportive of suicide attacks. In this case, the attacker is transformed into the ultimate "smart bomb". Standard defensive mechanisms to counter attacks on the environment are likely to be ineffective and thus improved technological and intelligence gathering will be required.

Major industrial accidents around the world can serve as useful proxies or harbingers of what could be the outcome a planned sabotage operation. In 1984, a major accident occurred at the Union Carbide plant, Bhopal, India, immediately adjacent to a densely populated area. The release of 40 ton of Methyl Isocyanate gas created a toxic cloud killing 20,000 people and injuring 500,000.

In 2000, 22 people died in a massive fireworks depot explosion in Enschede, The Netherlands. About 400 homes were destroyed and 1,500 homes damaged, leaving 1,250 people homeless.

In 2001 an explosion of 300 ton of ammonium nitrates in the AZF fertilizer factory, Toulouse, France, left a crater 30 m deep and 200 m in diameter. It killed 30 people, 2,500 seriously wounded and with 8,000 light casualties. Two-thirds of the city's windows were shattered. About 40,000 people were homeless for several days. In the case of the Toulouse explosion, the French environment minister at the time, Yves Cochet, remarked that it could have been a terrorist attack, based on information gathered during the initial investigation [26]. Subsequently, however, no firm basis to the suspicions was found.

The Chernobyl nuclear accident in 1986 was an exceptional event that led to an extensive radioactive atmospheric plume that covered the western part of the former Soviet Union and most of Europe. Although the direct number of deaths was under 50, it is anticipated that several thousand people may die prematurely from having been exposed to the radiation.

In 2010, the Lambro River in Italy absorbed an estimated 600,000 l (5,100 barrels) of petrol and oil released from a former refinery. Reports indicated that this spill was caused by sabotage [10]. The more recent BP offshore oilrig well rupture of April 2010 led to an estimated 4.9 millions of barrels of crude oil flowing into the Gulf of Mexico over a 3 month period. Though labeled an accident, it does show how vulnerable such oilrigs are to attack. In comparison, the largest oil spill recorded occurred during the First Gulf War in 1991, when 5.7 millions of barrels are estimated to have been released into the Persian Gulf.

We may consider harm to the environment as a strategy or use of the environment as a vector to harm a non-combatant population. Urban areas can be prime targets. The United Nations Population Fund noted that in 2008 about 50% of the world's population – about 3.3 billion people – lived in cities and towns, and that this number would grow to an estimated five billion by 2030 (i.e. 60%). Such urban settings serve as attractive targets because of the concentration of individuals and industry. However, rural areas are no less a target since they support agriculture, animal rearing, forests, and water supplies.

2.2 Background and Definitions

The terms "terror" or "terrorism" have their origins in the 1790s and were used to describe violence and repression carried out by the Jacobin party in the French Revolution, ironically with a goal to support justice, democracy and equality. Over the last two centuries "terror" has metamorphosed such that the Concise Oxford Dictionary of Politics defines terrorism as "…life-threatening actions perpetrated by politically motivated self-appointed sub-state groups", while The American Heritage Dictionary provides a more detailed definition as "The unlawful use or threatened use of force or violence by a person or an organized group against people or property with the intention of intimidating or coercing societies or governments, often for ideological or political reasons". Ullman [44] proposed a terror definition as action or sequence of events that "threatens drastically and over a relatively brief span of time to degrade the quality of life for the inhabitants of a state, or threatens significantly to narrow the range of policy choices available to the government of a state or to private, nongovernmental agencies (persons, groups, corporations) within the state". Gibbs [22] defines terrorism as violence or threats of violence but with the following five characteristics; intention to change norms of a population, secretive as to participant identity and location, not used for permanent defense, unconventional attacks, generating fear of violence in the population. Terror definitions remain in dispute and especially over what the term excludes, for example "armed resistance".

Because of the varied and interchangeable use of eco-terrorism and environmental terrorism, a key-word search (Table 2.1) was carried out using the ISI Web of Science search engine for journal-related publications. The results revealed a paucity of articles – about 50 – published from 1965 to 2010. This may be due to a lack of attention to the subject matter or for a preference to incorporate the issue into the more general encompassing term "terror". A similar but more restricted study was carried out by Wagner [52] of words related to "ecotage" used in six US national newspapers, to study how the newspaper media reported on such actions.

Table 2.1 ISI Web of Science journal literature search 1965–2010 using key words and permutations dealing with eco-terrorism/enviro-terrorism, with/without hyphens

ecocide =12	eco-sabotage = 2	environmental militants = 1
eco-defense = 1	eco-saboteur = 0	environmental sabotage = 2
eco-extremism = 0	ecotage = 1	environmental saboteur = 0
eco-insurgent = 0	eco-terror = 1	environmental terror = 0
ecological sabotage = 0	eco-terrorism = 2	environmental terrorist = 0
ecological terrorism = 0	eco-terrorist = 0	environmental terrorism = 1
ecological terrorist = 0	ecoteur = 0	environmental warfare = 6
eco-militant = 0	eco-vandal = 0	pyro-terrorism = 2
eco-radical = 1	eco-violence = 0	radical environmentalism = 19
eco-raiders = 0	eco-warfare = 0	warfare ecology = 1
eco-rebel = 0	eco-warrior = 0	

The values indicate the number of citations found for a given key word occurring in the journal title or abstract. Note that some key words had overlapping citations

The different applications of the terms eco-terrorism and environmental terrorism are outlined, below.

The roots of eco-terrorism (or eco-sabotage) go back to 1811–1812 when skilled English textile artisans destroyed automated looms that were making them redundant. They came to be known as Luddites, named after their apparent leader Ned Ludd. The second half of the twentieth century saw the introduction of a variation of the terror theme in the form of what is also called eco-terrorism. In this case, the term refers to damage or destruction of an ecosystem or to the environment for political gain or during warfare. Thus it can apply to the actions of President Saddam Hussein of Iraq for setting alight oil wells in Kuwait during the first Gulf War in 1990–1991, as well as acts of vandalism or sabotage (whether mild or severe) by environmentalists protesting industries that may be damaging the environment or ecology of an area or perceived to cause needless harm to animals.

Alexander [6] defined ecoterrorism as “the use of force or threat directed at the environment or ecosystem to terrorize of frighten people” and used the term in the context of threats to military forces. Beck [11] defined eco-terrorism as “the clandestine use of force or threat of force outside the normal routines of political action intended to influence targets for an environmental cause”.

For [50], the term eco-terrorism has been applied to combat environmental activists to create “an association between terrorism and radical environmentalism, planting the specter of another group of fanatics and mass murderers out to destroy ‘our’ way of life in the public mind”. He cites a USA anti-environmentalist activist, R. Arnold, as having coined the term eco-terrorism in 1983. According to [51], “Ecotage refers collectively to a variety of criminal acts (e.g., vandalism, arson, and threats) undertaken in the name of protecting nature while specifically not harming humans”. Amster [7] however notes that one of the early proponents of radical “ecodefence” explained that it was about “nonviolent resistance to the destruction of natural diversity and wilderness. It is never directed against human beings or other forms of life. It is aimed at inanimate machines and tools that are destroying life”. Vanderheiden [50] defined ecotage as “the extralegal tactics of radical environmental groups seeking to inflict targeted economic harm upon individuals and firms regarded as causing serious ecological damage”.

The Chief of the United States Federal Bureau of Investigation (FBI) Counterterrorism Division, J.F. Jarboe, stated that “The FBI defines eco-terrorism as the use or threatened use of violence of a criminal nature against innocent victims or property by an environmentally-oriented, subnational group for environmental-political reasons, or aimed at an audience beyond the target, often of a symbolic nature” [20]. Over US$200 million of damage is attributed by the FBI to eco-terrorism carried out between 2003 and 2008 in the USA.

Eco-terrorism has also been used to refer to environmental warfare, defined as “where the environment is manipulated for hostile military purposes” [53]. For example, in 1944 the German army deliberately flooded 200,000 ha of farmland in the Netherlands. Along the same lines, Dutch [17] claimed that the largest scale incident of environmental warfare in history appears to be the June 1938 Nationalist

Chinese destruction of the Yellow River dykes. The purpose was to hinder the advancing Japanese army but the tactic destroyed 11 cities and over 4000 villages, and led to the deaths of 800,000 people. Farmland was inundated, leading to the destruction of the topsoil and crops [37].

A more recent example concerns the end of the 1991 Gulf War, when the Iraqi military retreating from Kuwait deliberately set on fire about 700 oil wells and released crude oil from Kuwaiti oil wells, oil terminals and tankers. This action severely contaminated the soil and the marine environment of the Persian Gulf. It is estimated that up to 11 million barrels entered these waters, not withstanding emissions of soot from burning oil wells that entered the Gulf too [3]). As [2, 4, 5] have noted, such warfare can be labeled an "environmental crime".

Zirschky [55] defined environmental terrorism as "the deliberate use or threat of use of physical, chemical, nuclear, or bacteriological agents in the commission of a terrorist act in which either the agent is delivered to a target population by use of an environmental medium (such as air, water, or soil) or the agent is used to render a natural resource unsuitable for a desired use". Rohrman [36] wrote a short opinion piece entitled "Environmental terrorism" but the context was about extremists in the environmental movement going from activism to terrorism, or what he then terms "eco-terror". The same applies to [8] in his paper "Environmental terrorism – a case-study". However, [8] shows how activism metamorphisized into life-threatening actions such as high-explosive attacks on dams, cutting power transmission lines, and attacking nuclear facilities.

As argued by [38], terrorism must be considered in the context of wartime and peacetime and "a distinction must be made between acts of terrorism in which the use of the environment is merely incidental (e.g. when pipelines and or dams are targeted), and acts of terrorism in which the terrorist is explicitly attempting to create concern over the environment…Environmental terrorism should be reserved for incidents in which the environment is disrupted or threatened by a perpetrator as a symbol that elicits trepidation in the larger population over the ecological consequences of the act".

Schofield [38] defines an environmental terrorist as the "utilization of the forces of nature as weapons", and that "Environmental terrorists deliberately destroy or manipulate the environment in the name of political or ideological zealotry". He defines ecocide as "the intentional or reckless manipulation or destruction of any aspect of the physical environment" and went on to state that "Environmental terrorism includes both the targeting of the environment itself, such as the deliberate contamination of water or agricultural resources, and the use of the environment as a conduit for destruction, such as releasing chemical or biological weapons into the atmosphere".

Kavanagh (quoted in [7]), in warning against melding environmental activist groups and terrorism, wrote that by "equating… [environmentalist] direct actions with the deadly attacks of terrorist groups fuels the anti-environmental rhetoric of the right and irresponsibly conflates two very different kinds of criminal activity. What we lose in the process is our grasp on both the real nature of environmentalism and the real nature of terrorism."

To distinguish between environmental terrorism and environmental destruction, [38] identifies three characteristics, namely deliberate versus unintentional, symbolic versus non-symbolic, and the context of wartime versus peacetime. He goes on to create a taxonomy of environmental destruction to discern “environmental terrorism”, as he defines it. Environmental destruction for [38] can be called terrorism when the action/threat:

a) violates national and/or international laws governing the disruption of the environment during peacetime or wartime.
b) has specific objectives and the violence is aimed at a symbolic target.
c) uses the environment as a means of instilling fear in the general population over the ecological consequences.

We must keep in mind that we are not referring to the preparations and aftermath of warfare on the environment or ecology [25, 33], but rather a strategy of using the environment or ecology to cause harm and/or to devastate the environment or ecosystem as part of a weapons arsenal.

2.3 The State as an Eco-Terrorist/Enviro-Terrorist

There is much controversy over whether a state can be terrorist, how to define it, and what forms state terrorism could take [39]. This concept has also been applied to allegations of state involvement in eco-terrorism/enviro-terrorism. Three examples are provided, below.

During the Vietnam War, the US army used the Agent Orange herbicide and defoliation spray to reduce dense jungle cover and crops that could be used by the North Vietnamese forces. Between 1962–1971 about 77 million liters of Agent Orange were sprayed by helicopter, covering about 20% of the territory of South Vietnam The Vietnamese government has attributed exposure to Agent Orange for the deaths or disabilities of 400,000 people and causing birth effects to a half-million children. The term “ecocide” appears to be first coined in 1970 in reference to this intense environmental destruction.

In July 1985, the French intelligence service sank the “Rainbow Warrior” ship operated by the Greenpeace organization. The ship was to comprise part of a flotilla protesting French nuclear tests in the Mururoa Atoll. Explosives attached to the hull killed one person on board [13].

In Iraq, between 1991–2003 President Saddam Hussein of Iraq targeted the “Madan” Marsh Arabs, as well as opponents to his rule that had fled to the marshes, in order to eliminate any Shiite political uprising. The Iraqi marshlands were the largest wetland ecosystem in the Middle East. This was carried out by constructing upstream dams and extensive drainage schemes (canals and embankments) that diverted water flow away from the marsh region. Of the 20,000 km^2 of marshlands, by 2003 about 90% were transformed into bare land and salt crusts and the Madan population dropped from about 250,000 in 1991 to an estimated 20,000 in 2003 [45].

Since 2003 there appears to have been a 50% recovery [46, 47] due to dedicated efforts by the United Nations Environment Programme to restore the marshlands.

2.4 Fire as a Preferred Future Weapon of Choice

The Chinese military general Sun Tzu, who apparently lived about 2,500 years ago, is believed to have authored what became an influential book on military strategy, called "The Art of War". As noted by [4], Sun Tzu offered five applications of fire that could be used in warfare. This consisted of burning supplies, equipment, storehouses, weapons, and people.

There are a variety of biblical and historical examples of fires being used as an agent to induce harm or destruction to the natural environment in order to fight against an enemy, or deprive an enemy of resources such as shelter or food. The Biblical Samson is sometimes cited for taking revenge upon his foes by destroying their agricultural fields. In the Book of Judges 15:4–5, it states that:

> And Samson went and caught 300 foxes, and took torches, and turned tail to tail, and put a torch in the midst between every two tails. And when he had set the torches on fire, he let them go into the standing corn of the Philistines, and burnt up both the stocks and the standing corn, and also the olive yards.

The Battle of Hittin in 1187, near the Sea of Galilee, was where the Muslim leader, Saladin, defeated the Crusaders using fire as a tactic [18].

> There was a big swathe of grass in the plain…and the wind got up strongly from that direction; the Saracens [Muslims] came and set fire to it all around so that the fire would cause as much harm [to the Crusaders] as the sun.

Napoleon Bonaparte's invasion of Russia in 1812 led to the famous strategy of Russian General Mikhail Kutusov, which was to abandon Moscow and set it on fire, as well as devastating other territories. The purpose was to deprive the French army of any benefits that could have accrued by having left them intact.

During the Second Boer War (1899–1902), the Boers burned wide areas of grassland to prevent the British army from making use of it forage [16].

Joseph Stalin copied this tactic in 1941 during World War II against the Nazi army that was advancing into Russia. By destroying sources for food, buildings and infrastructure, the German army was burdened with providing logistical support for its troops.

In the last decades, deliberately set fires in forests and fields have become attractive weapons of terrorism [9, 15]. Arson is quite simple to carry out in that it requires little in resources; only a small amount of fuel, matches, or can be ignited remotely through the use of a clock or other mechanism. Because of the vast expanses, large forested regions cannot be monitored closely to detect arson perpetrators. The forests are porous in terms of multiple entry and exit options, generally little populated, and the death of the perpetrator(s) is not an intended outcome of the action. An individual, possibly trained on the internet, need not be part of a larger group and thus less chance of detection from law enforcement agencies. The timing of such fires can take advantage of hot rainless seasons, droughts, and strong afternoon breezes to whip up and spread the flames quickly.

Although forest ecosystems can recover over time, such fires cause both short- and long-term impacts on the local/regional economy through multi-billion dollar losses in forest industry resources (wood and paper industries), tourism-related income, damage or destruction of property and homes, harm to farming communities and animal life, air pollution, fire-fighting costs, insurance company liabilities, and of course the fatalities.

Baird [9] appears to have coined a new term, pyro-terrorism, as the "the use of incendiary attacks to intimidate or coerce a government, the civilian population, or any segment thereof, to advance political or social objectives". According to [12], pyro-terrorism relies on four central tenets of terrorism:

– targets civilians or non-combatants.
– politically motivated.
– encourages violence and mayhem to impart psychological impacts on the general population.
– dedicated agents.

In particular, [9] recognized that massive forest wildfires in the USA – and elsewhere – have the potential for devastation that can approach that of a weapon of mass destruction. The internet can inadvertently assist pyro-terrorists by providing them with routinely-available and up to date fire hazard advisories. Accordingly, an individual or group could plan conflagrations to deliberately coincide with optimal conditions for their goals. Baird [9] goes one step further by warning such groups could also obstruct evacuation routes and endanger fire brigades, police units and civilians.

The Age (Melbourne) newspaper Sept 7, 2008, wrote that [24] American intelligence agencies identified a website calling on "Muslims in Australia, the US, Europe and Russia to "start forest fires", claiming "scholars have justified chopping down and burning the infidels' forests when they do the same to our lands". The website claimed that lighting fires:

– was an effective form of terrorism justified in Islamic law
– caused economic damage and pollution
– tied up security forces

This news story reemerged 5 months later following the February 2009 massive bushfires in Victoria, Australia, which left over 200 people dead and 500 injured, destroyed 2,000 homes and 1,500 buildings, displaced over 7,500 people, and burned an area equivalent to 4,500 km^2 [12]. Although no links whatsoever were attributed to al Qaeda or other extremist radical organizations, it did highlight that terrorist groups could learn from such fires that arson is an effective and simple tool to implement their doctrines.

Similar wide-spread and destructive arson actions have taken place in Europe. Spain has suffered from massive fires set every summer over the past 5 years.

The extensive fires in Greece in August 2007 led to the government declaring a state of emergency, with $7 billion in damage and about 70 deaths.

In Israel only about 4% of the landscape is covered by forest, with most of it found in the central and northern half of the country. There are numerous incidents of arson each year, largely attributed to nationalistic origins of the middle-east conflict. It is estimated that about one-third of all forest fires in Israel are politically motivated. According to the Jewish National Fund Afforestation Division, in 2007 about 300 arson-related forest fires were set and destroyed an estimated 40,000 trees [28]. The summer 2006 Hizbollah-Israel military conflict had rocket barrages from Lebanon fired into northern Israel. The exploding rockets ignited hundreds of fires such that about 3,000 acres (app 12 km^2) of old woodland were destroyed [30]. In all, it is estimated that about 120 km^2 of forest, nature reserves, national parks, and other landscapes were burned [21].

According to [9], “It may only be a matter of time before an unconstrained eco-terrorist uses fire to create mass destruction in the [US] nation’s forests and the dwellings surrounding them”.

The only consolation from the aftermath of a massive fire is that it may take decades before the landscape regains its potential destructive power.

2.5 Prospects and Countermeasures: The Future Eco/Enviro-terrorist?

Schofield [37] quotes a terrorism expert as saying that “The old view was that terrorists were concerned about public opinion, now they’re preoccupied more with their rewards in the next life, not this one, and they view it to be a sacred obligation…. to bring civilization to its knees”. For Schofield, “It is for this new brand of terrorist that the destructive forces of nature may have irresistible appeal”. Schofield [37] continues by commenting that “Groups and individuals motivated by apocalyptic religious or ideological zeal…are more likely to engage in environmental terrorism because they believe that they are morally justified in doing so”.

The Earth Liberation Front (ELF) and Animal Liberation Front operating in the USA have been prominent organizations attacking property to further their ideological views on the use and protection of the environment. Their targets have focused on laboratories, corporations, and the forestry industry, using arson, sabotage and vandalism. Leader and Probst [31] point out that the ELF could shift their targets to include the nuclear industry. Because such groups rely on “leaderless resistance”, and encourage the formation of autonomous activist cells, there is no central authority for law enforcement agencies to shut down. Even if a cell could be penetrated, the number of people to be arrested would be few.

Ackerman [1] believes that radical environmentalists could jump from property attacks to threats to people. As an example, he cites an ecological extremist group, RISE, who had declared their intention in 1972 to release infectious diseases to destroy Mankind and thus save the Earth’s environment. This view is not supported by [41, 42]. Assessments [11, 49, 50] of whether there has been a radicalization in eco-terrorism also reject Ackerman's [1] viewpoint based on lack of evidence. Ackerman [1], however, may have a valid point in that the RISE group was indeed able to produce some infectious diseases with little expertise and that there is no reason to assume that radical groups may not one day "mutate" into extreme violence.

We may thus envisage the intensification of two separate but overlapping trends involving eco-terror and enviro-terror. The activists involved in traditional actions against industry or governments for perceived or real harm to the environment will likely continue in their mainly localized tactics. There is a risk that such individuals will "graduate" into extremely violent actions with international dimensions because of the globalization of companies. There may be a convergence where pressing environmental problems may radicalize individuals or groups to resort to large-scale actions in order to curtail real or perceived environmental damage. In addition, we must consider that well-meaning individuals or organizations may inadvertently be used as a cover by outside parties in order to allow lethal actions to take place. Individuals who are emotionally adrift and isolated may be more susceptible for recruitment by hostile organizations that can offer "a purpose" in their lives. As an example, attacks on nuclear power plants may be justified by environmental militants but without realizing the potential harm from a successful operation.

The internet is increasingly providing an anonymous means for disseminating ideas and "how to" kits to individual and disconnected closely-knit groups to carry out acts involving forest fires, water, air and soil contamination, bacteria release, etc. In 2010, a British white supremacist became the first person in Britain to have been caught and sentenced for manufacturing the deadly ricin poison. He had studied how to produce it online using easily available ingredients and had co-written a book on bomb-making advice that was available on a leading online retailer [52].

Potential enviro-terrorist "hard" targets are likely to include nuclear reactors and power supply, water delivery systems, water reservoirs and dams, chemical and petroleum factories, fuel depots, oil pipelines, and forests/bushland arson. According to [32], US chemical manufacturing plants have inadequate security to prevent or respond to a terrorist threat or attack. They [42] refer to literature indicating that 123 US chemical facilities can each put over one million people at risk to a toxic gas cloud release, with a further 700 chemical sites that could each put 100,000 people at risk.

In a similar vein, a US Congress report by the Commission on the Prevention of Weapons of Mass Destruction Proliferation and Terrorism [48] claimed that the US government had not yet built a quick-response capability for handling disease outbreaks from bioterrorism. The AUM Shinri Kyo Cult carried out a nerve gas attack in 1995 on the Tokyo subway that left 12 dead and 5,500 injured. They believed that a chemical attack would set off the Apocalypse. Police investigations revealed that the Cult's lab had a technical capacity to produce enough nerve gas to kill four million people. According to [29], bioterrorism is attractive as an environmental weapon because the materials are easy to procure, relatively simple to manufacture at a low cost, can be dispersed with low technology, and can overwhelm medical response and treatment due to the sheer potential number of casualties.

"Soft" targets would encompass derailments of train freight lines carrying chemicals or toxic cargo, trucks with toxic materials, biological/chemical releases into urban transport vehicles (metro, busses, trains), air ventilation systems in buildings, and computer cyber attacks shutting down or controlling environmental support systems. Economic terrorism should not be discounted whereby the tourist industry is targeted.

There are three ways to combat such terror potential. The first is the traditional need for safeguarding vulnerable facilities through improved security and management practices. The second is enhanced military and civilian intelligence to acquire information on likely threats, monitoring of communications and possible infiltration into radical groups. The third will rely on technological innovations in the security field.

The European Union Seventh Framework Programme (FP7) has adopted security of its citizens as one of its priorities and a wide-range of research has been initiated in this direction. Several projects are in progress that might be of value to counter eco-/enviro-terror and includes [19]:

- combining human behavior models with automatic analysis of video and audio surveillance data.
- evaluating possible security threats from new technologies such as nanotechnology and biotechnology, robotics, materials science.
- rapid detection of chemical, biological, radiological, and nuclear contaminants in the drinking water supply and determination of the point source(s).
- sensors to detect and identify airborne bacteria, spores, viruses and toxins.
- surveillance system to detect and assess chemical signatures within a wide urban area.
- portable optical technologies to identify improvised explosive devices.
- cyber-terrorism causing remotely-controlled industrial or military accidents.

There is an urgent need, in parallel, for an emergency response preparedness strategy [23]. This would include a pre-existing fast response crisis management command to cope with an emergency and to initiate countermeasures. The efficiency and capabilities of such command centers will dictate the extent to which disaster can be prevented or mitigated. This should include provisions for emergency food, water and shelter delivery.

Geographic Information Systems (GIS) can be an indispensable tool for assessing vast sets of information and can manipulate various databases such as topography, geology, land use, landscape attributes, population density, meteorology etc., to provide decision-makers with the means to choose between several response options. Mathematical models can be coupled with GIS to carry out disaster simulations such as transport and dispersion of chemical or biological releases from a single point or from multiple point sources, decay of the released agent into the environment, deposition onto surfaces, and a hazard estimate [40]. This would facilitate appropriate medical response decisions under conditions of great stress but also the rate of decay of a released agent, i.e. hours, days, months, etc. Given the significant dangers posed by forest pyro-terrorism, remote sensing tools may be needed to provide real-time monitoring of forest conditions [27]. GIS can be especially useful for forest fire spread prediction [34].

2.6 Concluding Comments

When we reflect on environmental security and terrorism issues, the security perspectives we may wish to consider include: for whom, from whom/what, provided by whom, timeframe (short-/long-term), response (emergency and disaster units) and intervention/prevention (military, intelligence).

Globalization of terrorism has brought with it the possibility that Nature can be used as a tool to carry out military or ideological objectives. The capability of an individual or small group to achieve substantial destruction to the environment is compounded by the added difficulties of identifying small self-sustaining attack units. Countermeasures will become costly and require more human intelligence gathering as well as technological surveillance and detection capabilities. Protecting the environment during times of war can make use of existing or new international treaties and conventions [16] but this assumes conventional war between nations and not irregular organizations or combatants working from outside such agreements.

To paraphrase Wendell Phillips (American writer and lawyer, 1811–1884), eternal vigilance is the price of “environmental security”.

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Chapter 3
Ecoterrorism: An Ecological-Economic Convergence

Ganna Kharlamova

Abstract Ecoterrorism is a challenging term because neither threats nor responses are easily defined. Instead, this problem can be solved only by complex means and applying interdisciplinary approaches. Here, we propose modeling ecological-economic complex systems to calculate the possible negative impacts of pollution – and especially intentional pollution – that could be classified as ecoterrorism. The combination of ecological and economic approaches has the potential to establish ecologically safe development of states and regions.

Keywords Ecological-economic systems • Ecoterrorism • Ecological-economic modeling

3.1 Introduction

The environment is everything that isn't me.

(Albert Einstein)

The distinction between "natural" and "human-dominated" ecosystems is becoming increasingly blurred. Moreover, the role of humans in our coupled socio-ecological systems is no longer understood to be supportive of and complimentary to natural system operations but is, instead, positioned in opposition to natural systems maintenance through practices such as littering and even intentional destruction. This situation is complex, and thus complex models are required for decision-making [5].

G. Kharlamova (✉)
Kiev National Taras Shevchenko University, Kiev, Ukraine
e-mail: akharlamova@ukr.net

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We may consider ecological education as one method to combat ecological crises and terror. As such, the population of any nation should be sufficiently knowledgeable such that every individual can detect threats to ecological components of the environment. The absence of information about the ecological state of the environment, reasons for its worsening, culprits causing contamination, and measures accepted for the improvement can lead to inadvertent potential complicity by a population in support of ecoterrorism and ecological pollution. A high level of environmental awareness and advanced ecological education of the public, the leaders of enterprises, and government officials is vital but it is especially crucial for transitional states and regions facing high ecological risk (like Azov, Uzbekistan territories, Chernobyl, etc.).

To achieve such knowledge, education in geology, hydrology, biology, and other environmental sciences is not sufficient in itself as we live in coupled socio-ecological systems. Economic and political factors can contribute to harming of natural systems and serve as a bridgehead for ecological terror. The absence of effective laws for environmental protection can allow a kind of invisible support for ecological threats including the effects of pollution.

The issue of safety and security across regions is vital, although defining acceptable levels is difficult. Optimization of ecological safety over space in terms of risk reduction requires improvements in the making of risk factor estimates. Such estimation should be a mixture of two modern and advanced approaches – economics and ecological estimation. The base conceptual mechanism for such a convergence is the principle of safety, but the task of providing safety in modern terms requires dynamic adjustments in the development of concepts of optimization as different fields of knowledge are integrated methodologically.

3.2 Terminological Issues: Ecoterrorism and Its Threats

> Let every individual and institution now think and act as a responsible trustee of Earth, seeking choices in ecology, economics and ethics that will provide a sustainable future, eliminate pollution, poverty and violence, awaken the wonder of life and foster peaceful progress in the human adventure.
>
> (John McConnell, founder of International Earth Day)

There is no universally accepted definition for ecoterrorism. Some scientists have used this term even for the mass infection of children at a camp. Is this really an act of terror or is it just the result of poorly washed fruits? Here, we try to analyze and summarize all peculiarities and common features for determining an ecoterroristic act.

Ecoterrorism is a term believed to have been coined by Ron Arnold, the Executive Director of the Center for the Defense of Free Enterprise. Ecoterrorism usually refers to acts of terrorism, violence, or sabotage committed in support of ecological, environmental, or animal rights causes against persons or their property [2, 8]. However, here is no strict dividing line: is nature an object on which an act of terrorism is directed, or is nature a reason to commit an act of terrorism?

Eco-terrorism is defined by the US Federal Bureau of Investigation as "the use or threatened use of violence of a criminal nature against people or property by an environmentally-oriented, subnational group for environmental-political reasons, or aimed at an audience beyond the target, often of a symbolic nature." This language, too, is broad, and not sufficient to provide a definitive meaning.

Compounding the problem of an agreed-upon definition is that there are contradictions within the philosophy of radical environmentalism, which is often taken as the intellectual foundation for ecoterrorism practice [7, 9]. In particular, there is the proposition or belief that human society is responsible for the degradation of the environment. Again, we are faced with the question – is the environment an object for terror or a reason for terror?

Glancing over the list of organizations that have been labeled as "ecoterrorists" in the United States,

- the Animal Liberation Front (ALF)
- the Earth Liberation Front (ELF)
- Greenpeace
- the Sea Shepherd Conservation Society
- Earth First!
- the Coalition to Save the Preserves
- the Hardesty Avengers

it is possible to conclude that these groups have a cause of protecting nature. The methods used in this fight, however can still harm nature itself and jeopardize lives. As such, they put Man outside the ecological system of the world. Here, we find a major mistake in this philosophy – as no one but Man can save this inherently coupled socio-ecological system. In any case, it is hard to apply the term of ecoterrorism to these actions.

The idea in the present paper is to approach the term "ecoterrorism" from a linguistic basis. The word "terror" comes from the Latin *terrere* meaning "to frighten", thus the main idea of a terrorist act is to *frighten* rather than to annihilate or to destroy. Even an announced threat (such as to set forest fires or the intention to destroy a chemical factory) can be considered as a terrorist act if it presses on human consciousness.

Below some key characteristics of terrorism are defined, as outlined by Hoffman [3]. By distinguishing terrorists from other types of criminals and terrorism from other forms of crime, terrorism is:

- ineluctably political in aims and motives;
- violent – or, equally important, threatens violence;
- designed to have far-reaching psychological repercussions beyond the immediate victim or target;
- conducted by an organization with an identifiable chain of command or conspiratorial cell structure (whose members wear no uniform or identifying insignia) and
- perpetrated by a subnational group or non-state entity.

The organizations listed above cannot be called ecoterroristic using these criteria. However, it is still open to debate.

The target of ecoterrorism – as opposed to terrorism – is the environment (nature) and living organisms (particularly people), with the only aim being political. In this way, ecoterrorism is outside terrorism as an ideology (such as anarchism, communism, narcoterrorism, nationalist religious (Islamic, Christian, Jewish) radicalism [4]). This kind of terrorism differs from other types not by ideology but by threats, tactics, and targets. The environment is in such a way not a reason for demolition, but a system that is destroyed for political reasons. The types of destruction can be:

- Agro-terrorism;
- Bioterrorism;
- Nuclear piracy;
- Propaganda of the deed (to pollute or to destroy factories, the burning of which can generate toxic releases harmful to people and the environment);
- Suicide attack (to cause an ecological catastrophe).

3.3 Economic Aspects for Ecological Security

To express these ideas in terms of mathematical symbols, we can propose some form of function: F(E) = (political impact, economic costs) → minimum. The challenge is to model and to optimize (minimize) the function of possible economic costs and political "costs" from ecothreats and ecoviolence (from ecoterrorism). The first possible approach is to develop environmentally benign technologies.

Here is the exact place where convergence principals appear – ecological problems of the modern world have a basis in economics. Every ecoterroristic attack is estimated not from the political impact it had but from the economic losses it created. This calculation has, at a minimum, two participants – the party who experienced the ecoterroristic act, and the party (national or regional government) who will pay for rehabilitation and making amends to those harmed.

Without a convergence of knowledge between economic and ecological theories and modeling, it is impossible to calculate these costs (Fig. 3.1).

The most well-known example of using this approach is the Environmental Kuznets Curve (EKC) [1], which shows pollution at first increasing and then decreasing as income increases. The main benefit of the EKC approach for environmental security is that for every dozen EKC papers, there might be one that seriously looks at how changes in regulatory structures and incentive systems in place across different political jurisdictions could be used to improve environmental quality in places where the population is increasing, income is improving, and technology from around the world is potentially available. Thus the challenge is in identifying factors that can translate some of the increased income from growth into improved environmental quality.

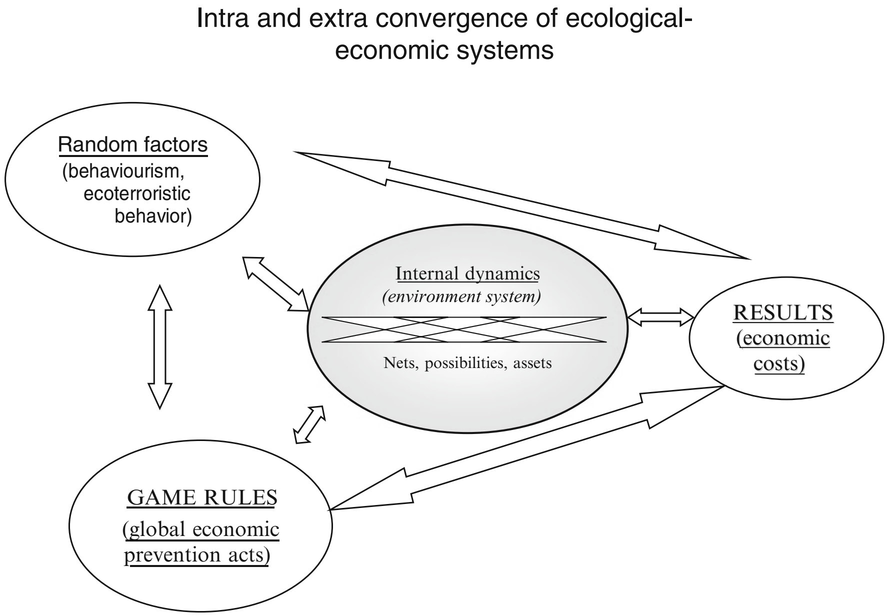

Fig. 3.1 Example of complex dynamics of knowledge in ecological-economic systems

Two production functions (Pething's and Siebert's) were combined [10, 12–13] to allow modern macroeconomic model resource and social-ecological limits to be included as endogenous in economic growth model [11]. These functions analyze production in terms of limits on production resources, on the one hand, and permit consideration of production as a factor of external costs, on the other hand.

A synthesis of these approaches leads to a production function with ecological ingredients:

$$Q = F\left\{K, L, \sum(R_i - R_i^r),\quad \sum(S_i - S_i^r)\right\}, \tag{3.1}$$

where K – capital;

L – labor;

R_i – natural-material resources (ecological factor) (including land), for production usage;

R^r_i – resources for pollution decreasing;

S_i – negative external effects of production;

S^r_i – softened external effects of production.

Following Solow's idea [14], such a function can be proposed by reducing factors of economic growth to vector L (labor):

$$Q/L = F\left\{K/L, 1, \sum\left(\sum R_i/L - \sum R^r{}_i/L\right)\left(\sum S_i - S^r{}_i\right)/L\right\}, \tag{3.2}$$

where *Q/L* – productivity of economy (*y*) – is determined: $y=f(k, r, r^r, s^{er})$,
where k – capital productivity (K/L);
r – resource supply of production (counting on 1 employed) (R/L);
r^r – resource supply of production for "softening" of its external effects;
s^{er} – factor of social risk, caused by degradation of ecological component of life-support.

To continue reasoning about the equilibrium state of economy, the terms of equilibrium can be given as equality of supply and demand:

$$f(k,r,r^r,s^{er}) = c+i \text{ or } f(k,r,r^r,s^{er}) = i/s. \tag{3.3}$$

In this model the total demand is determined by consumption (c) and investments (i) ($c+i$) counting on 1 employed – without accounting for social-mental motivations of estimation of ecological danger at the choice of consumed product or in accordance with the saving rate (*i/s*). Market supply of goods is determined by the production function: $y=f(k, r, r^r, s^{er})$.

Dividing the left and right sides of Eq. 3.1 on the yield, we receive such expression:

$$1 = F\left\{K/Q, L/Q, \sum \Delta R/Q, \sum \Delta S/Q\right\}, \tag{3.4}$$

where $K_q = K/Q$ – capital capacity,
$L_q = L/Q$ – labor capacity;
$R_q = \sum\Delta R/Q$ – resource capacity of production, and also
$S_q = \sum\Delta S/Q$ – ecological compatibility of production, that determines the efficiency of production with the type of technology

Consequently, the role of efficiency of labour, economy of capital, and sources of raw materials rises under conditions of resource limitations. Decline of labour- and resource-capacities of products means development of science and technological progress (STP) as a factor of potential economic growth.

Investigating the state of steady economic development, function (3.1), can be given as:

$$Q^* + S^* = F(K, L, R^*) \tag{3.5}$$

where the factor of contamination is examined as a concomitant product of production ($Q = Q^* + S^*$), and resources are fully used on the production of goods and the "softening" of their external effects ($R^* = R^p + R^r$).

When all resources (capital, labour, and natural resource base) are limited, the optimization of resource usage and minimization of external effects of production rises on the basis of exploitation of natural properties of assimilation. In this case production will be determined as:

$$Q^* = F\{K, L, (R^p + R^r)\} - S^* \tag{3.6}$$

Stated differently, the higher the properties of environment assimilation of the district where production is located, the lower the real emissions and their associated external effects. These, in turn, determine the increase in allocation of material resources for production. However, they do not change the allocation for cleaning or other nature protection measures. Resource limitations limit production volumes and the possibility of the economy to minimize its external effects. In this context, there is a list of international resource allocation problems of natural resources usage in all forms of consumption.

3.4 Conclusions

An ecological crisis results when the operating mechanisms of society fail to adapt to social and environmental contexts. At a global scale, lack of cooperation regarding Earth's ecosystem can result in large-scale deaths. There is an urgent need to reform the current vector of limited (or non-) cooperation and establish authorities and institutions capable of mediating our relationships with the environment [6].

Ecodevelopment has requirements and principles that give it special social significance. As such, it contributes to a number of important goals of the nation-state. Unfortunately, in many nations awareness is lacking and progress on educating leaders and citizens is proceeding slower than required.

Only the convergence of modern approaches can be useful for handling ecothreats.

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Chapter 4
Food Defence and Security: The New Reality

Alexandra Veiga

Abstract Very few food terrorist attacks have been reported so far with the most famous occurring in 1984 in Oregon, USA, when members of a religious cult contaminated food in two salad bars with the aim to influence local elections. However, some recent historical events have awakened Governments worldwide to the vulnerability of the food chain, and its potential to be a target for terrorist attacks. Food crises in the 1990s and the events of September 11 2001 have brought to mind that many vectors, food included, could be used to deliver a pathogenic agent. This new scenario needs to be addressed, having in mind *Food Defence* concerns. Activities aiming at protecting food products and food supply from intentional contamination are being outlined by both national and international organisations. The present situation concerning food defence will be discussed.

Keywords Food defence • Food terrorism • Food safety • Foodborne disease • Biological agent • Chemical agent

4.1 Biological and Chemical Agents in Food

Foodborne illnesses are diseases, usually either infectious or toxic in nature, caused by agents that enter the body through the ingestion of food [32]. Every person is at risk of contracting a foodborne illness. Some figures very expressively transmit the importance of such diseases, whose global incidence is difficult to estimate. It has been reported that in 2005 alone 1.8 million people died from diarrheal diseases. A great proportion of these cases can be attributed to contamination of food and

A. Veiga (✉)
Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa,
Av. da República, Oeiras 2780-157, Portugal
e-mail: aveiga@itqb.unl.pt

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drinking water [32]. In industrialized countries, the percentage of the population suffering from foodborne diseases each year has been reported to be up to 30% [32]. WHO estimates that foodborne and waterborne diarrheal diseases taken together kill about 2.2 million people annually, 1.9 million of them children [31].

Several biological agents can be delivered through food to cause disease. *Salmonella* and some *Campylobacter* species are among the most important bacteria, but others such as enterohaemorrhagic *Escherichia coli* (causing intestinal bleeding) and *Listeria* have emerged over the last decades. Cholera remains a major public health problem in developing countries, also causing enormous economic losses, and is due to *Vibrio cholera* [32].

Some other types of agents are also likely to cause foodborne illness, in particular naturally occurring toxins, Persistant Organic Pollutants (POPs), and heavy metals. Mycotoxins, marine biotoxins, cyanogenic glycosides and toxins occurring in poisonous mushrooms are naturally occurring toxins that periodically cause severe intoxications. POPs, like dioxins and PCBs (polychlorinated biphenyls), are compounds that accumulate in the environment and in the human body and may result in a wide variety of adverse effects in humans. Heavy metals, such as lead and mercury, cause neurological damage in infants and children, and exposure to cadmium can cause kidney damage, usually seen in the elderly [32]. Less common are physical and radionuclear agents whose occurrence in food has been reported sporadically.

Usually, the presence of biological and chemical agents in food is unintended and great efforts to minimize it have been made, in particular, by putting in place highly demanding prevention-based food safety systems such as Hazard Analysis of Critical Control Points (HACCP). However, some of these agents might be added to food for malicious purposes by criminals trying to bypass such controls.

4.2 When Undesirable Bugs and Chemicals Are Intentionally Added to Food

The fear that food would be used to poison someone is very old and it was common among ancient emperors and kings to have a taster testing the food. This was the case for Cleopatra and led to the death of at least one of her tasters. Other situations where food was used to harm people have been referred to, although in most cases they lack confirmation.

Probably the most famous incident occurred during the Roman Empire when Emperor Claudius's death was attributed to his scheming wife, Agrippina, who did not wish to wait for her son, Nero, to inherit the throne and thus poisoned Claudius with mushrooms. Some researchers, however, claim that there is no clear proof that he was a victim of murder [36]. In the early sixteenth century Lucrezia Borgia was said to be in possession of a hollow ring that she used frequently to poison drinks.

In present times, a major case was the 1984 Rajneeshee bioterror attack, in The Dalles, Oregon, USA. Salad bars at ten local restaurants were deliberated contaminated with *Salmonella*. A leading group of followers of Bhagwan Shree Rajneesh (now known as Osho) had hoped to incapacitate the voting population of the city so that their own candidates would win the 1984 Wasco County elections [7]. The incident was the first bioterrorism attack in the USA, and the single largest bioterrorist attack in USA history. A total of 751 people, including members of the Wasco County Commission, became ill with nausea, diarrhoea, headaches and fever. Forty-five people were hospitalized, but no one died [12]. The chosen biological agent was *Salmonella enterica* Typhimurium, which was first delivered through glasses of water to two county commissioners, and then delivered on a larger scale at salad bars and in salad dressing.

In 1996 there was an outbreak of *Shigella dysenteriae* type 2 among laboratory workers in USA due to intentional food contamination. A hospital employee fed co-workers with poisoned pastries and 12 people were affected [35].

Some years later, in 2004, the illness of the president of the Ukraine, Viktor Yushchenko, was attributed to an alleged dioxin poisoning during a dinner. However, controversy on the real cause of his illness still exists, and consensus that dioxin poisoning through food was its origin is far from being confirmed [15].

Quite recently, in February 2010, two employees of a fast food restaurant in the USA were arrested for intentionally poisoning hamburgers with hydrocodone, an orally active narcotic analgesic (pain reliever) and antitussive (cough suppressant) [19], an overdose of which can cause serious side effects including coma or even death [13]. Police believe that the employer poisoned the food because he was furious about a recent suspension for misconduct [19].

A curious case happened in Chile. A phone call to the USA Embassy in Santiago in 1989 claimed that Chilean grapes due to be exported were poisoned with cyanide. The USA and four other countries banned Chilean grape imports, resulting in an estimated US $300 million losses for Chile to this important industry. However, the Food and Drugs Administration, USA (FDA) tested the grapes and found that only two had non-lethal trace amounts of cyanide. It was never clear if there was a real threat of poisoning to humans [2].

Dalziel [2] did a survey and analysed the incidents involving the malicious contamination of the food supply chain from 1950 to 2008 and observed that chemical agents accounted for the majority of the registered cases. Of the 365 cases recorded, only a total of nine involved the use of biological agents and all of them occurred towards the lower end of the food supply chain. Despite press reports over the past few years of terrorist plots involving ricin, Dalziel [2] only found one case, stating that this observation highlights perhaps the dubious nature of a ricin threat.

Radiological agents accounted for eight incidents, and the Litvinenko case was the only one where there was a confirmation of the use of radiological material in a foodstuff to kill an individual and the only one where radiological material used in minute quantities could be considered fatal [2]. Alexander Litvinenko was a former officer of the Russian Federal Security Service, who escaped prosecution in

Russia and received political asylum in the United Kingdom. He authored two books, “Blowing up Russia: Terror from within” and “Lubyanka Criminal Group”, where he accused the Russian secret services of staging Russian apartment bombings and other terrorism acts to bring Vladimir Putin to power. On November 1 2006, Litvinenko suddenly fell ill and was hospitalized. He died 3 weeks later, becoming the first confirmed victim of lethal polonium-210-induced acute radiation syndrome [14, 27]. According to doctors, “Litvinenko’s murder represents an ominous landmark: the beginning of an era of nuclear terrorism” [38].

After examining the recorded cases, Dalziel [2] concluded that almost 98% occurred downstream in the food supply chain, at retail outlets, home and workplace. Most of them took place at consumer’s level (home or workplace) but cases at the food service point have had the largest impact on public health. Typically, the agents used are commonly available household, agricultural, or industrial chemicals. For the cases where more esoteric agents were used, the perpetrators often worked in a facility using such agents, and had access and knowledge of their use [2]. An average of 6 incidents per year, resulting on average of almost 7 deaths and 75 injuries per year, were registered between 1950 and 2008. Most commonly used materials are also those easiest to acquire (pesticides, rat poisons).

The public health impact from reported cases of biological, chemical or radiological contamination cases is very small. Only 3% of the cases could be considered mass casualty incidents and the actual capability of a terrorist group to replicate the effects of a large scale food safety incident is unclear [2].

4.3 What Has Changed with the Turn of the Century?

Some recent historical events have awakened European governments to the vulnerability of the food chain, and its characteristics as a potential target for a terrorist attack.

In first place the food crisis in the 1990s, with the outbreak of Mad Cow Disease in the United Kingdom and other European countries and the dioxin crisis in Belgium, shook consumer confidence in food and highlighted the vulnerability of this system. As a result, a White Paper on Food Safety was published by the European Commission in 2000 [5] and the General Food Law – Regulation EC/178/2002 [39] – was published setting up the European Food Safety Authority (EFSA), an organization in charge of performing an independent food (and feed) risk assessment and communication. Furthermore, the scope and procedures of the Rapid Alert System for Food and Feed (RASFF) were redefined by this Regulation. As a consequence of all these changes in the food safety approach in the European Union, some Member States felt the need to re-organize their food Risk Analysis structures (Risk Management, Risk Assessment and Risk Communication) in order to make them able to fit the requirements of the Commission and to respond to more demanding consumers, as well as to effectively act as a contact point for the EFSA.

Secondly, the events of September 11 2001, followed by bioterrorist menaces consisting mainly of mailed envelopes containing white dust, allegedly with spores of the potentially lethal bacterium *Bacillus anthracis*, brought to mind that many vectors could theoretically be used to deliver a pathogenic agent, food included.

It dawned, then, that it would be important to look at the food chain supply in a different way, as a potential target for a terrorist attack.

4.4 Food Safety, Food Security and Food Defence

When referring to food and warranties that no harm will arise from its consumption, different expressions might come across giving rise to confusions and misunderstandings. “Food Safety”, “Food Security” and, more recently, “Food Defence”, are terms widely used but not always with the correct meaning. In particular, food security is very often misused: depending on the context, it could be related to food access or to food terrorism. It is thus important to present, below, the agreed definitions of these expressions.

Food safety is the assurance that food will not cause harm to the consumer when it is prepared and/or eaten according to its intended use [21]. This is a very important issue like the above-mentioned figures on people suffering from foodborne illnesses show. Routine food safety measures, in place throughout the food system, are not designed to prevent or mitigate deliberate contamination of food.

Food security’s definition has been changing over time, but a broad consensus was reached to consider it as a situation that exists when all people, at all times, have physical, social and economic access to sufficient, safe and nutritious food that meets their dietary needs and food preferences for an active and healthy life [6]. This means that apart from guaranteeing situations where there is access to enough food, it goes even further when having an asset that food safety should be a requirement and that this food should meet the dietary needs and food preferences. Therefore, this is a more inclusive concept.

The expression ***food defence*** started being used after the events of September 11, to avoid the misleading “food security” term. Yoe et al. [45] reviewed the way this expression has been used. They concluded that there has been a pervasive and growing usage, without a definition widely agreed upon.

Some definitions that have been used are as follows:

– The **U.S. Food and Drug Administration (FDA)**’s defines food defence as “the collective term used by the FDA, USDA, DHS, etc. to encompass activities associated with protecting the nation’s food supply from deliberate or intentional acts of contamination or tampering. This term encompasses other similar verbiage (i.e., bioterrorism (BT), counter-terrorism (CT), etc.)” [23].
– Marc L. Ostfield, **U.S. Department of Homeland Security**, states that “the term Food Defence encompasses the steps taken to minimize or mitigate the threat of deliberate contamination of the food supply, and includes identifying points of vulnerability and working to strengthen infrastructure, thereby, making the food

supply a less attractive and, more importantly, less vulnerable target. Controls in support of Food Defence include physical security – monitoring the premises for suspicious activity, or locking chemical storage facilities; personnel security-screening employees, use of name badges; and operational security monitoring production to prevent sabotage, use of tamper-evident packaging" [37].

– In its guidance document "Developing a Food Defence Plan for Meat and Poultry – Slaughter and Processing Plants," **USDA's Food Safety and Inspection Service** responds to the question of what is food defence with: "Food defence is not the same as food safety. Food defence focuses on protecting the food supply from intentional contamination, with a variety of chemicals, biological agents or other harmful substances by people who want to do us harm. These agents could include materials that are not naturally-occurring or not routinely tested for. An attacker's goal might be to kill people or disrupt our economy. Intentional acts are generally not reasonable and are hard to predict" [41].
– More recently, this same organisation – **USDA's Food Safety and Inspection Service** – is defining food defence as "the protection of food products from intentional adulteration by biological, chemical, physical, or radiological agents. It addresses additional concerns including physical personnel and operational security" [24].

Yoe et al. [45] deeply discussed the outcome of the **MITAGS Workshop**, that took place to address the recommendation of the National Center for Food Protection and Defence conference that was held in April 2007, that there should be developed/promotion of common definitions and metadata terms to achieve consistency, interoperability and clarity in educational programs to help students, industry, etc. Participants in this workshop ended up proposing the following definition of food defence: "Food defence means having a system in place to prevent, protect, respond to and recover from the intentional introduction of contaminants into our nation's food supply designed specifically to cause negative public health, psychological, and/or economic consequences" [45].

As can be inferred from the above-mentioned definitions, although there is no agreed definition adopted by an international organisation, consensus exists that food defence relates to measures taken aiming at protecting food products from intentional contamination. The likely hazards to the food or food facilities include biological, chemical, radiological, physical (or financial hazards). The physical hazards include damage and destruction to infrastructure and equipment as well as the entire range of physical materials that can be added to food. A mere threat or claim of an attack could be sufficient to inflict economic damage on a producer.

4.5 How Can We Be Prepared?

When having in mind food defence, apart from preventing food from accidental hazards (HACCP or similar systems would guarantee it), food business operators would have to take measures to prevent intentional hazards. These include the security of the premises, the surveillance and monitoring of activities so that identification and prevention of acts intended to disrupt food supply can be implemented, personnel security, and emergency responses.

Food business operators are quite diverse ranging from big multinationals to very small units, some of them run by one or few members of a single family. This heterogeneity together with the increasingly complexity of the food chain supply does not make the task of putting these practices in place particularly easy. Food production would be more demanding, requiring additional skills and, in some cases, changes in facilities. An increase in the costs associated with production will be most probably an outcome. These kind of measures are usually not compulsory and, most probably, they will not be in the future. But pressures to implement them might come from insurance companies, in order to decrease the insurance premiums. This factor is presently particular important in multinational companies.

On the other hand, governmental institutions should be prepared to prevent or to minimize the effects of a terrorist attack to food and provide support to producers where needed.

This new way of looking at the food chain supply requires a strong articulation between all the players, including national and international organizations that have a determinant role in providing support to the food sector.

4.5.1 International Organizations – WHO

Immediately after the events of the September 11 2001, and the acquired awareness that food could be a potential target for a terrorist attack, the World Health Organization (WHO) started working on a document aiming at addressing this “new” threat. In December 2002, WHO published Terrorist Threats to Food, which was intended primarily for policy-makers in national governments with responsibilities for ensuring food safety, and was designed to assist them in incorporating considerations of food terrorism into existing food safety systems [43]. In June 2007, the revised International Health Regulations (2005) entered into force across the globe for WHO Member States. The revised Regulations have dramatically changed the way that key public health events of international significance are handled by the international community. As a consequence, this guidance has been updated and expanded, especially to inform responsible authorities in WHO Member States of their new obligations concerning foodborne disease under the revised Regulations. Certain incidents, potentially involving deliberate contamination of food, may be considered of international significance and subject to these Regulations. The WHO International Food Safety Authorities Network (INFOSAN) functions within the framework of the IHR and is utilized to manage food safety events, as appropriate [44].

WHO considers that taking sensible precautions coupled with establishing and strengthening surveillance and response capacity, constitute the most efficient way of countering food terrorism as well as other food safety emergencies. This document provides guidance to Member States for integrating consideration of deliberate acts of food sabotage into existing programmes intended for assuring the safe production of food. It also provides guidance on strengthening existing communicable disease control and prevention systems to ensure that surveillance, preparedness and response systems are sufficiently rapid and sensitive to meet the threat of food terrorism. Such systems will increase the capacity of Member States to reduce the burden of foodborne disease and help to address food terrorism, but resources allocated should be proportional to the size and nature of the threat [44].

Since prevention is best achieved through a cooperative effort between government and industry, this document provides guidance for working with the food industry, including specific measures for their consideration.

It also provides policy advice on strengthening existing emergency alert and response systems by improving links with all the relevant agencies and with the food industry. This multi-stakeholder approach serves to strengthen disease outbreak surveillance, investigation capacity, preparedness planning, effective communications and responses.

This document complements other guides and advice developed by WHO, the Food and Agriculture Organization of the United nations (FAO) and other international agencies related to terrorist threats to food [44].

4.5.2 American Approach

Before the events of September 11 2001, food production plants in the USA used to pay attention to nothing but accidental hazards. Subsequently, the need to be concerned about intentional hazards was felt. Issues like building security, personnel security, and surveillance and monitoring of activities to prevent acts to disrupt the food supply, all started being addressed.

In order to help the players along food chain systems, from food producers to Federal Agencies, policy measures were taken and governmental bodies started working on documents and tools aiming at helping them to address these new issues.

In 2002, the Public Health Security and Bioterrorism Preparedness and response Act was published [29]. This is an act to improve the ability of the USA to prevent, prepare for, and respond to bioterrorism and other public health emergencies.

The Homeland Security Presidential Directive 7, published in December 2003, established a national policy for Federal departments and agencies to identify and prioritize critical infrastructure and to protect them from terrorist attacks. The directive defined relevant terms and delivered 31 policy statements. These policy statements defined what the directive covered and the roles various federal, state, and local agencies would play in carrying it out.

In 2006, the USDA's Food Safety and Inspection Service [41, 42] defined a food defence plan as follows: "A food defence plan is a document that sets out control measures developed by an establishment to prevent intentional adulteration of product.

A food defence plan should be developed, written, implemented, tested, assessed, and maintained if it is to be functional. All establishments are encouraged to operate with a food defence plan" [42]. The elements of such a food defence plan include the following [41]:

- *Assessment.* As part of the assessment the establishment: looks for vulnerable points at the establishment, determines what the risk factor is for each point, develops defence measures at each point that it has identified as high risk, and creates a written plan to implement defence measures.
- *Implementation.* The food defence plan is implemented when the defence measures identified in the plan are in place and used as intended.
- *Test.*The establishment tests the written plan by monitoring periodically to evaluate the effectiveness of its defence measures.
- *Assessment.* The establishment assesses the plan by reviewing the plan and revising it as necessary whenever new risks are discovered.
- *Maintenance.* The establishment maintains its plan by ensuring that the defence measures it implements continue to be effective.

In November 2007, the FDA introduced the Food Protection Plan as a complement to the interagency Import Safety Action Plan [8, 40]. The Food Protection Plan emphasizes three core elements:

- *Prevention*: Promotion of improved food safety and defence capabilities throughout the product lifecycle.
- *Intervention*: Coordinate risk-based interventions among federal, state, local and foreign agencies.
- *Response*: Development of rapid and comprehensive methods to communicate with consumers and other agencies before, during and after an event.

The FDA and the U.S. Department of Agriculture's (USDA's) Animal Plant Health Inspection Service (APHIS) developed an offensive targeting prioritization tool named *CARVER + Shock* [22]. This tool was launched online on December 2009 to help farmers and producers keep food safe from a terrorist attack [22]. It was adapted from the military version of CARVER, used to identify areas that might be vulnerable to attack, for use in the food industry and can be used to assess the vulnerabilities within a system or infrastructure to an attack. It allows the user to think like an attacker to identify the most attractive targets for an attack. By conducting a CARVER + Shock assessment of a food production facility or process, the user can determine the most vulnerable points in their infrastructure, and focus resources on protecting the most susceptible points in their system.

What does C-A-R-V-E-R + Shock mean? CARVER is an acronym for the following six attributes used to evaluate the attractiveness of a target for attack:

- *Criticality* – measure of public health and economic impacts of an attack
- *Accessibility* – ability to physically access and egress from target
- *Recuperability* – ability of system to recover from an attack
- *Vulnerability* – ease of accomplishing attack

- *Effect* – amount of direct loss from an attack as measured by loss in production
- *Recognizability* – ease of identifying target

A seventh attribute, Shock, has been added to the original six to assess the combined health, economic and psychological impacts of an attack within the food industry.

With this tool, the attractiveness of a target is ranked on a scale from one to ten on the basis of scales that have been developed for each of the seven attributes. Scoring the various elements of the food sector infrastructure of interest for each of the CARVER-Shock attributes can help identify where an attack is most likely to occur in that infrastructure. Federal agencies, such as FDA and the Food Safety and Inspection Service (FSIS) of the United States Department of Agriculture (USDA), have used this method to evaluate the potential vulnerabilities of farm-to-table supply chains of various food commodities. The method can also be used to assess the potential vulnerabilities of individual facilities or processes [22].

4.5.3 European Approach

In Europe, the food supply chain has received much attention in what concerns food safety issues and terrorist attacks in general, but less to the reduction of the potential consequences of deliberate attacks to the food chain. Nevertheless, diverse systems that somehow contribute to the safety/security of the food chain supply are in place.

The **Health Security Committee (HSC)** was established by the Council of the European Union in 2001, on the occasion of a discussion following the bioterrorist attacks in the USA where the cardinal role of public health bodies in the fight against bioterrorism was recognised. The Committee was given the responsibility to exchange information on health-related threats and to share information and experience on preparedness and response plans and crisis management strategies. Following a communication from the European Commission to the Council of the European Union in November 2006, it was agreed in February 2007 on the transitional prolongation and extension of the mandate of the Health Security Committee to focus on three areas: influenza preparedness and response, public health preparedness and response to chemical, biological and radio nuclear (CBRN) attacks, and generic preparedness and response for public health emergencies. The HSC is chaired by the European Commission and consists of officials of the EU Members States, officials of the Directorate General for Health and Consumers and other relevant Commission services and agencies [17].

In order to ensure a rapid and effective response by the European Union to a wide range of emergencies, the European Commission has put in place a number of **early warning and rapid alert systems**. These systems are based on an information exchange network for receiving and triggering an alert as well as exchanging other relevant information. These systems are active and efficiently working to guarantee that information flows smoothly through Member States and Associate Countries. Each of these systems covers a specific health threat field.

The Rapid Alert System for Food and Feed **(RASFF)** provides the control authorities with an effective tool for exchange of information on measures taken to ensure food safety [9].

The Rapid Alert System for Biological and Chemical Agents Attacks **(RAS-BICHAT)** is used for exchanging information on health threats due to deliberate release of chemical, biological and radio-nuclear agents (notification of confirmed or suspected events, exchange of information and coordination of measures among partners). The system links the European Commission with the designated competent authority and 24 h operational contact points of each Member States. It has been established to serve in particular the Health Security Committee members, nominated by Health Ministers to address and coordinate together with the Commission all preparedness and response issues in terms of public health related to attacks in which biological and chemical agents might be used [11].

Since a crisis rarely affects only one sector of activities, the European Commission decided to create a general European rapid alert system called **ARGUS**, with the capability to link all specialized systems for emergencies, and a central crisis centre (CCC) which would bring together all relevant Commission services during an emergency. Although emergencies management is mainly the responsibility of the Member States, the European Commission has nevertheless a role to play when it is related to its domains of competences and can also offer its support to Member States. ARGUS has been set up with the aim to assure a coordinated and effective management of major multi-sectoral crisis that require a reaction at the European Community level. It is an internal network. Member States and external bodies are connected through sector-specific rapid alert systems [10].

Moreover, **food laws** that set down the general obligation for food operators to take measures to ensure that food products are safe for consumption, and legislative provisions for controls on food and feed by the border authorities, as well as the obligation to be able to trace a food product – traceability, also contribute to increase the security of the food chain supply.

In 2007, the Green-paper on biopreparedness was published [16]. Bio-preparedness is a term used in generic way covering all aspects such as prevention, protection, prosecution of criminal/terrorist, surveillance, response and recovery. The term also covers the steps taken to minimise the threat of deliberate contamination of the food supply through biological agents. The aim of this green paper was to stimulate a debate and launch a process of consultation at European level on how to reduce biological risks, and to enhance preparedness and response.

Recently, a project was sponsored by the European Commission with the aim to overview strategies adopted in the EU to prevent criminal, and specifically terrorist attack against the food supply chain – SecuFood – Security of European Food supply chain [18]. In his authors' opinion, although excellence elements can be identified, specific European Union prevention mechanisms are missing. Moreover, due to the multi-disciplinarily of the topic, several organisations (e.g. law enforcements, food safety agencies, health organisations, food firms, etc.) in each one of the Member States are in charge with different strategies and potential solutions, which limits the problem-sharing capability at European Union level.

The final results of this project were presented in the "Fourth Annual IFIP WG 11.10 International Conference on Critical Infrastructure Protection" held in Washington, DC, USA, in March 2010 [26]. The authors observed that although many food operators think their process is secure and their controls adequate, they admit vulnerabilities in their process. Moreover, many of them are more aware of the negative publicity that would come from the idea that their food could be maliciously manipulated than on effective possible attacks. They concluded that countermeasures for the food safety developed by the European Commission and by each Member State provide a valid food defence of the supply chain, but they appear to be unsatisfactory in what concerns food manipulation at consumer/retailer level, and in the case of chemical agents [26].

Individually, most Member States have specific fora to address food defence concerns. Since this is a very sensible issue, information on countries' strategies is rarely available.

4.5.4 Other Countries Worldwide

Attempts to understand which kind of measures are being taken outside the North American and the European arenas are very often frustrated since there is no easily accessible information available in English.

An Australian case was presented by Alan Edwards in the Food Defence Workshop organized by the Centre of Excellence for National Security (CENS) at the Rajaratnam School of International Studies (RSIS), Singapore, in February 2009 [28]. He mentioned that the Australian government adopts a holistic array of strategies comprising pre-boarder, border and post-border tactics, and explained that the government placed added importance on border measures because of Australia's largely costal demographic spread. This put Australia at a greater risk to food-chain vulnerabilities that may enter via the border. Examples of concrete measures were given. Pre-border tactics include active surveillance programmes and deeper committed roles in regional and international bodies. For border strategies, large investments are made to bolster the number of quarantine staff as well as the screening process. Imports are closely monitored and a high percentage of incoming passengers as well as mail are screened thoroughly. Post-border measures include rigorous training programmes as well as nation-wide simulation exercises for both industry and government [28]. A Trusted Information Sharing Network (TISN) was established in 2003, and forum, critical information and infrastructure protection arrangements are coordinated between government and industry [28].

4.6 Is Food Terrorism a Real Threat?

Is food terrorism a real threat? This is a question frequently addressed since statistics show that only very few cases of food chain attack have been reported. One thing is certain: if a food attack is successful, the consequences could be extremely serious.

Natural occurring outbreaks can give clues for what would be the impact of an intentional attack to the food chain.

In May 1981, disease broke out in Spain and quickly became of epidemic proportions, although the incidence of the disease was limited to a relatively small area around Madrid. The epidemic affected more than 20,000 people in Spain and claimed about 400 lives between May 1981 and October 1983. The cause was industrial rapeseed oil illegally added to consumer cooking oil [34].

Among the largest reported outbreaks caused by biological contamination was an outbreak of *Salmonella typhimurium* infection that sickened approximately 170,000 people in 1985 and was linked to post-pasteurization contamination of milk from a USA dairy plant [33]. Tainted clams affected nearly 300,000 people in China in 1991 and may have been the largest foodborne disease incident in history [33]. In 1994, an outbreak of *Salmonella enteritidis* linked to a contaminated ice-cream pre-mix affected an estimated 224 000 people in 41 states of USA. About 8,000 children in Japan in 1996 became ill and some died after eating *Escherichia coli* O157:H7- tainted radish sprouts served in school lunches [33]. In 2008 in the USA, *Salmonella* Saintpaul in tomatoes affected over 1400 people and generated around US $100 million in losses to the tomato industry. In 2008 at least three babies died and 53,000 children fell ill in China from drinking milk products tainted with melamine [25]. Melamine is a chemical compound commonly used in the manufacture of resins, plastics and glues. In Europe, melamine is approved for manufacturing plastic materials and articles, but the addition of melamine in food and animal feed is prohibited [20]. Government officials say the melamine was added to milk products by suppliers to artificially boost protein count in milk that had been diluted. Babies and children who regularly drink the tainted milk can develop kidney stones after several months [25].

These incidents happened accidentally or, in the case of the melamine in milk, with criminal purposes but not triggered by terrorist motivations. Had they had been a consequence of deliberate contamination of the foodchain, one would have felt the strong impact of such an attack.

Tommy Thompson, former Secretary of the U.S. Department of Health and Human Services, said at his farewell news conference in December 2004: "I, for the life of me, cannot understand why the terrorists have not, you know, attacked our food supply because it is so easy to do" [30]. This was a very strong statement that reflects deep concerns of a man positioned in a central place that receives information and awareness of the situation relating to food menaces.

In fact, there are a handful of reasons that, even for people without access to all the information official entities might have, help to understand such a statement. The food supply chain is an easy target since the security of installations and staff is low, and 100% of the people eat 100% of the time which increases the chance of exposure to the hazard. On the other hand, a food chain attack can affect food supply without killing people, can destroy a product brand, and can lead to misleading interpretation: food terrorism can easily be interpreted as an accident, which can be useful for certain purposes such as economic. Moreover, although food and water are becoming safer, the big concentration of retailers and production systems makes sabotage easier.

Some important information points to the need for being attentive to the likelihood of a food chain attack. Material allegedly found in 2001 at the Tarnak Farms training camp in Afghanistan indicated interest on the part of al-Qaeda in plant and animal diseases, doing little to dispel fears of such threats [2]. Widespread media reports in 2007 regarding the safety of overseas food exports, along with large-scale food safety breakdowns, increased the perceptions of vulnerabilities in the global chain food supply [2]. Food defence principles were signed by 21 member countries of APEC – Asian-Pacific Economic Cooperation [2]. In the World Health Report 2007, the natural accidental and deliberate contamination of food has been identified as one of the major global public health concerns in twenty-first century [24].

Although this raises worries concerning the possible occurrence of a food chain attack, some voices argue that it is most unlikely to occur. The combination of a set of factors has to be met. In particular, a food terrorist must have technical skills and be good enough to avoid detection of spoiled food during retailing to succeed, which might not be easy if having in mind all the control steps.

Even some governmental and international organisations have strong doubts on the real threat food terrorism represents. The USA Department of Homeland Security states that "limitations on the survivability of some possible threat agents, security measures to prevent product threat abroad, and careful quality control for many imported goods, combine to reduce vulnerabilities" in the food chain [4]. This same Department said they lack "credible information to indicate transnational terrorist planning for an attack against food and agriculture" on al-Qaeda's part [3]. Moreover, the UK's Centre for the Protection of National Infrastructure (CPNI) is confident that "undertaking a major attack on the food supply chain is much more difficult than at first it may be believed" [1].

According to Dalziel [2], the retail/food service point of the food chain may be the most effective point in the food supply chain to cause more than just minimal causalities. He thinks that intentional contamination for economic gain (rather than for malicious goals) may be the larger threat to public health in this area than that from terrorist organisations [2].

Fortunately, major food terrorist attacks have not been registered so far, and food defence is still a subject that reflects worries more than a response to specific past events. However, all these concerns should be considered pertinent, since a relaxed attitude could have a heavy price in the future should a food terrorist succeeded in a massive attack through the food chain.

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Chapter 5
Theoretical Issues of Food Chain Security and Case Studies in the Czech Army

Ales Komar and Jiri Dvorak

Abstract The chapter outlines the general philosophy of food chain security with respect to food subsistence in the military sector. Methods of risk management are applied to the army of the Czech Republic. The main case studies aimed at food chain security during deployment are presented together with the outcomes of major research into catering. A basic risk catalogue was compiled after risk identification and assessment. A map of risks in the catering process was also developed with the illustrative risks and activities of top priority in Ministry of Defence catering services. A user manual is the result of a risk management process on the basis of which measures can be taken in order to minimize and eliminate the occurrence or undesirable impacts of risks and their transfer to another entity.

Keywords Military sector • Food Service • Food subsistence • Security • Risk management • Catering

5.1 Introduction

This chapter describes Ministry of Defence (MoD) insights into the very broad topic of food chain security. It focuses on the challenges in the fields of food safety, food security and food defence. Attention is paid to the role of MoD in food research projects. Risk management is described in relation to Food Service in the Czech Armed Forces [6].

A. Komar (✉) and J. Dvorak
University of Defence, 65 Kounicova, Brno, The Czech Republic
e-mail: ales.komar@unob.cz; jiri.dvorak@unob.cz

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5.1.1 General Considerations

A safe food is the one without contaminants and which does not cause disease and detriment to consumer health. Food chain safety guarantees a shelf life of food during its life cycle from farm to kitchen. Food supply system is an extremely complex issue. Both starvation and overeating have been acknowledged as global challenges. Food system and food supply exist as terrorist vehicles of risk to health and safety. Either intentional or accidental contamination may be considered as far as raw materials and food products are concerned. The vast majority of contamination is accidental and includes microbial, physical, chemical and nuclear contamination. Accordingly, there is a new paradigm for threats to food safety, defence management and catering in the army. Indigenous food and soldiers' welfare are basic prerequisites for good military performance. There is also the European Union (EU) initiative on Green Public Procurement (GPP) in food and catering services, which will supposedly affect armies through the cost increase [3].

Food safety: Food safety deals with an unintentional food poisoning in daily routine. The existing threats are real, but food-borne illnesses requiring hospitalizations are known and deaths are rare. There are routine procedures to cope with unexpected situations. A system failure typically follows the occurrence of disease. The Swine flu pandemic was an illustrative example of routine, out of food subsistence.

Food safety may be achieved through the safety system on Hazard Analysis of Critical Control Points (HACCP) and, eventually, through Good Manufacturing and Hygienic Practices (GMHP) implemented in food production and distribution and prevention of system failure. System failure could be prevented under the following conditions: (a) when impact is severe and exposure likelihood is low, medium or high; (b) when exposure likelihood is low and impact severe, moderate or mild. The HACCP prevents a safety system failure if the impact is moderate and mild and the exposure likelihood is medium and high (Table 5.1). The system also offers some protection against deliberate incidents of contamination.

Safety is a hot topic in the news given 76 million estimated and 6,500 actually reported cases of food-borne illnesses each year. Among them, alimentary infection diseases (gastroenteritis), bacterial enteral infections and poisoning (intoxication) are common food-borne illnesses in the army as well.

The incidence of salmonella (diagnosis A02) decreased five times to 106 cases per 100,000 inhabitants in the Czech Republic between 1998 and 2005. On the other hand, the incidence of viral infections (diagnosis A08) and other enteral infec-

Table 5.1 Preventing safety system failure

	Exposure likelihood		
Impact	Low	Medium	High
Severe		HACCP	HACCP
Moderate		HACCP domain	HACCP
Mild		HACCP	

Table 5.2 Preventing system attack

	Exposure likelihood		
Impact	Low	Medium	High
Severe	Defence domain		
Moderate			
Mild			

tions (diagnosis A04; campylobacter was a causative agent of enteritis in 86 % of cases) increased three times to 287 cases per 100,000 inhabitants in the same period [1,9].

In the contingents of the Czech Army deployed in the Middle East, there are up to 50 cases of hospitalizations, 650 cases of quarantine after withdrawal and 20–30 % of soldiers suffer enteric diarrhea annually. In 2006/2007, 14 occurrences of Listeria were observed and, in 2008, Shigella occurred in the 4th Field Hospital Contingent, fortunately without any deaths.

Food security: There are two main reasons impacting food security: (1) access by all people at all times to enough food for an active, healthy life (the term concerns mainly the elimination of hunger) and (2) food security can be breached by contamination at any point in the food chain [10]. When the food security system fails, it causes alimentary deficiency. Social incompetence can be considered as a main reason for such deficiency around the world.

Food defence: Food safety considers protection of the supply chain against intentional, criminal, sporadic, unknown, plausible/unpredictable threats to food chain from farm to fork. That approach is common in the US Armed Forces, when the event has the above-mentioned features [2]. The prevention of attack against the system is successful in case of severe impact and a low likelihood of exposure. Such protection belongs to the defence domain (Table 5.2).

Food terrorism: Food terrorism is an act or threat of deliberate contamination of food for human consumption with chemical, biological or radioactive agents for the purpose of causing injury or death to civilian populations and/or disrupting social, economic or political stability [11].

5.1.2 Food Risk Management

Food risk management is based on the following main principles in the area of food subsistence in the military sector: food quality, food safety, food defence, and food protection including animal and crop protection and catering management. Catering management may be considered as a new Czech contribution to the Food Service.

All hazards on the way from farm to consumption have to be identified [5]. Food risk management is based on the identification and prioritization of existing risks – probability of risk and consequences of system failure (i.e. impact). The goals of justified interventions are to reduce/eliminate the potential for system failure, use economically viable or regulatory requirements and repeat analysis/intervention cycle until the cost/benefit ratio is acceptable.

Challenges for defence food risk management depend on risk perception. The identification and prioritization of risks is based on vulnerability only as economic impact lacks the probability function. The implementation of justified interventions requires regulation/command or other motivation and it is difficult to prove the intervention value. Rapid detection methods are missing and expensive.

5.1.3 Unique Challenges and Defence Strategies of Military Food System

Food safety is a high profile target for conditions of the Czech Army (two vendor recalls in 2005; now only four are in business) and has been one of the reasons to put catering risks in the army on the agenda. Nowadays, only one-third of units operate catering through outsourcing. Deployed military food sources are combined because subsistence has two streams: own support and NATO support. The main requirements include shelf-stable food and Czech-sourced foods (e.g. Meals Ready to Eat) in stock, and Czech and locally-sourced perishable foods (Kosovo Forces, KFOR). The Czech final products are prepared either in own military kitchens (e.g. KFOR) or the Czech Armed Forces use NATO catering, e.g. the US subsistence (Middle East, International Security Assistance Forces, Multinational Forces in Iraq). Food contamination could result in mission failure. For example, the Czech Army suffered a food-borne illness outbreak in 2005 in the Middle East from locally purchased food. It resulted in a change in the system of food subsistence [8].

In order to comply with the NATO STANAG 2937 (Survival Emergency and Individual Combat Rations, concerning mainly nutritional values and packaging), the Czech military food system concentrates on the following areas:

- Implementation of Combat Food Rations, CFRs, (I, II, Special) and Unitized Group Rations;
- Development of CFRs IV and V;
- Complete development of the modernized Czech field kitchen POKA 4;
- Proposal of premixes to be used safely and efficiently for bread production in field conditions; and
- Development of mobile field bakery.

The potential for unforeseen events must be reduced in the Czech Armed Forces by the following measures: rendering the targets unattractive, rapid and accurate detection of failures, responding effectively to emergencies in order to minimize consequences, rapid delivery of effective recovery efforts, implementation of the Code of Hygienic Practice for Precooked and Cooked Foods in Mass Catering [4], training of new professional soldiers in food service management (considered to be a priority), and conducting the food subsistence research projects within the reform of the Czech Armed Forces.

5.2 Food Safety in Research Projects of the Army of the Czech Republic

The food safety research projects at the University of Defence are dedicated to food safety subsistence in the military sector. One of their objectives is long-term subsistence within a security establishment. The latest topics included Combat Food Rations I and II, Unitized Combat Food Ration, Development of Durable Bread, Incidence of Alimentary Diseases, Economy and Technology in the Operation of Small Bakery, and Military Food Service and its Risks. These projects have already been completed.

The current research projects are focused on food safety and catering during NATO-led operations and the subsistence of bakery products during peace support operations.

5.2.1 Food Rations

The raw material and industry production control, as well as veterinary intervention, are the tasks of military subsistence management, which were pursued during the research. The demands for rations include safe packaging suitable for easy preparation and consumption. The NATO Standards require proper and healthy nutritional levels. It should be easy for food rations to be transported, stored and checked. They also should have a prolonged shelf life and national identification is required (Safety labeling, RFI – Radio Frequency Identification).

5.2.2 Incidence of Alimentary Diseases

The occurrence of alimentary diseases caused by *Salmonellas* in the Czech Republic was the highest in the EU, partially due to the good hygienic practice allowing detection of incidence. In the research project, the comparison of the incidence of salmonelosis, shigellosis (decline) and campylobacteriosis (increase) in the Czech Republic was performed. The incidence of other bacterial enteral infections, including campylobacteriosis, was monitored among civil population and compared with that among the Czech Army personnel. It showed similar tendencies both in civilian and military sectors. Detailed diagnoses of infections and intoxications were carried out with special focus on rising campylobacteriosis. Chickens were identified as the food vehicles for infection. The relevant substitutions of chicken, such as turkey and duck, were proposed. The Principles of Good Practice were implemented and food posted from home was banned. Table 5.3 confirms the prognosis of increasing occurrence of diseases [1] and shows that viral enteral infections are becoming a new phenomenon.

Table 5.3 Incidence of infections (number of cases) [9]

Infection	1999	2005	2008
Other salmonella infections (A02)	44,845	32,927	11,009
Shigellosis (A03)	519	278	229
Other bacterial intestinal infections (A04)	11,732	32,972	23,480
Other bacterial food-borne intoxications (A05)	524	45	85

5.2.3 Indigenous Durable Bread

The daily allowance of bread is 400 g per soldier per day in a food ration and is part of the Czech Army regulation. Durable bread with long-term shelf life and safe packaging was developed in our laboratories. The bread is sliced to provide easy and hygienic eating. Ordinary soldiers support the national culinary preparation of traditional brand bread in own field bakeries.

5.2.4 Catering During Missions

The objectives to be met in the area of soldiers' welfare are traditional, genuine food and national cooks. Notably, arable crops exclude a control mechanism. A containerized military kitchen was developed in our research centers and the containerization of the field bakeries started. It is effective to monitor nutritional characteristics during the mission, such as balance of energy and levels of calories, proteins, carbohydrates, fatty acids, calcium, fiber, etc. Soldiers' personalized healthy nutrition has been proposed for body condition, being assessed on the basis of body mass index and body fat content. The implementation of Good Hygienic Practices and Good Manufacture Practices has recently started in the military units.

5.2.5 Military Food Service and Risk

The combat rations assemblers authenticity control (vendor, prime vendor) and food quality control (nutritional, hygienic) are orders of the day. A long-term framework is required for subsistence pre-conditioned by the authenticity and reliability of supplier and transport. Requirements for supplier's communication readiness and own transport or patrol become a part of contract as well as governmental contracts with host nations.

A completion of container surveillance and the use of tagging, such as trans-informative barcodes, are among the new recent tasks. The utilization of local water treatment facilities is not considered during missions. Only Czech potable bottled water is consumed. Food composition should reflect the requirements for healthy food with a long-time shelf life and storage and should not include any food known as a disease medium. Good Food Service management in subsistence must exclude risks caused by market volatility.

5.2.6 Military Kitchen and Mess Hall

The transposition of EU legislation into the Army involves the implementation of HACCP, compliance with either the Czech Critical Control Points regulation (regarding catering) or the Principle of Good Practices (regarding manufacture, hygiene and operation in military kitchen) and respect of the Alimentary Codex. All the standards play an important role in the management control mechanism. Students at the University of Defence, Brno, are familiarized with all the necessary standards.

5.3 Risk Management in Food Service: Case Study

Implementation of risk management provides a basis for faster quality improvement in Food Service. There are numerous invisible risks connected to the quality of catering service. The implementation of risk management results in functional and efficient mechanisms and can adjust the price and benefit of service. In general, risk management must be routinely accepted in the army [7]. Furthermore, the MoD and the entire defence sector are obliged to follow good practice of the state administration and governmental bodies. Since 2005 there has been a professional army comprising logistically dependent units in the Czech Republic. Reorganization and re-dislocation changes created new risks to contract catering in the last few years.

Here, the study of risk management during a catering contract negotiation is presented. The goal of the research was to explore this field having been a *Terra incognita* so far.

5.3.1 Risk Management in Catering Operation

Logistic Food Service involves administrative, organizational, financial, technical, material and information activities. The objectives of Food Service are sustenance management, organization of catering, nutritional and sensory value of food, security of potable water, safety and sanitation.

Our catering analysis focused on acts and regulations relating to military feeding, risk management, the ways of catering in the Armed Forces, the state of risk management in catering service, risk identification and evaluation, and risk of counter-measures and their effects.

The aims of the work were to analyze the current state of catering services, define risks of possible harm, damage, destruction, loss, and other possible disasters and propose a systematic approach to the risk management. The risk identification was carried out, the identified risks were completely analyzed and a map of risks in the catering process in the Czech Department of Defence was designed on the basis of analyses. A user manual dealing with the declining, monitoring and controlling of risks was developed. Procurements for risk avoidance, minimization of risk occurrence and mitigation of the unexpected results of risks can be implemented on the basis of this document.

5.3.2 Material and Methods

Legislative sources include: (1) the Ministry of Finance (MoF) EU Directive on the System of Risk Management in Governmental Bodies fully applicable to the MoD Sector to comply, (2) the MoD Decree No 5/2003 regarding the Financial Control in the Military Sector implemented to fulfill the Directive of MoF, (3) the Czech Republic Government Decree obliging the creation of maps of risk control and to establish an organization performing risk control in the defence sector.

Notably, risk identification arises from the transposition of the EU legislation and is obligatory for the military sector. A more detailed description is out of scope of this paper.

The Delphi method and risk maps were used to establish the order of risk factor priority. Data acquisition was conducted primarily by interactive discussions with employees (85 respondents) involved in subsistence processes at military facilities and catering companies. Some data were collected by means of inspection.

The Pearson test and paired comparison of probabilities were used for statistical analysis of the distribution of probabilities at nominal samplings.

The matrix calculus employed here for risk assessment was based on the risk analysis matrix rating. There are various estimations of risks. The corresponding Czech Armed Forces' approach could be presented in simplified form as follows. On a linear scale, the indices for the rating of *risk probability* are: 1 – improbable, 2 – exceptional, 3 – occasional, 4 – probable and 5 – certain. The indices for the rating of *risk consequences* for impact assessment with a geometric sequence of numbers are: 1 – manageable, 2 – minor, 4 – moderate, 8 – major, 16 - extreme.

The calculation of *risk significance* is carried out by multiplying the probability (P) and the consequence (C):

$$\text{Significance} = \text{Probability} \times \text{Consequence}\,(\text{Impact}).$$

Subjective assessment was also used for determining the probability of loss, while applying the assessment scale, which quantifies the probability of risk as high, medium and low. The high probability means that risk will probably occur, the medium one indicates that risk will occasionally occur, and low probability implies that the occurrence of risk is unlikely, but possible. A map of risks illustrating the significance of major risks was used as a two-dimensional chart with the coordinates of probability and impact of risks.

The risk management strategies proposed for the four levels of risks, such as critical, high, medium and low, were as follows.

Critical risk/risk avoidance: It is prohibited to undertake risky activities and procedures in case the risk is too high and it is not possible to eliminate, mitigate, or prevent it by introducing further control of uneconomic, ineffective and inefficient allocation of resources. Risk may be avoided by not undertaking the activities connected with such a risk, if the activities are not given a priority in order to fulfill the approved goals.

High risk/risk reduction: If the risk is high, it may be mitigated by implementing the specific measures, while adhering to economic, effective and efficient allocation of resources. The risk may also be mitigated by transferring it to another entity, e.g. through insurance.

Medium risk/risk mitigation: Specific improvement activities and strategy of maintaining the current level of risk must be accomplished by accepting the risk without other activities. This is suitable in case the implementation of measures connected with such a risk is acceptable.

Low risk/risk abatement: Routine procedures aimed at risk prevention due to low level of risk. Ineffective, inefficient and uneconomical use of resources should not be applied.

A Catalogue of Risks was developed to ensure proper risk management of the assessed risks. The risks were coded into particular subgroups. The indexing expresses impact, probability and significance of risks as well as procedure aimed at avoiding them. In practice, the Czech Ministry of Defence uses an electronic version of the catalogue.

5.3.3 Results

The most serious risks in catering service provided through outsourcing are introduced here. The classifications of predictable, controllable and non–controllable risks were proposed, and their impact on food chain security are presented below. The main attention was paid to such risks in the catering service, which can be mitigated or controlled. External risks, such as political, legislative and juristic, regulatory, financial and budgetary, cultural, demographic, natural disasters, and military actions were considered as non-controllable risks without scrutiny.

5.3.3.1 Predictable and Controllable Risks

The list of predicable and controllable risks includes the following 11 groups of risk factors: food service system, legislation, economy, way of messing, food preparation, personnel, real estate, machinery and equipment, occupational health safety, health surveillance, and other risk factors. Risk factor is described using risk identification, while implementing the indices of probability and consequence:

$$\text{Risk factor} = \text{Probability} \times \text{Consequence}.$$

A number of major risks are observed in the areas of health and food preparation, but only the most significant risks are analyzed here in more detail. Limitation stems from the fact that, according to the provisions laid down by legal regulations, the catering service is obliged to introduce the system of GHMP[1] and Critical

[1] Good Hygienic and Manufacturing Practice means providing support to all the activities related to catering service in compliance with the valid legal regulation.

Table 5.4 Number of risks arising from individual activities

Risks description	Number of risks from activities
Food service system	7
Legislation	13
Economy	31
Way of messing	9
Food preparation	26
Personnel	17
Real estates	7
Machinery and equipment	3
Occupational health safety	7
Health surveillance	21
Other risk factors	3

Control Points in food production. Although it is absolutely necessary to pay attention to the risks in the areas of hygiene, epidemiology and food preparation, they are controlled quite well by introducing the system of HACCP.

5.3.3.2 Identified Risks

Thorough risk identification resulted in the primary file containing 418 risks. The identified risks were re-assessed. Duplicities and the risks insignificant for catering service were eliminated. The catalogue of 154 risks was made from the primary file and the risks were divided into 11 groups according to various activities. Individual activities and the number of risks arising from them are shown in Table 5.4.

It is clear from the table that the most risks were identified in economic activities, food preparation and health surveillance.

5.3.3.3 Risk Assessment

The assessment shows that, according to the respondents, there are about 30 most significant risks, 9 of which directly affect the security of the food chain. They are particularly related to infectious diseases, microbial contamination and broken hygiene standards. The values presented in Table 5.5 are the arithmetic means calculated from the respondents' replies.

5.3.3.4 Statistical Assessment of Risk Perception

Based on the outcomes of tests carried out with 95 % reliability, it may be stated that the perception of individual risks differs depending on people's assignments, i.e. whether they are at managerial or executive posts. The risk perception is the highest in health surveillance activity and reaches 19 % and 21 %, respectively, and both groups perceive health risks as the most significant. The assessment differs in other

Table 5.5 Survey of critical risks

No	Code	Description of risk	C	P	R
1	1008	The change of resource framework followed by downsizing	14.89	4.69	69.90
2	1265	Ignorance of accounting standards	14.18	4.76	67.50
3	1305	Hidden overcharging of food purchase prices	15.04	4.33	65.10
4	1221	Insufficient or incorrect specification of public contracts for supplying services or food	15.15	3.64	55.10
5	1701	Insufficient supply of large-scale kitchen equipment	7.86	4.85	38.10
6	1702	Obsolete machines and equipment	7.84	4.81	37.70
7	1606	Neglected maintenance of real estate	7.72	4.75	36.70
8	1941	Alimentary diseases caused by staff	14.87	2.32	34.50
9	1426	Exceeding the recommended shelf life of items in stock	14.11	2.41	34.00
10	1464	Breaching the hygiene standards for food output	14.67	2.28	33.50
11	1270	Fines and penalties	8.28	4.02	33.30
12	1007	Organizational changes	8.19	4.04	33.00
13	1924	Indirect contamination	14.28	2.28	32.60
14	1943	Alimentary diseases caused by suppliers	14.49	2.25	32.60
15	1232	Own failure to keep the deadlines	8.19	3.96	32.50
16	1944	Alimentary diseases caused by food	14.52	2.21	32.10
17	1004	Incorrect setting of pilot project	14.27	2.25	32.10
18	1923	Direct contamination	14.54	2.14	31.10
19	1324	Lack of food stock for crisis situations	14.46	2.13	30.80
20	1001	Wrong analysis of initial state	14.46	2.12	30.60
21	1002	Incorrect concept of catering service	14.11	2.15	30.40
22	1303	Breaching the weight of dishes set in contract	7.76	3.91	30.30
23	1427	No anti-theft protection	14.02	2.15	30.20
24	1323	Breaching the weight of dishes in military kitchens	7.44	3.92	29.10
25	1445	Food contamination during food preparation	14.07	2.06	29.00
26	1603	Construction and technical requirements non-conforming to the hygiene standards	7.51	3.86	29.00
27	1266	Infringement of accounting regulations	7.35	3.86	28.40
28	1304	Breaching the contractual prices	7.35	3.80	27.90
29	1524	Negligence	7.75	3.31	25.60
30	1015	Data falsification (intentional and unintentional)	7.51	3.38	25.30

C consequence, *P* probability, *R* risk significance

areas. For example, the operators perceive the risks in the areas of food preparation, machinery and occupational safety as significant, while the top managers lay emphasis on economic, systematic and legislative risks. All respondents consider risks to be the most significant in the areas of health (20 %) and food preparation (15 %).

5.3.4 Map of Risks in Catering Services

The risks caused by the following activities are presented in the maps of risks: catering (Fig. 5.1 and Table 5.6), food preparation and the sub-activities of receiving

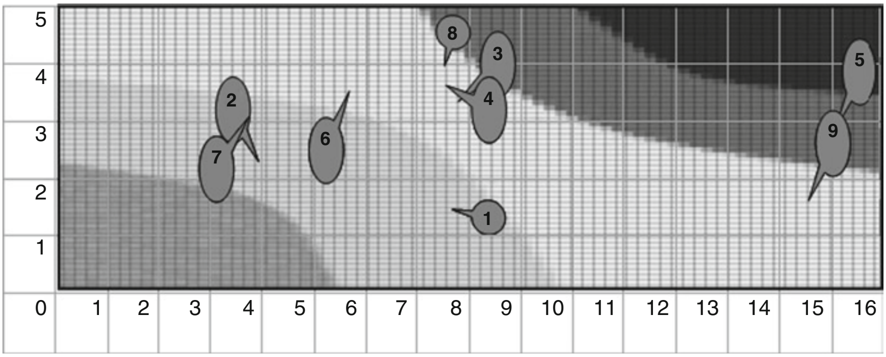

Fig. 5.1 Map of risks in catering

Table 5.6 Survey of catering risks

No	Code	Risk description	C	P	R
Subgroup 'Catering through outsourcing':					
1	1301	Insufficient authority to inspect the fulfilling of obligations	7.62	1.36	10.40
2	1302	Breaching the hygiene and sanitation standards	3.93	3.00	11.80
3	1303	Breaching the weights of dishes	7.76	3.91	30.30
4	1304	Breaching the contractual prices	7.35	3.80	27.90
5	1305	Food purchased for excessive prices	15.04	4.33	65.10
Subgroup 'Own kitchen facility':					
6	1321	Insufficient inspection	5.88	3.20	18.80
7	1322	Breaching the hygiene and sanitation standards	3.82	2.94	11.20
8	1323	Breaching the weight of dishes	7.44	3.92	29.10
9	1324	Lack of food stock for crisis situations	14.46	2.13	30.80

C consequence, *P* probability, *R* risk significance

and storing the food (Fig. 5.2 and Table 5.7), food production and output (Fig. 5.3 and Table 5.8), and some health risks (Fig. 5.4 and Table 5.9).

Catering risks: These are the risks arising from the two basic forms of catering in the military sector, i.e. catering through outsourcing and catering provided in own military facilities. The risk of procuring food for excessive purchase prices is shown under No. 5 in the map of risks (Fig. 5.1) and was assessed by the respondents as another most significant risk from the entire catalogue of risks.

The analysis of the risks of breaching the hygienic and sanitation standards in both catering through outsourcing and own catering (depicted by No. 2 and 7) demonstrated that they are approximately of the same value and are not significant. However, it is desirable to monitor them due to their practical importance.

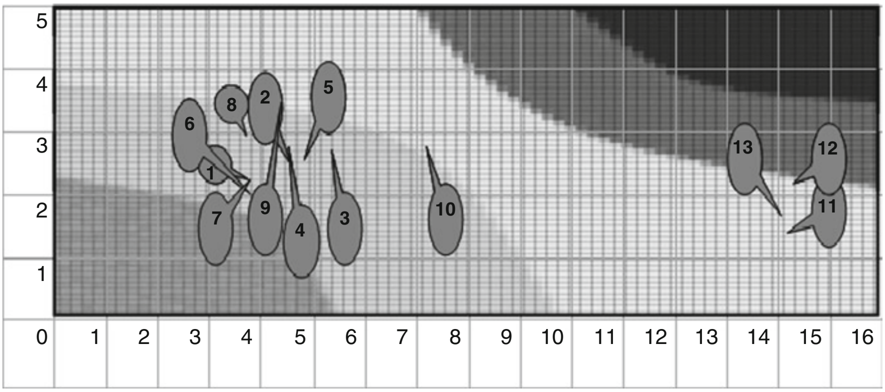

Fig. 5.2 Map of risks linked to food preparation, subactivity of food reception and storage

Table 5.7 Survey of risks linked to food preparation, subactivity of food reception and storage

No	Code	Risk description	C	P	R
Subgroup 'Food reception':					
1	1401	Unsealed packages	3.88	2.12	8.20
2	1402	No control of health certificates	4.66	3.13	14.60
3	1403	Acceptance of food after expiry date of shell life or consumption	5.27	2.33	12.30
4	1404	Breaching the prescribed transport conditions	4.42	2.27	10.00
5	1405	Incorrect quality receipt	4.71	3.21	15.10
6	1406	Incorrect quantity receipt	3.92	2.72	10.60
Subgroup 'Food storage':					
7	1421	Breaching the regulations regarding the layouts of warehouses according to the stored items	3.98	2.11	8.40
8	1422	Cross-contamination in storage	3.61	2.86	10.30
9	1423	Stock conditions (temperature, moisture, light, direct sun radiation, ventilation)	4.25	2.94	12.50
10	1424	Pest attack of food in stock	7.09	2.34	16.60
11	1425	Food after expiry date used for food production	14.02	1.80	25.20
12	1426	Exceeding the recommended shell life of items in stock	14.11	2.41	34.00
13	1427	No anti-theft protection	14.02	2.15	30.20

C consequence, *P* probability, *R* risk significance

Risks linked to food preparation, subactivity of food reception and storage: Exceeding the recommended shelf life of items in stock (No. 12), no anti-theft protection (No. 13) and food used for food preparation after the expiry date

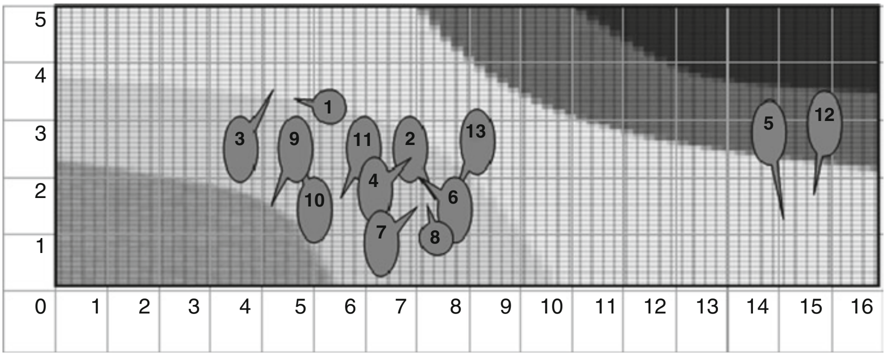

Fig. 5.3 Map – Food preparation, subactivity food production and food output

Table 5.8 Survey of risks linked to food preparation, subactivity of food production and output

No	Code	Risk description	C	P	R
Subgroup 'Food production':					
1	1441	Breaching the manufacturing procedures	4.38	3.27	14.30
2	1442	Breaching the minimum time for thermal treatment	7.34	2.19	16.10
3	1443	Breaching the recipe – weight	4.26	3.22	13.70
4	1444	Breaching the hygienic standards	6.99	2.26	15.80
5	1445	Food contamination during food preparation	14.07	2.06	29.00
6	1446	Unprepared food due to the interrupted supply of energy or potable water	6.99	2.04	14.20
7	1447	Unprepared food due to insufficient staffing	7.27	1.24	9.00
8	1448	Unprepared food due to the failure of large-scale kitchen equipment	7.27	1.28	9.30
Subgroup 'Food output':					
9	1461	Exceeding the time of output of hot dishes (4 h after the end of heat treatment)	4.05	2.08	8.40
10	1462	Breaching the required food temperature of at least 63°C during serving	4.61	2.35	10.90
11	1463	Breaching the required food temperature of at least 65°C during transport and distribution	5.55	2.22	12.30
12	1464	Breaching the hygienic standards for food output	14.67	2.28	33.50
13	1465	Possibility of contamination	7.62	2.27	17.30

C consequence, *P* probability, *R* risk significance

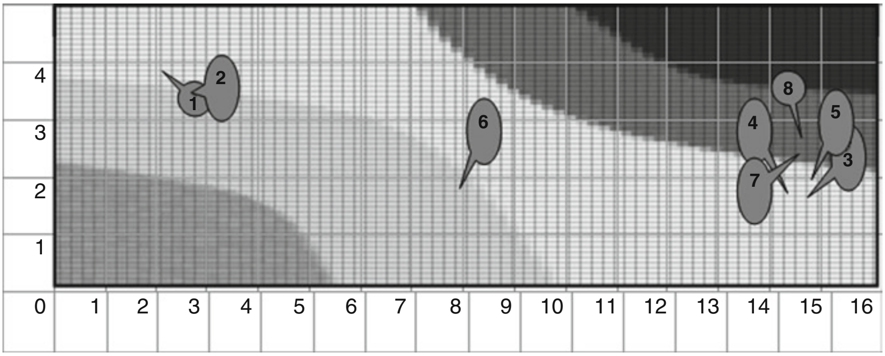

Fig. 5.4 Map of health risks in subgroups of food contamination and alimentary infections

Table 5.9 Survey of health risks in subgroups of food contamination and alimentary infections

No	Code	Risk description	C	P	R
Subgroup 'Food contamination':					
1	1921	Chemical contamination	2.11	3.96	8.30
2	1922	Biological contamination	2.61	3.82	10.00
3	1923	Primary contamination	14.54	2.14	31.10
4	1924	Secondary contamination	14.28	2.28	32.60
Subgroup 'Alimentary infections':					
5	1941	Alimentary infections caused by personnel	14.87	2.32	34.50
6	1942	Alimentary infections caused by boarders	7.93	2.34	18.60
7	1943	Alimentary infections caused by suppliers	14.49	2.25	32.60
8	1944	Alimentary infections caused by food	14.52	2.21	32.10

C consequence, *P* probability, *R* risk significance

(No. 11) are the highest risks, which could be found on the map of risks (Fig. 5.2) and are therefore described in the Risk Management Guidelines in more detail.

Other risks, such as damage to packaging, were assessed as low level risks. They are monitored, but not thoroughly analyzed.

Risks linked to food preparation, subactivity of food production and output: Breaching the hygienic standards for food output (No. 12) and food contamination during food preparation (No. 5) are the risks shown as unacceptable on the map.

Other risks were assessed as middle level risks as shown in Table 5.8. It is necessary to monitor them due to their significance regarding possible contamination

Health risks in subgroups of food contamination and alimentary infections: It is clearly seen from Fig. 5.4 that the staff working in the catering service considers any risk of alimentary infections and direct or indirect contamination of food as unacceptable. Such risks are shown in Table 5.9 under No. 3, 4, 5, 7, and 8.

Other monitored health risks were the risks from subgroups of hygiene, occupational safety and other risks, such as environmental risks and risks caused by not introducing HACCP. They are not presented here as they were not included in the risk survey as risks of the highest significance.

5.4 Conclusions

The risk analysis presented here, i.e. risk identification and assessment in the MoD catering service, resulted in the development of a basic catalogue of risks. Such a catalogue has been missing in practice so far. The maps of risks clearly show which risks and activities are the subjects of primary attention and worth further analysis. It was determined that health risks and risks caused by food preparation have the biggest impacts on food chain security. The final outcome of the risk management process is the proposal of Risk Management Guidelines dealing with elimination and mitigation of the risks, or with their transfer to another entity. The Guidelines will be annexed to a new Czech MoD regulation, which will become effective on January 1, 2012.

The Risk Management Manual implements the Czech MoD strategy of risk reduction. It is decisive to cover the costs for impact verification and absorption impacts. The recommended procedures are as follows:

1. Avoid extreme risks that cannot be mitigated or prevented
2. Avoid risk by dropping operations that are not target priorities
3. Mitigate high risk via procedural improvement
4. Mitigate high risk via its transfer to another entity, e.g. insurance company
5. Accept risk when current procedural measures are proper
6. Decrease control activities with regard to low-level risks in order to avoid ineffective expenditure of resources

Risk identification and assessment in Food Service is a qualitative tool for the prevention and mitigation of risks in food chain security. System management is focused on risk elements in catering as a new part of the food service management security concept. Risk identification and management provides effectiveness, i.e. security, efficiency, hygiene and sanitation, for a safe food service system.

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Chapter 6
Impact of Pesticides as Organic Micro-Pollutants on the Environment and Risks for Mankind

Faruk Bozoglu

Abstract Because of health concerns, persistence, and long-term environmental effects, the impact of pesticides on agriculture and public health has been the subject of considerable research. Organophosphorus pesticides exert their acute effects by inhibiting acetylcholinesterase in the nervous system with subsequent accumulation of toxic levels of acetylcholine. Herbicides have widely variable toxicity. In addition to acute toxicity from high exposures, there is concern over possible carcinogenicity as well as other long-term problems. Improper use of herbicides may damage crop plants, especially if too large a dose is used, or if spraying occurs during a time when the crop species is sensitive to the herbicide. There are also apprehensions about the toxicity of some herbicides, which may affect people using these chemicals during the course of their occupation. The use of herbicides and other pesticides carries risks to humans through exposure to these potentially toxic chemicals, and to ecosystems through direct toxicity caused to non-target species, and through changes in habitat. People exposed to pesticides had over a fourfold increased risk to Non-Hodgkin's lymphoma (NHL), neuroblastoma, child brain development defects, Parkinson's disease, prostate cancer, leukemia in children, male infertility and miscarriage.

Keywords Pesticide contamination • Human health • Environment risk and ecological risk assessment

6.1 Introduction

Pesticides play a large role in agriculture, industry, home/garden maintenance and public health. Of course these benefits are offset by potential risks to human health and the environment due to pesticide toxicity, potency, and persistence in the

F. Bozoglu (✉)
Department of Food Engineering, Middle East Technical University, Ankara, Turkey
e-mail: Bozoglu@metu.edu.tr

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environment. Organophosphate pesticides represent the largest class of pesticides in use today. These compounds affect the nervous system by disrupting the enzyme that regulates acetylcholine, a neurotransmitter. Most organophosphates are insecticides. Organophosphates, in general, are acutely toxic and many compounds were developed as nerve agents and used in World War II. These compounds include sarin and isopropyl methylphosphoric acid (IMPA). Organochlorine insecticides were commonly used in the past, but many have been removed from the market due to their health considerations, persistence, and long-term environmental effects (e.g. DDT and chlordane). Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non-target species, such as air, water, bottom sediments, and food. Pesticide contaminates land and water when it escapes from production sites and storage tanks, when it runs off from fields, when it is discarded, when it is sprayed aerially, and when it is sprayed into water to kill algae. The amount of pesticides that migrates from the intended application area is influenced by the particular chemical's properties, its propensity for binding to soil, its water solubility and its resistance to being broken down over time.

If herbicides are not used properly, damage may be caused to crop plants, especially if too large a dose is used, or if spraying occurs during a time when the crop species is sensitive to the herbicide. Unintended but economically important damage to crop plants is sometimes a consequence of the inappropriate use of herbicides. Unfortunately, the use of herbicides and other pesticides carries risks to humans through exposure to these potentially toxic chemicals, and to ecosystems through direct toxicity caused to non-target species, and through changes in habitat. Herbicide resistant strains have evolved, whose weed population cannot be controlled by the herbicide at the normal recommended application rate.

6.2 Classification of Pesticides

In the past, organochlorine insecticides (e.g. DDT and chlordane) were commonly used but many have been removed from the market due to health concerns, persistence, and long-term environmental effects. They were replaced in developed countries by organophosphates and carbamates by 1975.

Below is a chronology of pesticide development [15].

Period	Example	Source	Characteristics
1800–1920s	Early organics, nitro-phenols, chlorophenols, creosote, naphthalene, petroleum oils	Organic chemistry, by-products of coal gas production, etc.	Often lack specificity and were toxic to user or non-target organisms

(continued)

Period	Example	Source	Characteristics
1945–1955	Chlorinated organics, DDT, HCCH, chlorinated cyclodienes	Organic synthesis	Persistent, good selectivity, good agricultural properties, good public health performance, resistance, harmful ecological effects
1945–1970	Cholinesterase inhibitors, organophosphorus compounds, carbamates	Organic synthesis, good use of structure–activity relationships	Lower persistence, some user toxicity, some environmental problems
1970–1985	Synthetic pyrethroids, avermectins, juvenile hormone mimics, biological pesticides	Refinement of structure activity relationships, new target systems	Some lack of selectivity, resistance, costs and variable persistence
1985–	Genetically engineered organisms	Transfer of genes for biological pesticides to other organisms and into beneficial plants and animals. Genetic alteration of plants to resist non-target effects of pesticides	Possible problems with mutations and escapes, disruption of microbiological ecology, monopoly on products

Pesticides can be classified based upon their biological mechanism function or application method. The Class of pesticides in use today are the Organophosphate pesticides. These compounds affect the nervous system by disrupting the enzyme that regulates acetylcholine, a neurotransmitter. The resulting accumulation of acetylcholine causes continuous stimulation of the muscles, glands, and central nervous system. Carbamate pesticides also affect the nervous system by using an acetylcholine disrupter. There are several subgroups within the classification of carbamate pesticides, including aldicarb, carbaryl, carbofuran, and others.

In biochemistry, cholinesterase is a family of enzymes that catalyze the hydrolysis of the neurotransmitter acetylcholine into choline and acetic acid, a reaction necessary to allow a cholinergic neuron to return to its resting state after activation.

There are two types of cholinesterases:

- Acetylcholinesterase (AChE), also known as RBC cholinesterase, erythrocyte cholinesterase, or (most formally) acetylcholine acetylhydrolase, found primarily in the blood and neural synapses.
- Pseudocholinesterase (BChE or BuChE), also known as plasma cholinesterase, butyrylcholinesterase, or (most formally) acylcholine acylhydrolase, found primarily in the liver.

Among the most common acetylcholinesterase inhibitors are phosphorus-based compounds, which are designed to bind to the active site of the enzyme.

The structural requirements are a phosphorus atom bearing two lipophilic groups, a leaving group (such as a halide or thiocyanate), and a terminal oxygen.

Mammalian and non-mammalian toxicity of pesticides usually expressed as LD_{50} ("Lethal Dose": concentration of the pesticide which will kill half the test organisms over a specified test period). The lower the LD_{50}, the greater the toxicity; values of 0–10 are extremely toxic.

Measured half-life is referred to the time required for the ambient concentration to decrease by 50%. Modern pesticides tend to have short half-lives that reflect the period over which the pest needs to be controlled. The degradation process may lead to formation of "degradates" which may have greater, equal or lesser toxicity than the parent compound. Persistence is determined by biotic and abiotic degradational processes. Biotic processes are biodegradation and metabolism; abiotic processes are mainly hydrolysis, photolysis, and oxidation [4].

6.3 Ecological Effects of Pesticides

Pesticides are included in a broad range of organic micro-pollutants that have ecological impacts. Different categories of pesticides have different types of effects on living organisms, therefore generalization is difficult. Although terrestrial impacts by pesticides do occur, the principal pathway that causes ecological impacts is that of water contaminated by pesticide runoff. Artificial fertilizers, pesticides and herbicides are applied on wide swaths of land in copious amounts by agribusinesses and farmers. These chemicals are then washed off the land by rain and end up in groundwater and rivers, where they accumulate in sediment and water, and thus, in fish, animals and humans, through our drinking water and eating the animals and fish that eat/drink the contaminated food/water [14].

An important problem with broadcast applications is that they are non-selective – they affect many plants and animals that are not weeds – the intended target of the treatment. This is especially true of herbicides, because they are toxic to a wide variety of plant species, and not just the weeds. Therefore, the broadcast spraying of herbicides results in broad exposures of non-pest species, which can cause an unintended but substantial mortality of non-target plants.

The ecological effects of pesticides (and other organic contaminants) are varied and are often inter-related. Effects at the organism or ecological level are usually considered to be an early warning indicator of potential human health impacts. The major types of effects are listed below and will vary depending on the organism under investigation and the type of pesticide. Different pesticides have markedly different effects on aquatic life which makes generalization very difficult. The important point is that many of these effects are chronic (not lethal), are often not noticed by casual observers, yet have consequences for the entire food chain.

- Cancers, tumors and lesions on fish and animals.
- Death of the organism.

- Suppression of immune system.
- Reproductive inhibition or failure.
- Cellular and DNA damage.
- Teratogenic effects

6.4 Human Health Effects of Pesticides

Herbicides have widely variable toxicity. In addition to acute toxicity from high exposures there is concern of possible carcinogenicity as well as other long-term problems such as contributing to Parkinson's disease. Some herbicides cause a range of health effects ranging from skin rashes to death. The pathway of attack can arise from intentional or unintentional direct consumption, improper application resulting in the herbicide coming into direct contact with people or wildlife, inhalation of aerial sprays, or food consumption prior to the labeled pre-harvest interval.

Farm workers have special risks associated with inhalation and skin contact during preparation and application of pesticides to crops. These include:

- skin contact: handling of pesticide products
- inhalation: breathing of dust or spray
- ingestion: pesticides consumed as a contaminant on/in food or in water

However, for the majority of the population, a principal vector is through ingestion of food that is contaminated by pesticides.

It was reported that cancerous human breast tissue contained the chemical heptachlor epoxide (found in the common home pesticide chlordane) at levels four times higher than non-cancerous breast tissue, indicating a breast cancer link to home pesticide chlordane [5]. Babies born to families living near wheat growing agricultural areas using chemical pesticides have been found to have a 65% greater risk of having birth defects related to the circulatory/respiratory system [3]. The pesticide category believed to be the culprit is known as chlorophenoxy herbicides that contain the chemical 2,4-D. A three- to ninefold increased risk of developing Non-Hodgkin's lymphoma (NHL) was noted for patients receiving treatment with alkylating agents or radiotherapy. The most extensive data related to pesticides and the occurrence of NHL suggest that exposure to phenoxy herbicides, particularly 2,4-D, is linked to NHL. Flour millers exposed to fungicides and fumigant pesticides had over a fourfold increased risk of NHL; a long-term follow-up indicated this risk increased to ninefold [6].

Results of another study showed that there was approximately a twofold greater risk of having a stillbirth if the mother lived within 1 mile from an agricultural area that used organophosphate, pyrethroid, carbamate, or chlorinated pesticides. Mothers who lived near crops where certain pesticides were sprayed faced a 40–120% increase in risk of miscarriage due to birth defects [2]. The risk for developing lymphoblastic lymphoma was 12.5 times greater after a child's exposure to household insecticide use. The risk of developing Burkitt lymphoma was observed to be 9.6 times greater after occupational exposure to pesticides. The risk for developing large cell lymphoma or Burkitt lymphoma was 6.7 and 8.0 times higher, respectively, after professional insect extermination [9].

The pesticide MCPA, used as an ingredient is some lawn pesticides, has been found to damage a part of the brain known as the blood brain barrier. Low doses of chlorpyrifos target the developing brain during the critical period in which cell division is occurring, effects which may produce eventual cellular, synaptic, and behavioral aberrations after repeated or prolonged subtoxic exposures [16]. Although the primary hazard to humans associated with pesticide exposure is acute poisoning, among male applicators, prostate cancer mortality was significantly increased [7]. Children who live in homes where indoor or outdoor pesticides are used face a far greater chance of developing leukemia. The results showed the children living in the pesticide treated homes had nearly a four-times greater risk of developing the disease. If the children lived in homes where pesticides were used in the garden as well, the risk of developing leukemia was 6.5 times greater [12].

Pesticide applicators employed for 20 or more years found they had nearly three times the risk for developing lung cancer. The same study also showed the pesticide applicators had twice the risk for brain cancer. There was no increased cancer risk when applicators were studied for only 5 years, implying it takes over 5 years to accumulate enough damage to the genetic structure to develop the cancers. The blood brain barrier is the brain's primary defense system, which works to keep toxic substances out of the brain cells and is literally protecting all of us from developing immediate neurological illness [1].

Mortality from Parkinson's Disease (PD) as the underlying cause of death was higher in agricultural pesticide-use counties than in non-use counties [13]. A dose response was observed for insecticide use per county land treated when using 1982 agricultural census data, but not for amounts of restricted pesticides used or length of residency in a country prior to death. Parents exposed to pesticides may be damaging their children's chance of becoming parents.

A new study involved exposing rats to two common agricultural chemicals – the fungicide vinclozolin and the pesticide methoxychlor that are chemically related to natural hormones, and have been tentatively implicated in reproductive disorders in both animals and humans [11]. When the rats gave birth, their male offspring tended to have low sperm counts and low fertility.

Because the environmental burden of toxic chemicals includes both agriculture and non-agricultural compounds, it is difficult to separate the ecological and human health effects of pesticides from those of industrial compounds that are intentionally or accidentally released into the environment. However, there is overwhelming evidence that agricultural use of pesticides has a major impact on water quality and leads to serious environmental consequences and health effects.

6.5 Ecological Risk Assessment

For some crops it is not cost-effective to remove weeds by physical means such as tilling, a time-consuming and expensive process, yet care is required so that the herbicide does not harm the crop plant or the environment. Crop plants genetically-engineered to be resistant to one very powerful herbicide could help prevent environmental damage by reducing the amount of herbicides needed. For example, Monsanto has created a strain of soybeans genetically modified to be unaffected by their herbicide product Roundup®. When farmers grow these soybeans, which then only require one application of weed-killer instead of multiple applications, it reduces production costs and limits the dangers of agricultural waste run-off. With the advent of genetically modified crops that are tolerant to broad-spectrum herbicides, adverse impacts on non-target habitats are not likely to improve.

The advantage of using herbicides from an agronomic point of view has been extensively considered. What is frequently neglected in the cost/benefit equation is the adverse impact of herbicides on the environment, such as the unwanted phytotoxicity that frequently occurs following herbicide applications. An example would be injury to natural vegetation in the vicinity of field crops, which may have repercussions at various trophic levels – invertebrates, amphibians, birds, and mammals. Regardless of the method of application, it is generally accepted that, when herbicides are being applied, there will always be some misplacement through drift, volatilization, runoff, leaching, or displacement of soil particles through wind erosion.

Most herbicides are specifically plant poisons, and are not very toxic to animals (there are exceptions, however, as is the case with the herbicide paraquat). However, by inducing large changes in vegetation, herbicides can indirectly affect populations of birds, mammals, insects, and other animals through changes in the nature of their habitat. Similarly, the herbicides most commonly used in forestry are not particularly toxic to animals. Their use does, however, cause large changes in the habitat available on clear-cuts and plantations, and these might be expected to diminish the suitability of sprayed sites for the many species of song birds, mammals, and other animals that utilize those habitats.

In an ecological risk assessment, the likelihood that exposure to one or more pesticides that may cause harmful ecological effects are evaluated. The effects can be direct (e.g., fish die from a pesticide entering waterways, or birds do not reproduce normally after ingesting contaminated fish), or indirect (a hawk becomes sick from eating a mouse dying from pesticide poisoning).

Irrigated agriculture, especially in tropical and subtropical environments, usually requires modification of the hydrological regime, which in turn creates a habitat that is conducive to breeding of insects such as mosquitoes which are responsible for a variety of vector-borne diseases. In addition to pesticides used in the normal course of irrigated agriculture, control of vector-borne diseases may require additional application of insecticides such as DDT which have serious and widespread ecological consequences. In order to address this problem, environmental management methods to control breeding of disease vectors are being developed and tested in many irrigation projects.

In addition to ecological impacts in countries of application, pesticides that have been long banned in developed countries (such as DDT, toxaphene, etc.), are consistently found in remote areas such as the high Arctic. Chemicals that are applied in tropical and subtropical countries are transported over long distances by global circulation. The global situation has deteriorated to the point where many countries are calling for a global convention on “POPs” (Persistent Organic Pollutants), which are mainly chlorinated compounds that exhibit high levels of toxicity, are persistent, and bioaccumulate [8].

6.6 Natural Factors That Degrade Pesticides

Metabolism of pesticides occurs principally by oxidation, and hydrolysis by esterases and by reaction with glutathione. Demethylation and glucuronidation may also occur. Oxidation of organophosphorus pesticides may result in more or less toxic products. In general, phosphorothioates are not directly toxic but require oxidative metabolism to the proximal toxin. The glutathione transferase reactions produce products that are, in most cases, of low toxicity.

Two principal biological mechanisms exist that cause degradation of pesticides in addition to chemical and photochemical reactions. These are (1) microbiological processes in soils and water and (2) metabolism of pesticides that are ingested by organisms as part of their food supply.

Degradation of pesticides in soil: This process is mineralization and results in the conversion of the pesticide into simpler compounds such H_2O, CO_2, and NH_3. While some of this process is a result of chemical reactions such as hydrolysis and photolysis, microbiological catabolism and metabolism is usually the major route of mineralization.

Soil microbiota utilize the pesticide as a source of carbon or other nutrients. Some chemicals (for example 2,4-D) are quite rapidly broken down in soil while others are less easily attacked (2,4,5-T). Some chemicals are very persistent and are only broken down slowly (atrazine).

Process of metabolism: Metabolism of pesticides in animals is an important mechanism by which organisms protect themselves from the toxic effects of xenobiotics (foreign chemicals) in their food supply. In the organism, the chemical is transformed into a less toxic form and either excreted or stored in the organism. Different organs, especially the liver, may be involved, depending on the chemical. Enzymes play an important role in the metabolic process and the presence of certain enzymes, especially “mixed” function oxygenases (MFOs) in liver, is now used as an indicator that the organism has been exposed to foreign chemicals.

While both processes are beneficial in the sense that pesticide toxicity is reduced, metabolic processes do cause adverse effects in, for example, fish. Energy used to metabolize pesticides and other xenobiotics (foreign chemicals) is not available for other body functions and can seriously impair growth and reproduction of the organism.

Bioremediation involves microbial digestion of certain organic chemicals used in land farming, biostimulation and bioaugmentating soil biota with commercially available microflora. Clean-up or remediation is assessed by environmental scientists who utilize field measurement of soil chemicals and also apply computer models to analyze the transport and fate of soil chemicals.

6.7 Concluding Remarks

Weeds do not hit the news headlines in the same way as droughts, insect plagues or even swine flu, but cause substantial human misery, quietly and continuously, notes one of the UN Food and Agriculture Organisation's (FAO) most renowned weed experts, Ricardo Labrada-Romero. He quotes figures produced by a leading environmental organization, Landcare Research (New Zealand), which indicates that uncontrolled weeds cause crop losses equivalent to 380 million tonnes of wheat every year. As the FAO reckons that more than one billion people in the world are hungry, this has a huge impact. At today's prices, $95 billion translates into some 380 million tonnes of wheat, or more than half of world production expected in 2009, and of those $95 billion, $70 billion are estimated to be lost in poor countries [10].

Equivalent wheat land lost (in million hectare) by weeds is 135, from disease 121, from insects 65, and from birds/rodents 3.

Modern weed management techniques involve the integrated use of herbicides, crop rotations, and using good quality crop seed uncontaminated by weed seeds.

However, over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non-target species, air, water, bottom sediments, and food. Pesticide contaminates land and water when it escapes from production sites and storage tanks, when it runs off from fields, when it is discarded, when it is sprayed aerially, and when it is sprayed into water to kill algae. Surface runoff of pesticides contaminating bodies of water can change the natural ecosystems by annihilating or permanently damaging several groups of organisms. These further collect and accumulate in the food chain, not just invading the surroundings but also causing harm to humans.

The advantage of using herbicides from an agronomic point of view has been extensively considered. What is frequently neglected in the cost/benefit equation is the adverse impact of herbicides on the environment, such as the unwanted phytotoxicity that frequently occur following herbicide applications. An example would be injury to natural vegetation in the vicinity of field crops, which may have repercussions at various levels to invertebrates, amphibians, birds, and mammals. Regardless of the method of application, it is generally accepted that, when herbicides are being applied, there will always be some misplacement through drift, volatilization, runoff, leaching, or displacement of soil particles through wind erosion. Progression of pesticide development has moved from highly toxic, persistent and bioaccumulating pesticides such as DDT, to pesticides that degrade rapidly in the environment and are less toxic to non-target organisms is a promising approach for the environment.

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Chapter 7
Environmental Lead Contamination as Eco-Terrorism and a Threat to Ecosystems and Public Health

Alexander Omelchenko

Abstract Lead is an element that is non-essential and toxic to the physiology of living organisms. It exerts detrimental effects on the central nervous, cardiovascular, gastrointestinal, reproductive, renal and immune systems, and causes cancer. Lead contamination also threatens the ecosystem of the planet reducing the availability of safe food and water. Thus, the continuous environmental lead pollution could be qualified as an act of eco-terrorism. Currently, the world population is still exposed to a dangerous level of environmental lead. Although, starting from 1976, the blood lead level (BLL) among the USA population is monotonically decreasing, it is asymptotically approaching the BLL of 1 μg/dL, suggesting a sustained human lead intake of about 25 μg/day. Such seemingly low BLLs are documented to be unsafe for adults and, especially, for children. In a majority of European and developing countries between 2003 and 2007, BLL in the population exceeded USA levels. The sources of lead in the environment, such as gasoline, paint, drinking water, food supplements, some recreational activities, etc., and the pathways of its world-wide distribution are analyzed here. Analysis of European data shows that, despite unequal atmospheric lead emission by European countries, atmospheric fallout is normally distributed among them with some countries emitting more lead than taking in. The total atmospheric fallout over Europe is two times more than total lead emission. This necessitates undertaking efforts towards strong international cooperation and collaboration in fighting environmental lead pollution.

Keywords Environmental lead contamination • Atmospheric emission • Atmospheric fallout • Lead • Blood lead level • Gasoline • Lead-based paint • Drinking water • Public health

A. Omelchenko (✉)
Department of Physiology, Institute of Cardiovascular Sciences, St. Boniface General Hospital Research Centre, University of Manitoba, Winnipeg, MB, Canada
e-mail: omelca@sbrc.ca

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7.1 Introduction

Eco-terrorism is often defined as acts that endanger living species and threaten the ecological system of the planet. Accordingly, environmental pollution can certainly qualify as eco-terrorism. Firstly, exposure to environmental pollutants produces adverse health effects including elevated blood pressure, reduced endothelial function, coronary atherosclerosis, certain neurological, respiratory and renal diseases, etc. [11, 23, 62, 65]. For example, the occurrence of cardiovascular diseases (CVD) shows regional specificity in the USA, with West Virginia, Puerto Rico, and Kentucky having the highest proportion of residents with heart diseases, whereas Hawaii, Colorado, and the Virgin Islands have the lowest [54]. In the USA, the increased risk of fatal and non-fatal cardiovascular events in postmenopausal women was associated with greater long-term exposure to the fine particulate air pollution, $PM_{2.5}$, i.e., airborne particles less than 2.5 μm in diameter regardless of any other risk factors for CVD [44]. The study of a large cohort of adults aged 45–74 years has shown that living near busy roads increases incidents of coronary atherosclerosis [20, 31]. Recently, first evidence of a causal link between brief exposure to diesel fumes during physical exercise and myocardial infarction has been obtained [45]. A short-term exposure to ozone as a component of smog, at concentrations typical for many regions of the USA, contributes to premature deaths especially among people with chronic lung or heart disease or other risk factors [50]. The Canadian Medical Association forecasts that about 20,000 Canadians, mostly seniors, could die annually in upcoming years from both short- and long-term exposures to air pollution [71]. As recently found, the average person develops some morbid cardiovascular events, such as the narrowing of the brachial blood vessel diameter and increased systolic blood pressure, within only one or two days of the exposure at or below levels recommended in the current US Environment Protection Agency (EPA) guidelines [93]. Overall, air pollution is the 13th leading cause of death worldwide [93].

Secondly, it is well documented [11] that environmental pollution inevitably reduces the availability of clean air, safe food and water not only leading to adverse health effects in the human population but also creating dangerous geopolitical effects. In modern society, population health has become a key determinant of peace and security [74]. Reduced access to clean environment and associated diseases create a solid ground for social tension at local and international levels, which eventually could translate into extreme violence commonly associated with acts of terrorism and, on a larger scale, war.

Exposure to environmental lead, arsenic, cadmium, pollutant gases, solvents, and pesticides had been linked to increased incidence of CVD and other diseases [11, 66, 79]. The adverse effects of lead on cardiovascular health, sources and distribution of environmental lead have been previously discussed by the author in [60, 61]. In this communication, toxic effects of lead, the current levels of the human lead exposure and major sources of environmental lead contamination are reviewed in accordance with recent data. The main objective here is to emphasize that environmental lead can be considered as an example of eco-terrorism and a threat to the ecological system of the planet and to public health.

7.2 Health Effects of Environmental Lead

Lead is ubiquitous in nature and it was one of the first metals smelted and extensively used by humans. Today, lead is the most widely used non-ferrous metal, with global annual production of 9 million tons. The total amount of lead that has been dispersed into the world ecosystems through the atmosphere during last 2000 years is $2 \cdot 10^{10}$ kg [56, 97]. Assuming uniform distribution of that quantity over the Earth's surface, which comprises 510,065,600 km^2, the average area-specific load of lead amounts to about 40 kg/km^2. Principally, at least a fraction of that substantial amount of dispersed lead could be re-introduced into the atmosphere or dissolved in the aquatic systems due to various meteorological events and anthropogenic activities.

Lead is an absolutely non-essential and, moreover, toxic element for the physiology of living organisms. Only 1 g of lead in 20 m^3 of water makes it unfit for drinking. It is thought that lead poisoning greatly contributed into demise of the Roman Empire due to the neurological damage inflicted by lead upon the Roman governors [58]. The Romans employed lead pipes for plumbing and wine processing. Lead-containing compounds were used as wine sweeteners, food additives, components of cosmetics and glazed pottery. It is believed that some Romans might have consumed as much as 1 g of lead daily [58].

In extreme cases, short-term exposure to high levels of lead can cause vomiting, diarrhea, paralysis, convulsive seizures, coma or even death [70]. In Dakar, the capital of Senegal, 18 children were killed by mysterious illness before lead, left over from years of extracting it from old cars, was discovered in surrounding soil [8]. Acute lead poisoning causes various symptoms related to the nervous system: headache, irritability, abdominal pain, sleeplessness, restlessness, etc. Children may be affected by behavioral disturbances, learning and concentration difficulties. In severe cases, the affected person may suffer from acute psychosis, confusion and reduced consciousness [63]. Long-term exposure to environmental lead affects various vital systems: cardiovascular, nervous, renal, gastrointestinal, haematopoiethic, reproductive, immune, dermatological, and causes cancer [63].

Association between lead exposure and CVD in humans was recently emphasized in a number of original studies and reviews [21, 51, 81]. Specifically, cardiotoxic effects of lead are manifested as peripheral arterial occlusive disease, direct myocardial injury, myocarditis and sinus bradycardia. EKG abnormalities are reported in children and lead-exposed workers. Lead promotes hydroxyl radical generation and lipid peroxidation in cultured aortic endothelial cells and may induce the procoagulant activity of blood cells directly leading to thrombosis. Lead affects human erythrocytes and lymphocytes [80]. In erythrocytes, it could degenerate both the lipid and protein components and suppress hemoglobin synthesis.

In the brain, lead produces the toxic effects on neurons, vascular endothelial cells, astroglia, and oligodendroglia. It induces apoptosis and excitotoxicity as well as disturbances in the storage and release of neurotransmitters and second messengers. Long-term exposure to lead causes memory deterioration, prolonged reaction time and reduced ability to understand [67]. It reduces nerve conduction velocity and dermal sensibility. Lead exposure diminishes intellectual capacity in children [10].

For every 10 μg/dL increase in blood lead, IQ decreases by two points [95]. Notably, the mean IQ in the USA is 100 and people with IQ less than 70 are considered to be mildly mentally retarded. Chronic inorganic lead toxicity results in growth retardation, intellectual impairment, and hyperactivity [70].

Developmental exposure to lead up-regulates the expression level of amyloid precursor protein involved in Alzheimer's disease [9]. Other adverse effects of lead include: loss of muscle tone, intestinal colic, anemia, spontaneous abortion, increase of oxidative stress, down-regulation of nitric oxide production, interference with vitamin D metabolism and magnesium, calcium, iron and zinc homeostasis, etc.

Lead exposure is the most serious for younger children because they absorb lead more easily than adults and are more susceptible to its harmful effects. Even low level exposure may harm the intellectual development, behavior, size and hearing of infants. During pregnancy, especially in the last trimester, lead can cross the placenta and affect the unborn child. Female workers exposed to high levels of lead have more miscarriages and stillbirths.

Notably, a strong causative link is suggested between the level of children's exposure to lead and violent criminal behavior some 20 years later in their lives [48, 52, 53]. Speculatively, that violent criminal behavior, which comprises aggravated assault, robbery, rape and murder, could be readily translated into terrorist activity.

Remarkably, the absorption of lead from the environment by humans through gastrointestinal tract and respiratory ingestion has an accumulative character. There are strong evidences that the BLLs detected by routine blood analysis usually do not reflect total body burden [34]. In fact, the total lead body burden is mainly represented by the bone stores, and bone lead is a better biological marker of chronic lead toxicity. Lead, entering the human body by ingestion and/or inhalation, is transported through the hydrophobic barrier of cell membranes. Since specific natural membrane transporters for lead are doubtful, as this metal is physiologically non-essential and toxic, the ionized lead could take the pathways reserved for essential metal ions. Indeed, it was shown [12] that intestinal transporter for Fe^{2+} ions, DMT1, also mediates the transmembrane movement of Pb^{2+}. By mimicking calcium, magnesium, iron, zinc, and other essential metal ions, lead gets into the blood [12]. Once in the blood, lead binds mainly to erythrocytes and then moves to other organs via circulatory system. The half-life for lead in the blood is about 1 month. During this time, blood lead is distributed between various tissues and organs, including kidney, liver, spleen, heart, stomach, intestine, and nervous and reproductive systems. However, 90–95% of adult body lead resides in bones [63]. Human bones mainly consist of calcium orthophosphate (e.g. hydroxyapatite $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2]$), which makes up to 60% by weight of the human skeleton, comprising 99% of the total calcium of the human body [38]. Lead competes with calcium for the participation in the bone metabolic processes and, due to a lower solubility of lead orthophosphate [55, 59], could substitute calcium in bones. Rough calculations using values of solubility products of lead and calcium orthophosphates show that lead will not accumulate in bones at BLL a half-million times less than corresponding blood calcium concentration [60]. Physiological blood calcium concentration is about 2.4 mM [92]. Thus, BLL should not exceed

0.1 μg/dL as, otherwise, lead will be permanently accumulated in human bones. Although the above estimate seems quite approximate [26, 27], it probably has certain merits. Firstly, it closely relates to the natural BLL from geochemical data, i.e. 0.25 μg/dL [64]. Secondly, no threshold value for association between CVDs and lowest level of lead exposure has yet been found [51].

It is estimated that about 70% of blood lead comes from the skeleton [63]. The half-life of lead in bones ranges from a few years in the trabecular bone (e.g. the patella) to decades in the cortical bone (e.g. the tibia) [69]. Therefore, in some instances, bones could provide elevated BLL compared to lead from daily uptake and serve as an endogenous source of lead exposure in people with increased bone turnover [84]. Although both tibia and patella lead were associated with elevated risk of hypertension, a stronger correlation between tibia lead and hypertension was observed [32, 33]. Blood lead level could significantly increase when bones become less stable. For example, during pregnancy it may double due to mobilization from bones. Notably, fetus actively (i.e. against concentration gradient) absorbs calcium and, simultaneously, lead from mother. At the same time, pregnant women taking high levels of daily calcium supplements (about 1.2 g) showed significant reductions in BLL and breast milk lead suggesting a decrease of fetal and infant exposure [18]. The bone mass loss in postmenopausal women and in aged persons also could cause elevated BLL. In women, lead liberated from the bone as a result of postmenopausal bone loss caused an increase in both systolic and diastolic blood pressures and elevated the risk of hypertension [49].

Although routine population BLL testing is of great importance for determining the status of current environmental lead pollution [5–7, 47], it can hardly serve as a direct indicator of human health, as follows from the above considerations. Bone lead represents a "time bomb" that can be triggered by accelerated bone turnover due to certain pathological events. Thus, BLL, below which lead is not accumulated in bones, could be tentatively considered as the safe one.

7.3 Current Alert BLLs Set by the US Authorities Are Not Safe

Following the ban of lead in gasoline, paint, and the soldering of cans in 1975, geometric mean BLL among general US population decreased from 15.8 in 1976 to 1.6 μg/dL in 2002 [5–7, 47]. As was previously shown [61], the time-dependence of BLL in recent years is described by one-exponential function with offset:

$$BLL = 1 + 15 \times \exp\left(-\frac{t - 1976}{8}\right) \tag{7.1}$$

where t is the year (A.D.). It follows from the Eq. 7.1 that, although BLL has been recently declining two-fold every 6 years, even in infinite time it will only attain the constant level of about 1 μg/dL corresponding to a certain sustained level of lead intake by adults. This concentration seemingly looks harmless, as it is much smaller than the alert levels set by the US Occupational Safety and Health Association (OSHA) and other authorities, which are 40 μg/dL for general population and 10 μg/dL for children and pregnant women [40]. Currently, these standards are appreciated worldwide. However, such BLLs are dangerous because of accumulation of lead in bones, as was shown above. In fact, recent studies have demonstrated significant blood lead-dependence of all-cause mortality, CVD, cancer and impairment of children's intellectual functioning at BLL well below 5–10 μg/dL [35, 39, 43, 51, 78]. Increased occurrence of heart diseases and impaired cognitive functioning and academic achievement reported among children were observed at BLL less than 5 μg/dL [51]. Measurable pathological effect on kidneys was found at 1 μg/dL [19]. Moreover, recent data [13] suggest that a safe BLL level for children has not been demonstrated. Therefore a scientifically proven safe threshold BLL is unknown.

7.4 Sources of Environmental Lead Contamination

Blood lead leveled out at 1 μg/dL and corresponds to lead daily intake of 25 μg by adults [36]. Thus a majority of the USA population continues to intake not less than 25 μg of lead on a daily basis.

Gasoline (petrol) remains one of the major sources of lead in the environment. Tetraethyl lead is used in gasoline as an antiknock additive. In the USA, leaded gasoline is still legally allowed in aircrafts, trains, racing cars, watercrafts, and farm machinery [63]. In the words of a manager in 1982 working for Associated Octel Limited, currently the world's only producer of lead additives for gasoline, "Many funerals have been arranged for lead in petrol -1926, 1943, 1954, 1970, etc. – as I can recall. The grave has been dug, the service arranged, the coffin prepared, the parson and mourners instructed, but the body just would not lie down in the coffin" [37].

Among the two types of aviation fuels, unleaded is used in jet-engine aircrafts and leaded Avgas is utilized by piston-engine aircrafts. Avgas, mainly the 100 LL brand, contains tetraethyl lead, which is the only approved antiknock additive for aviation. Avgas contains 0.56 g/L of lead. In a single year of 2009, $7.3 \cdot 10^6$ L of Avgas were produced in the USA alone [86]. The lead emission from this amount was about 400 t. Since the population of the USA is about 307 million as of 2009, that emission could be translated into about 3,570 μg of lead per person per day. Obviously, not all that lead will be immediately consumed by people. However, it could be a major source of daily lead intake as indicated above, since 25 μg accounts for only 0.7% of that large amount. Fortunately, the usage of Avgas in the USA is constantly declining (Fig. 7.1) in accordance with the data of USA Energy Information Administration [86]. For the period from 1983 to 2009, the time-dependence is described by the formula:

$$Sales \approx 42266 - 21 \times t \tag{7.2}$$

where sales is given in 1,000 gal. per day, and t is the year (A.D.). Slightly different formula derived on the basis of the data from 1983 to 2006 was presented

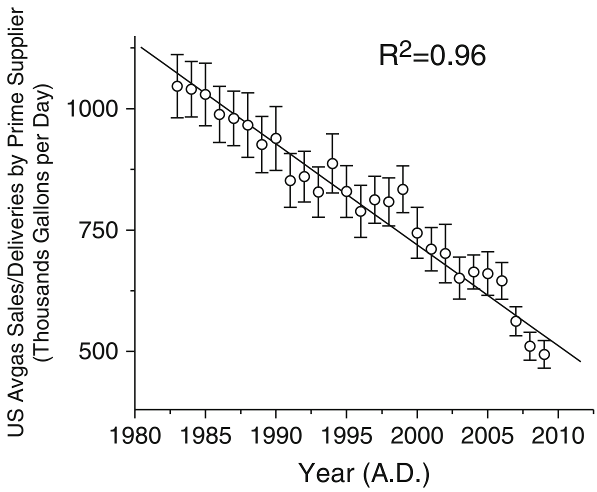

Fig. 7.1 Decline of USA Avgas usage between 1983 and 2009

previously [61]. Contrary to BLL, the usage of Avgas in the USA has declined linearly, and it will be tentatively terminated in about 2035 in accordance with Eq. 7.2.

Competition vehicles using leaded gasoline participate in car racing run by the National Hot Rod Association (NHRA), the International Hot Rod Association (IHRA), Champ Car, and the International Motor Sport Association (IMSA). The data on the amount of leaded gasoline used in the USA for car racing was not found in a literature and internet search. However, the import of leaded gasoline for competition vehicles into Canada increased by 54% between 2002 and 2006, reaching $1.34 \cdot 10^6$ L in 2006 [25]. In Canada, the legislative exemption for use of leaded gasoline in racing cars was recently extended until January 1, 2010, and the USA are not currently planning to ban or restrict the use of leaded fuels in racing events [16].

Only a handful number of countries legally banned the use of leaded petrol. As of 1996, 93% of all gasoline sold in Africa contained lead, 94% – in the Middle East, 30% – in Asia and 35% – in Latin America [94]. In Mexico City, about 4 million cars pumped about 32 tons of lead each day into the air. The kidney and brain damage in policemen and traffic controllers in Alexandria, Egypt, were positively correlated with duration of lead exposure from automobiles using heavy-leaded gasoline [46]. Some popular brands of petrol used in Russia are allowed to contain from 13 to 370 mg of lead per liter [4]. Hypothetically, even unleaded gasoline could be a source of lead. For example, the USA EPA allows unleaded gasoline to contain up to 13 mg/L Pb [17] on a basis that this level provides adequate protection for the car catalytic devices and is practicable for the petroleum industry. Although the use of lead additives in the production of unleaded gasoline is strictly prohibited, it may acquire traces of lead as it passes through the refinery and transport systems previously containing leaded gasoline. Therefore, in principle, it is possible that every single car emits up to a gram of lead every 1,000 km.

Another major source of lead intake is drinking water. In natural water, typical lead concentration lies between 0.2 and 1 μg/dL [85]. However, drinking water can acquire more lead at the original water source, during treatment and/or distribution through the plumbing system. In the USA, about 16–20% of the lead body uptake comes from drinking water [24, 63]. A close correlation between lead concentration in tap water and BLL was found in Hamburg, Germany [22]. Data from Glasgow and Liverpool indicated that over 10% of people exposed to an average water lead concentration of 10 μg/dL would have BLL above 25 μg/dL [68]. In Great Britain, about 45% of households in 1982 used water that had at some stage passed through lead pipes [83]. Some properties in Scotland in the 1970s had lead-lined water tanks [83]. About 100,000–120,000 apartments in Hamburg, Germany [22] and 70,000 residences in Paris, France [89], use lead-containing plumbing and, supposedly, are supplied with lead-contaminated water. In 1993, lead pipes were in use in some 50% of the houses in Southern Saxony, Germany [15]. There, the median and maximum lead levels in tap water were 2.4 and 260 μg/dL, respectively. In a study conducted in households in Trondheim, Norway, the highest values of lead were found in hot water from heaters, especially in older houses with old water heaters [82]. Between 1975 and 1976, 10% of households in England and Wales, and over one-third in Scotland had 'random daytime' water lead concentrations above 5 μg/dL [83].

In the USA, the use of lead solder and leaded pipes in public water supply systems was banned in 1986 by amendments to the federal Safe Drinking Water Act and lead content in faucets and other brass plumbing components was limited to less than 8% of lead. Nevertheless, leaded plumbing components continue to be used in schools and daycares creating elevated lead levels in drinking water. For example, in many Seattle public schools in 2004, an elevated water lead concentration (>2 μg/dL) was found [76]. About 57% of Philadelphia's public schools had water lead levels exceeding the USA EPA action level of 2 μg/dL, and about 29% of schools had water lead concentrations more than 5 μg/dL [14]. Interestingly, the EPA jurisdiction does not extend to drinking water in public school buildings and only the non-enforceable guidelines recommending that the drinking water lead does not exceed 2 μg/dL are provided [88]. In Washington, DC, of approximately 130,000 residences served by the District of Columbia Water and Sewer Authority, an estimated 18% have lead service pipes [1].

Human lead intake might also originate from lead-based paint. Since 1978, paint intended for domestic purposes (e.g. house paints, toys, furniture, etc.) in the USA may contain not more than 0.06% Pb. However, white house paint extensively used prior to the 1980s contained about 50% $PbCO_3$ by weight. Accordingly, 3 million tons of lead remain in 57 million US houses built prior to 1980 [30]. Persistence of lead paint in older homes still constitutes an enormous hazard to inhabitants and construction workers involved in sanding, scraping, and restoration of painted surfaces in these buildings. Lead-based paint is still allowed for industrial, military, marine, and some outdoor uses. In the USA, lead-based paints cover about 465 km^2 of non-residential surface area and almost 90% of the bridges [63]. Millions of

China-made toys were recalled in 2007 due to elevated level of lead in surface paint [90]. The head of a Chinese manufacturer, whose toys were recalled, committed suicide by hanging himself.

Dust and soil represent significant sources of lead contamination, especially for young children and workers exposed to lead. Lead in soil comes from the air or from erosion of lead-bearing rocks. Workers in smelters, refineries and other industries and their families living in the vicinity to these industrial enterprises may be exposed to high levels of lead. For example, in children living in the highly industrialized city of Duisburg, Germany, BLL was higher (3.1 μg/dL) than in those from the rural area of North Rhine Westphalia, Germany, (2.1 μg/dL) [91]. In another case, the villagers from Campo de Jales, Portugal, a place surrounding an abandoned Jales mine had significantly higher than usual BLL levels that were associated with higher prevalence of respiratory and irritation symptoms [42].

Traces of lead are found in almost all food [24]. Lead can enter food from lead-based glazes on glassware and ceramics, from containers painted with lead-based paint or from vinyl lunchboxes [63]. Elevated BLL was associated with storing of food in lead-glazed containers [73], whereas children's lunchboxes made of soft vinyl contained more than 90 times the legal limit for lead in paint [72]. Lead solder used in canned food produced outside the USA and Canada can also contaminate food [2]. Leaded crystal glassware could also be a significant source of dietary lead, especially when acidic beverages such as wine, port, fruit juices and soft drinks are served [24]. Lead salts are used as stabilizers in inexpensive PVC mini-blinds made outside the USA. These blinds were a significant factor contributing to 75% of North Carolina childhood lead poisoning cases in 1996.

Lead is present in some pharmaceutical products and dietary supplements [36], especially in those produced in China, India, the Middle East and Saudi Arabia [3, 63, 75]. Among 45 analyzed products, the highest content was in Teva's prescription multivitamins. If used as prescribed, this preparation will deliver about 2.7 μg of lead daily. Among two ibuprofens, the one purchased via Internet contained 60 times more lead that another produced by Interpharm®. Some herbal and mineral medicine products from Asia are the sources of lead exposure. Certain Ayurvedic herbal products were found to contain lead ranged from 5 to 37,000 μg/g.

An enormous amount of lead was used as fishing sinkers and jigs, and lead shots for hunting and target shooting [77]. At the end of the 1990s, about 5,000 tons of lead were sold annually in the USA and Canada as fishing sinkers and jigs. Additionally, about 1,600 tons of lead were released through spent lead shot from hunting and target shooting in Canada alone. Although lead weights for fishing and waterfowl hunting have recently been largely phased out, considerable lead was previously released into the environment with no chance of being recovered. In addition, lead use for upland hunting, shooting sports, and in fishing tackle remains common [87]. It was reported that in the areas of extensive angling activity, the elevated level of mortality was observed in turtles, waterfowls, and eagles, including California condors [77, 87].

7.5 The Fate of the Airborne Lead: Worldwide Lead Pollution

Atmospheric lead emission and deposition represent the greatest threat to the environment and public health because of the quantities involved and widespread dispersion. Airborne lead can be deposited on water bodies, soils and crops, thus entering animals and, eventually, the human food chain. It was shown that 7–40% of lead in blood is airborne by origin [41]. An average residential time of lead aerosols in the atmosphere is about 4–6 weeks [29], during which lead can travel long distances and be mostly uniformly distributed over space. Evidences for this can be found in ancient and modern times. For example, lead content of ice layers deposited in Greenland between 500 B.C. and 300 A.D. was about four times that of background, implying widespread pollution of the northern hemisphere by emissions from Roman mines and smelters [57]. Also, correlation between the chronology of anthropogenic lead emission and the lead content in seal hair, penguin droppings and snow was found in Antarctica [97]. In individuals living in remote regions of the Himalayas with no known lead exposure, BLL ranged from 0.78 to 3.2 μg/dL, whereas median BLL measured in 1999–2002 in USA adults aged 20–59 was 1.5 μg/dL [63].

Atmospheric lead deposition strongly depends on weather patterns. For example, two samples of air collected in Sutton, in the vicinity of London, UK, on two different days in the same year contained 29 μg and 7.733 mg of lead per gram of air dust [28]. It rained on both days. The observed 267-fold difference was due to the fact that on the first day the wind was from south-west, and on the second day the wind was from the north-east and London air was carried over Sutton. Notably, Sutton occasionally becomes covered by a thin grey-white deposit originating from the Sahara desert in North Africa. On one particular day, about 1 million tons of Sahara's dust were deposited over southern England and Wales [28].

In a majority of European countries between 2003 and 2006, BLL among children exceeded the USA levels [96]. Data on atmospheric lead emission and deposition over European and Trans-Caucasian Countries and Kazakhstan can be found on the website http://www.msceast.org/hms/emission.html#Spatial (accessed in April 2010) managed by the Meteorological Synthesizing Center-East (MSC) located in Moscow, Russian Federation. The MSC is an international center of the Co-operative Program for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP). The detailed analysis of the MSC database on atmospheric lead emission and fallout over 42 European countries shows that European countries emit lead non-equally (Fig. 7.2). The atmospheric lead emission in most countries in 2007 was less than 5 g/year per person. The area-specific lead fallout is not proportional to emission due to strong dependence on meteorological conditions. Indeed, atmospheric lead fallout calculated from data of the MSC was *normally* distributed in 2007 over 42 European countries with most countries getting about 1.6 ± 0.4 kg/year per km^2 (Fig. 7.3). The normal distribution of atmospheric fallout suggests very good air mixing over the European continent.

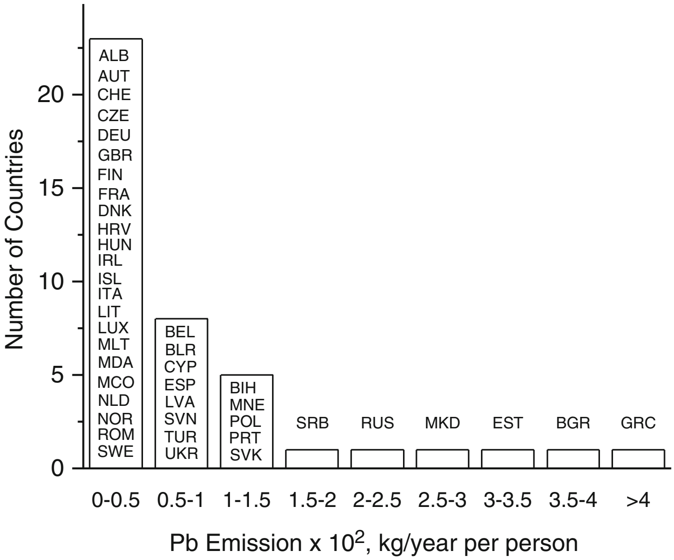

Fig. 7.2 Distribution of European countries by amount of atmospheric lead emission. *AUT*-Austria, *BEL*-Belgium, *BGR*-Bulgaria, *BIH*-Bosnia & Herzegovina, *BLR*-Belarus, *CHE*-Switzerland, *CYP*-Cyprus, *CZE*-Czech Rep., *DEU*-Germany, *DNK*-Denmark, *ESP*-Spain, *EST*-Estonia, *FIN*-Finland, *FRA*-France, *GBR*-United Kingdom, *GRC*-Greece, *HRV*-Croatia, *HUN*-Hungary, *IRL*-Ireland, *ISL*-Iceland, *ITA*-Italy, *LUX*-Luxemburg, *LTU*-Lithuania, *LVA*-Latvia, *MCO*-Monaco, *MDA*-Moldova, *MKD*-Macedonia (*FYR*), *MLT*-Malta, *MNE*-Montenegro, *NLD*-Netherlands, *NOR*-Norway, *POL*-Poland, *PRT*-Portugal, *ROM*-Romania, *RUS*-Russia, *SRB*-Serbia, *SVK*-Slovakia, *SVN*-Slovenia, *SWE*-Sweden, *TUR*-Turkey, *UKR*-Ukraine

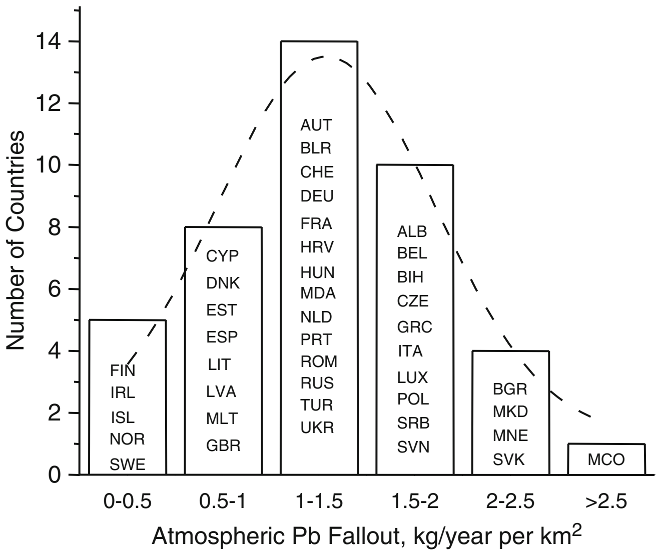

Fig. 7.3 Distribution of European countries by the amount of atmospheric lead fallout. Dashed line represents the best least-square non-linear fit to the normal distribution function

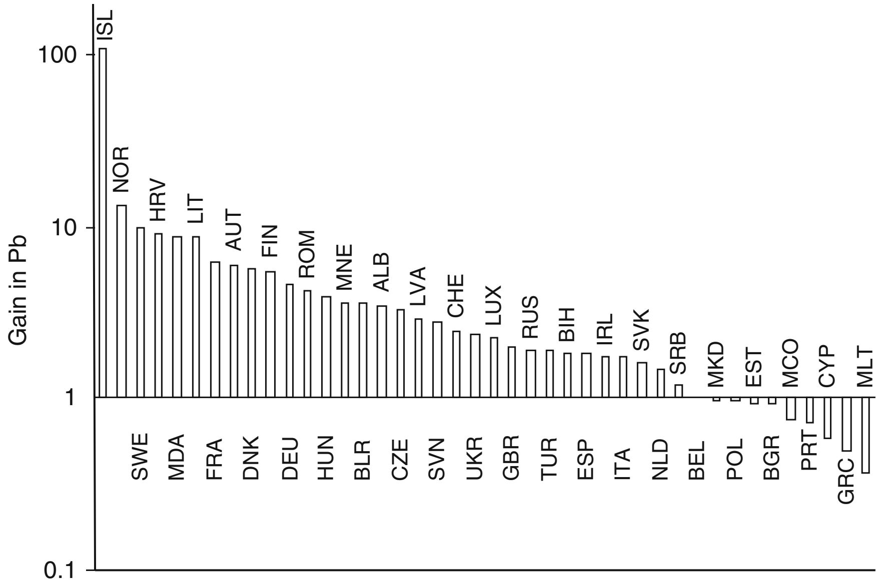

Fig. 7.4 The "lead gain" by the European countries. The dashed line corresponds to the ratio that equals unity

Figure 7.4 shows the "*lead gain*" for each country, i.e. the ratio of atmospheric fallout over emission. The value of the gain more than unity means that the country gets more atmospheric lead than it emits and, if the gain is less than unity, then the country gets less lead than it emits. Most countries acquire more lead than they emit. Notably, Iceland gets 108 times more atmospheric lead than it emits, whereas Greece, Cyprus, Malta get 2–3 times less than they emit. Interestingly, the total atmospheric lead fallout over Europe is twice more than the total European lead emission, Neighboring regions such as in the Mediterranean, sub-Saharan and Middle East countries, and even further, may be the culprits for this excessive lead fallout.

7.6 Conclusions

The current level of lead exposure endangers life on Earth and should be seriously taken as a factor of eco-terrorism. Environmental lead pollution and, associated with it, adverse health effects could create a sense of insecurity among populations. It also reduces the availability of safe natural resources and causes environmental degradation, which in turn can provoke major political controversy, tension, and violence. Human history demonstrates that access to resources frequently was a cause of war.

More fundamental studies are needed to estimate the true safe blood lead level in humans and the corresponding maximal permissible concentrations. Alert levels should be accordingly adjusted by the authorities. In a social sphere, dissemination and popularization of obtained scientific results on lead toxicity are necessary to raise the level of public awareness since such awareness is not widespread. Although there is growing evidence of the pathological effects of lead, its role as a health risk factor is not widely recognized, even by doctors.

Lead has a long history. Arguably, it was one of the first metals smelted and extensively used by Man. Today, lead is the most widely used non-ferrous metal due to certain excellent characteristics. Nevertheless, lead should not be used in products where, at any point of the product's life cycle, it could be digested, inhaled or absorbed through the skin by humans. Stronger legislative measures should be taken to limit lead content in the environment, food, water, and in products exposing lead to people on a daily basis. Lead should not be used in consumer goods, such as children's car seats, umbrellas, jewelry, hockey sticks, etc., just because of convenience.

In a political sphere, better regulations and tighter collaboration between countries are needed at a global scale to eliminate transboundary distribution of atmospheric pollutants.

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Chapter 8
Emergence of the Science and Technology of Electroactivated Aqueous Solutions: Applications for Environmental and Food Safety

Elena N. Gnatko, Vasilij I. Kravets, Elena V. Leschenko, and Alexander Omelchenko

Abstract Although the first attempts to apply electrolyzed aqueous solutions for water disinfection were performed in Russia in the late nineteenth century, the deficiencies in construction of electrolyzers and stability of electrodes did not allow for their broad practical use. The developments in technology and design led to applications of electrolyzed aqueous solutions in the former USSR starting from the 1960s. At present, this technology is being developed in numerous countries around the world. It is reflected in an increased number of publications in peer-reviewed journals and other information sources. Moreover, a number of companies were established to pursue commercialization of the technology. The possibility of their use as power disinfectants of potable water and swimming pools, bactericidal agents for disinfection and sterilization of living tissues, materials, medical and food processing equipment, etc. have been demonstrated in various trials. However, the broader application of the technology is hindered by the lack of profound theoretical and experimental studies of production of electroactivated aqueous solutions and the mechanisms of their activity. In particular, the interrelation between technological and constructional characteristics of the apparatus and functional properties of produced solutions is most poorly understood. We offer an array of figures-of-merit allowing a fair comparison between the electrolyzers of different design.

Keywords Electroactivated water • Superoxidized water • Electrolysis • Flow cylindrical electrolyzer • Disinfection • Sterilization • Figures-of-merit • Transport phenomena • Food equipment • Medical equipment

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E.N. Gnatko (✉), V.I. Kravets, and E.V. Leschenko
Ukrainian State University for Chemical Engineering, Dnepropetrovsk, Ukraine
e-mail: gelnik2011@mail.ru

A. Omelchenko
Department of Physiology, Institute of Cardiovascular Sciences, St. Boniface General Hospital Research Centre, University of Manitoba, Winnipeg, MB, Canada
e-mail: omelca@sbrc.ca

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8.1 Introduction

Electrochemical technology plays an important role in resolving of the modern ecological and socio-economical problems [69]. The electrochemical activation (ECA) represents a relatively novel, advanced technology of electrochemical treatment of aqueous solutions including drinking water [5].

The first attempts to use electrolyzed solutions of sodium chloride as disinfecting and bactericidal agents commenced in Russia in the late nineteenth century [24]. Koch and Mendelson in 1879 and Porokhovnik and Spaet in 1890 tried using such solutions for water disinfection. However, the material and constructional drawbacks attributed to their electrolyzers had not allowed for the practical use of the technology.

Developments in technology and design led to applications of electrolyzed NaCl solutions in the former Soviet Union starting from the 1960s and, soon after that, in Japan [4, 5, 17]. Up-to-date, investigations and applications of the technology are also reported in the USA, United Kingdom, Germany, Israel, South Africa, Greece, Spain, Mexico, China, Russia, Ukraine, Estonia, and India. The conducted trials demonstrated the possibilities for electrolyzed acid aqueous solutions as power disinfectants of potable water and swimming pools, bactericidal agents for disinfection of living tissues, materials, medical and other equipment, etc. [10, 34, 48, 52, 56]. At the same time, electrolyzed alkaline solutions have been used for washing and rinsing, watering plants and cattle [1]. Weak alkaline water routinely obtained by electrolysis of tap drinking water is shown to be beneficial for human health [16].

The ECA technology was tested in a most dramatic way during the Rwanda genocide in 1994. Poor sanitation and scarcity of food and, especially, safe drinking water were characteristic for the refugee camps and peacekeeping forces. The Japanese Self-Defense Forces and also British entrepreneurs from Enigma (UK) Ltd took with them small devices for producing electrolyzed strong acid aqueous solutions [33]. The Japanese used the device for disinfection of premises in their campground, washing hands, boots and vehicles; and for cleaning medical facilities. The British employed their device to turn polluted water into safe drinking water for refugees by the dilution (1:1,000) of electrolyzed acid solution. The electrolyzed solutions were also used in the treatment of burns, cuts, ringworm and other ailments. Both parties successfully completed their mission by stopping a potential epidemic of infectious diseases with neither infected personnel nor residual environmental pollution.

Notwithstanding the well-documented examples of beneficial uses of electrolyzed acidic and alkaline aqueous solutions, the faster development and broader application of ECA technology is currently hindered by the lack of profound theoretical and experimental studies of production of electroactivated aqueous solutions and the mechanisms of their activity. In particular, the interrelation between technological and constructional characteristics of the apparatus, from one side, and functional properties of produced solutions, from another side, are very poorly understood. The lack of detailed theoretical and experimental studies

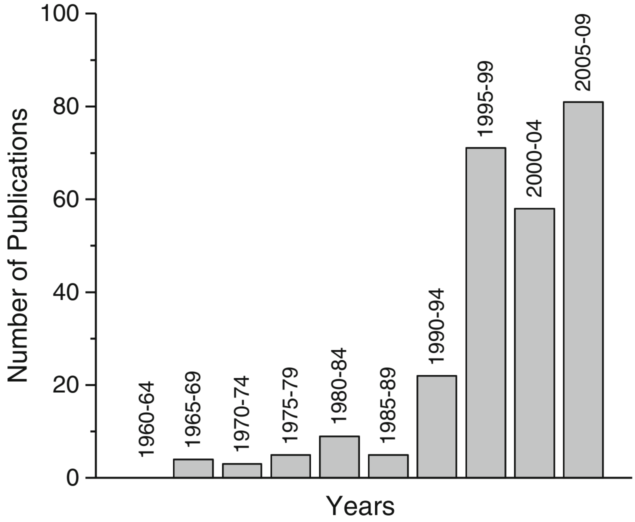

Fig. 8.1 Increasing number of publications dedicated to the science and technology of electroactivated solutions. The data were obtained from the Web of Knowledge using the keywords: electrolyzed water, super-oxidized water, oxidized water, and electroactivated water

into ECA technology is illustrated in Fig. 8.1, which shows that the number of peer-reviewed publications pertaining to the subject, although significantly higher than in the 1960s, is still relatively small.

Here we describe the modern state of the technology and application of ECA and outline the necessity of studying the intimate relationships between the working parameters of the electrochemical reactors and functional characteristics of the activated solutions. An array of figures-of-merit, allowing for a fair comparison between the electrolyzers of different design, is proposed.

8.2 Principals of the Electrochemical Water Activation

Principally, the technology can be described using the scheme depicted in Fig. 8.2. The electroactivated aqueous solutions are usually produced inside the continuous flow, diaphragmatic electrolyzer fed with the brine solution containing about 75 g/L NaCl. This solution is passed through the reactor where it is subjected to a mild electric charge. It emerges as a catholyte, an alkaline solution, which acts as a powerful washing, cleansing, and extraction agent, and as an anolyte, which can be used for disinfection, sterilization, purification, and killing bacteria. The catholyte might be fed back into the anode chamber where it can be treated to produce an anolyte having desirable functional characteristics. Depending on mineralization of the input solution, the weak and strong catholytes and anolytes can be produced. At the same time, depending on the amount of catholyte re-directed into the anode chamber, acid, neutral, and alkaline anolytes are manufactured. Usually, the strong

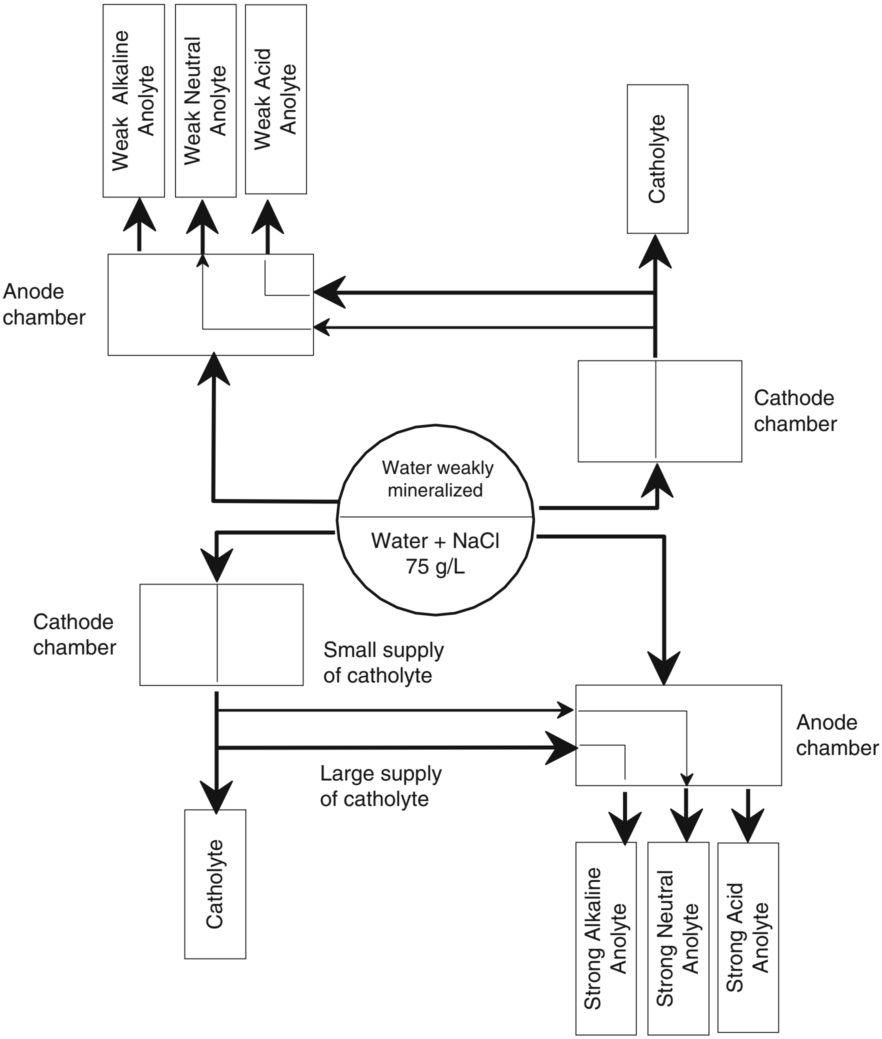

Fig. 8.2 Principal scheme of electrochemical water activation

acid anolytes are characterized by pH ranging 2.3–2.7, positive redox potential of 1,000–1,100 mV, and by about 30–50 ppm of dissolved chlorine [23, 39, 40, 54, 63]. The catholyte is characterized by pH 6.2 and negative redox potential −329 mV and by pH 8.8 and negative redox potential −390 mV, if produced by electrolysis of distilled water or 10^{-4} M NaCl, respectively [46].

To obtain alkaline ionized water, weakly mineralized water (e.g. tap drinking water) is subjected to electrolysis. It is important to keep produced solutions free of contaminants originating from corrosion of electrodes, especially anode, and decomposition of the diaphragm.

In a simplified form, the main electrode processes are as follows:

1. Oxidizing water on the anode:

$$2H_2O - 4\,e^- \rightarrow 4H^+ + O_2$$

2. Reducing water on the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

3. Formation on the anode of gaseous chlorine in chloride solutions:

$$2Cl^- - 2e^- \rightarrow Cl_2$$

4. Formation in the anode chamber of highly-active oxidyzers:

$$ClO_2,\ HClO,\ ClO^{\cdot}, Cl^{\cdot},\ Cl_2,\ O_2,\ O_3,\ H_2O_2,\ OH^{\cdot},\ \text{etc.}$$

5. Formation in the cathode chamber of highly-active reducers:

$$OH^-,\ O^{2-}\ HO^{2-},\ H_{aq},\ H_2O^{2-}$$

The electroactivated aqueous solutions could temporally exist in a metastable state possessing peculiar physicochemical properties and distinct biological activities, which are diminished during the relaxation period lasting days or even weeks [29, 30, 37, 46]. It is consistent with the notion that electroactivated and chemically prepared solutions, having the same concentrations of the oxidants, do not manifest the same redox potentials, pH, and functional characteristics [5, 20, 26, 39, 47, 72]. For example, a study of the interaction of electrolyzed or chemically modified waters with iron powder, serving as a reducing agent, revealed significant difference in the properties of foregoing solutions [28]. When 100 mg/L of powdered iron was added to the electrolyzed or chemically modified solution, it took longer for the redox potential reading of electrolyzed water to stabilize. It suggests that HOCl existing in the electrolyzed water is more stable comparing to that of chemically modified one.

Several factors suggested for explanation of anomalous activities of electroactivated media are as follows: (1) formation of metastable intermediate products of electrolysis, in particular, hydrogen peroxide and free radicals, which are able to exist in the medium for a long time due to the cyclic chain reactions; (2) modification of structural and energetic properties of water, and (3) formation and prolonged existence of gaseous microbubbles [29, 30, 33, 46, 47]. The increase of the ionic strength of catholyte and anolyte by addition of concentrated NaCl solution after the electrolysis significantly decreases the relaxation time [46]. Prolonged preservation of the catholyte and anolyte redox potentials could also be achieved by freezing.

8.3 Existing Applications of the Electrochemically Activated Aqueous Solutions

All electroactivated solutions are relatively environmentally safe [16]. Neutral anolyte, for example, has a biocompatibility with living cells similar to that of distilled water. Activated water is non-toxic, so users can apply it without wearing special protective equipment because there is no danger of skin or respiratory damage. The electroactivated solutions have a great potential to replace such harmful chemicals as chlorine and hydrogen peroxide in certain applications.

Currently, alkaline ionized water (AIW) is being used in Japan for drinking, cooking, preparing tea, coffee, and alcoholic drinks [22, 71]. Meat and other phosphate-containing acid foods tend to make blood and body fluid more acidic. It is thought that AIW could help to maintain alkalinity in living organisms and improve body disposition [16]. Scientists have also been studying the physiological role and mechanisms of action of AIW [22, 60].

Significant bactericidal activity of the electroactivated acidic water was found against various bacteria, viruses and fungi including *Acinetobacter baumannii*, *Acinetobacter calcoaceticus*, *Actinomyces israelii*, *Actinobacillus actinomycetemcomitans*, *Actinomyces naeslundii*, *Actinomyces viscosus*, *Aspergillus fumigatus*, *Bacillus cereus*, *Bifidobacterium bifidum*, *Candida albicans*, *Candida tropicalis*, *Clostridium difficile*, *Cryptococcus neoformans*, *Enterococcus faecalis*, *Escherichia coli*, *Eubacterium lentum*, *Fusobacterium nucleatum*, *Helicobacter pylori*, *Klebsiella pneumoniae*, *Lactobacillus acidophilus*, *Lactobacillus rogosae*, *Neisseria gonorrhoeae*, *Peptococcus niger*, *Peptostreptococcus anaerobius*, *Porphyromonas endodontalis*, *Porphyromonas gingivalis*, *Prevotella loeschii*, *Prevotella melaninogenica*, *Prevotella nigrescens*, *Propionibacterium acnes*, *Pseudomonas aeruginosa*, *Pseudomonas cepacia*, *Salmonella typhimurium*, *Serratia marcescens*, *Staphylococcus aureus*, *Staphylococcus* spp, *Stenothrophomonas maltophilia*, *Streptococcus intermedius*, *Streptococcus mitis*, *Streptococcus pneumoniae*, *Streptococcus pyogenes*, *Streptococcus salivarius*, *Streptococcus sanguis*, *Streptococcus sobrinus*, *Veillonella parvula*, *Xanthomonas maltophilia*, Coxsackievirus type B1, echovirus type 7, herpes simplex types 1 and 2, adenoviruses types 1, 2, and 3; poliovirus types 2 and 3; and human immunodeficiency virus HIV-1 [21, 41, 43, 55, 63, 65–67].

The viability and power of electrolyzed water have been demonstrated in agriculture [14, 53, 73], food processing [19, 27, 68], medical applications [23, 45, 55], fisheries [6, 13], and industry [8, 12, 35, 56, 61]. The strong acid anolyte was used in medical practice for cleaning the premises, for hand washing, skin care; and for the prevention and treating various infections, such as mediastinitis, peritonitis, intraperitoneal abscesses, infectious skin defects, decubitus ulcer, burns, cystitis, vaginitis, etc. [18, 23, 33, 51, 54]. The irrigation of porcine pancreases with acid anolyte during their harvesting from slaughterhouse for the purpose of islet xenotransplantation was effective in preventing of microbial contamination [38]. A successful treatment of the abdominal aortic graft infection by irrigation with strong acid anolyte has been presented in [44].

An acid anolyte was suggested as an alternative to hazardous glutaraldehyde for cleaning and disinfection of gastrointestinal endoscopes [2, 36, 39, 66]. In the United Kingdom and USA, such a solution was dubbed Sterilox. The investigation of the mechanism of Sterilox's action on *Escherichia coli* using protein and nucleic acid analysis revealed total destruction of chromosomal and plasmid DNA, RNA and proteins of the bacteria within 5 min of exposure [75]. The atomic force microscopy revealed swelling and rupture of *E. coli* cells with release of cytoplasm. The biocidal properties of Sterilox have been proposed to be due to the effect upon constituents of the bacterial cell including proteins and nucleic acids. Currently, Sterilox-producing technology is marketed by PuriCore [3].

The cleaning and disinfecting of hemodialysis equipment using strong acid anolyte have been studied in [64, 65]. The study indicated that the disinfecting action of strong acid anolyte proved to be faster and more effective than the other hazardous chemicals, such as NaClO, formalin, and Dialox (a mixture of H_2O_2, $CH_3CHOOOH$, CH_3COOH, and H_2O) conventionally used to clean and disinfect hemodialysis pipelines.

The electrolyzed water has been used in dentistry for disinfection of dental instruments [58], irrigation of root canals [15, 21] and gingival pockets [57], and as gargles [25]; in ophthalmology for disinfection of the ocular surfaces [59].

8.4 Constructional Figures-of-Merits of the Concentric Cylindrical Flow-through Electrochemical Reactor

The electroactivated aqueous solutions are produced worldwide by a variety of different electrolyzers. In Japan alone in 1999, there were about 30 manufacturers of apparatuses for water electroactivation [65]. The electroactivated water made by those machines has been said to vary subtly due to the differences in the water content, type of electrodes, inter-electrode distance, technological parameters, etc.

Electrochemical treatment of water and aqueous solution had been performed using the batch type [39, 42, 51, 62, 72] and flow-through electrolyzers with [39, 51, 61] or without porous diaphragm [42, 62]. In some cases, multiple and bipolar electrodes were employed [24, 61, 62]. A peculiar electrolyzer containing multiple magnetite or graphite electrodes is described in [56]. The electrolyzer comprised two columns filled with the grains of magnetite or graphite, each of which could virtually be considered as a bipolar electrode.

For the faster and broader application of ECA technology, profound theoretical and experimental studies of production of electroactivated aqueous solutions and the mechanisms of their activity are of paramount importance. Particularly, the interrelation between technological and constructional characteristics of the apparatus, from one side, and functional properties of the activated solutions, from another side, should be well understood for the production of the most effective solutions. It is difficult to achieve this goal without determination of the unifying principles applicable to the electrolyzers of different design. As a first step in establishing such a relationship, the major requirements for the state-of-art design and an array of figures-of-merit allowing for comparative evaluation of various electrolyzers are suggested below.

The general guidelines for designing an efficient electrochemical reactor are: (i) a large active electrode area per unit volume, resulting in a compact highly efficient reactor, (ii) an uniform distribution of the electric potential over the electrode surface, (iii) the high as possible current density, although this could affect the corrosion stability of the anode, (iv) a high rate of mass transport towards the electrodes, and (v) the low power consumption, which requires small inter-electrode distance and a thin conductive diaphragm [31, 32, 69, 70]. The above principles are largely determined by the constructional (geometrical) figures-of-merit.

An analysis presented here is carried out for the concentric cylindrical flow-through electrolyzer (CCFE) with diaphragm. Similar electrolyzers have been used in experimental and commercial settings for removing heavy metals and textile dyes, and for electroactivation of aqueous solutions [5, 7, 49, 73, 75]. The advantages of CCFE are as follows: (1) the uniform distribution of the electric potential over the electrode surfaces for better current efficiency, (2) compactness, (3) the use of external tubular electrode as external casing, (4) hermetical nature of each electrolyzer and a possibility of use it in a modular system, (5) a possibility of a separate electrolyte inflow into anode and cathode chambers, etc.

The analyzed CCFE depicted in Fig. 8.3 comprises anode with inner (if hollow and tubular) r_A radius, tubular cathode, and ceramic porous diaphragm.

All these components are the stationary cylinders electrically insulated at the ends, therefore they have the same effective working length L. The corresponding figures-of-merit are as follows.

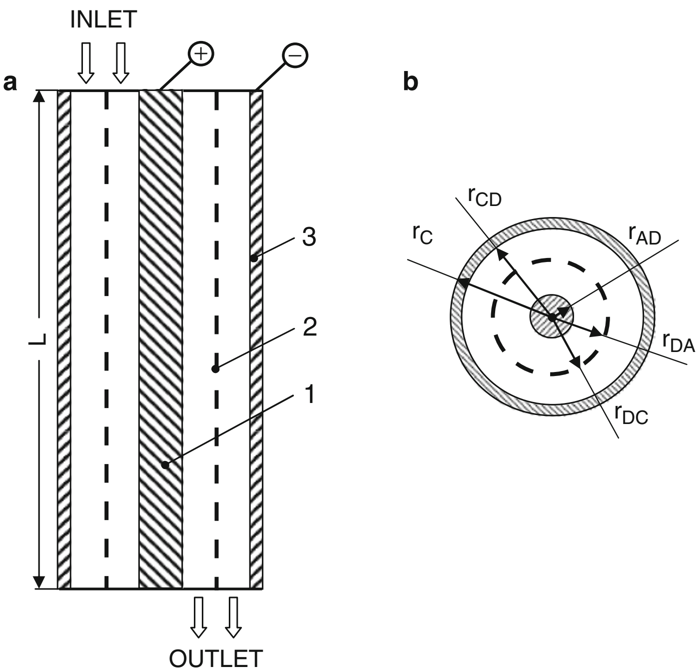

Fig. 8.3 Principal construction of the concentric cylindrical flow electrolyzer with diaphragm. r_{AD} is the anode outer radius; r_{CD} and r_C are the inner and outer cathode radii, respectively; r_{DA} and r_{DC} are the inner and outer radii of the ceramic porous diaphragm, respectively

Aspect ratio, *a*: The corresponding aspect ratios are defined as $a_A = r_A/r_{AD}$, $a_C = r_{CD}/r_C$, $a_{AD} = r_{AD}/r_{DA}$, and $a_{CD} = r_{DC}/r_{CD}$ for anode, cathode, anode chamber and cathode chamber, respectively.

Active electrode area per unit reactor volume (A_S, cm^2 cm^{-3}): Conventionally, this parameter is defined as ratio of the electrode surface area, A, to volume of the electrolyzer, V_R:

$$A_S = \frac{A}{V_R}$$

For diaphragmatic electrolyzers, it is useful to define the active electrode area per unit reactor volume with respect to the volumes of the corresponding chambers, i.e. A_{SA} and A_{SC} for the anode and cathode chambers, respectively. Obviously, the maximal magnitudes of the above parameters are desirable for designing the most compact, highly efficient electrolyzer. Since the anode, cathode and diaphragm are cylinders with the same effective length, one can show that the active electrode areas per unit reactor volume are independent of the length of the annuli and are given by:

$$A_{SA} = \frac{2a_{AD}}{r_{DA}(1 - a_{AD}^2)} \text{ and } A_{SC} = \frac{2}{r_{CD}(1 - a_{CD}^2)} \tag{8.1}$$

for the anode and cathode, respectively. A peculiarity of the cylindrical electrolyzers, which is important for engineering, could be found by the analysis of Eq. 8.1. For example, Fig. 8.4 shows the dependence of the active anode area per unit anode chamber volume on the inner radius of the diaphragm at some fixed outer anode radius calculated using Eq. 8.1. It can be seen that to change the size of the reactor, for example for increasing the productivity of the process, but to

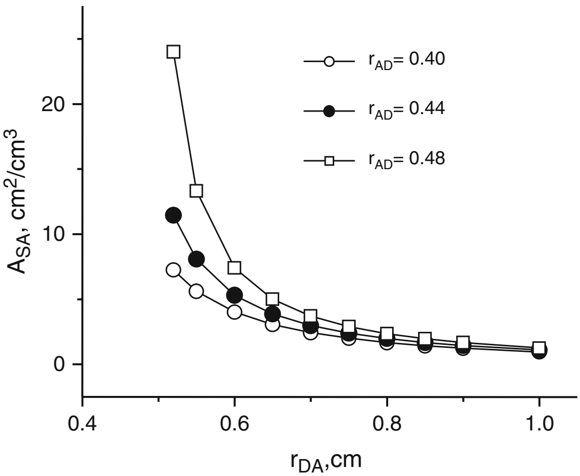

Fig. 8.4 Dependence of the anode area per unit anode chamber volume A_{SA} from the inner radius of the diaphragm r_{DA} for various fixed magnitudes of the outer radius of the anode r_{AD}

keep the corresponding figures-of-merit unchanged, it is necessary to alter the corresponding aspect ratios.

It is of interest to establish interrelationships between relative changes of the inner radii of the diaphragm and cathode and corresponding changes of the outer radii of the anode and diaphragm satisfying the condition of preservation of magnitudes of A_{SA} and A_{SC}. Such relative changes could be conveniently characterized using dimensionless scaling coefficients χ representing the ratios of the changed radius to the initial one calculated for the corresponding compartments of the electrolyzer.

From the condition $A_{SA1} = A_{SA2}$ and Eq. 8.1, the scaling coefficient for the outer anode radius χ_{AD} represents a positive root of the quadratic equation:

$$\chi_{AD}^2 + \left(\frac{1-a_{AD1}^2}{a_{AD1}^2}\right)\chi_{AD} - \left(\frac{r_{DA2}}{r_{AD1}}\right)^2 = 0,$$

where $\chi_{AD} = r_{AD2}/r_{AD1}$ and $a_{AD1} = r_{AD1}/r_{DA1}$; r_{AD1} and r_{DA1} are the initial outer and inner radii of the anode and diaphragm, respectively, r_{AD2} and r_{DA2} are the changed outer and inner radii of the anode and diaphragm, respectively. Thus,

$$\chi_{AD} = \frac{1}{2}\left\{\frac{a_{AD1}^2-1}{a_{AD1}^2} + \left[\left(\frac{1-a_{AD1}^2}{a_{AD1}^2}\right)^2 + 4\left(\frac{r_{DA2}}{r_{AD1}}\right)^2\right]^{\frac{1}{2}}\right\} \tag{8.2}$$

The dependence of the ratio $\chi_{AD}/\chi_{DA,}$ where $\chi_{DA} = r_{DA2}/r_{DA1}$ is the scaling coefficient of the diaphragm inner radius, from χ_{DA} calculated using Eq. 8.2 is concave (data not shown for brevity), which manifests the gradual weakening of the dependence between the anode and diaphragm dimensions upon increasing of the diaphragm radius.

From the condition $A_{SA1} = A_{SA2}$ and Eq. 8.1, the dependence of the scaling coefficient of the diaphragm outer radius χ_{DC} from the scaling coefficient of the cathode inner radius χ_{CD} is given by:

$$\chi_{DC} = \left[\left(\frac{r_{CD2}}{r_{DC1}}\right)^2 - \left(\frac{1-a_{CD1}^2}{a_{CD1}^2}\right)\chi_{CD}\right]^{\frac{1}{2}}$$

where $\chi_{DC} = r_{DC2}/r_{DC1}$, $\chi_{CD} = r_{CD2}/r_{CD1}$ and $a_{CD1} = r_{DC1}/r_{CD1}$; r_{CD1} and r_{DC1} are the initial inner and outer radii of the cathode and diaphragm, respectively, r_{CD2} and r_{DC2} are the changed inner and outer radii of the cathode and diaphragm, respectively.

The dependence of χ_{DC}/χ_{CD} from χ_{CD} is similar to that described by Eq. 8.2 (data not shown for brevity).

Active electrode area per unit electrode volume (A_E, cm^2 cm^{-3}): Conventionally, this parameter is defined as ratio of the electrode's surface, A, to its volume, V_E:

$$A_E = \frac{A}{V_E}$$

It is often desirable to have the larger values of this parameter for the more compact construction of the electrolyzer. At the same time, smaller dimensions should not interfere with uniform distribution of the electrolyte flow, electrode potentials and current densities, as this is important for securing the high current efficiency of the process.

For the cylindrical electrodes, these characteristics are independent of the electrode lengths and depend only on their radii:

$$A_{EA} = \frac{2}{r_{AD}} \quad A_{EA} = \frac{2}{r_{AD}(1-a_A^2)} \quad A_{EC} = \frac{2a_C}{r_C(1-a_C^2)} \tag{8.3}$$

for the solid anode, tubular anode and cathode, respectively. It follows from the Eq. 8.3 that, for the solid anode, increasing of the radius r_{AD} will be inevitably accompanied by a decrease in the active electrode area per unit electrode volume, whereas, for the hollow tubular anode and cathode, it is possible to keep this parameter unchanged by adjusting the magnitudes of the inner and outer radii, as was shown above.

Equivalent hydraulic diameter: This parameter is used for calculation of dimensionless numbers of the electrochemical reactors, such as the Reynolds number, used to characterize different flow regimes, i.e., laminar or turbulent flow, and Sherwood number [50]. In general, the equivalent hydraulic diameter for the channels of the different shapes is defined as [9]:

$$d_h = \frac{4 \times Crossection\,Area}{Wetted\,Perimeter}$$

Since the anode and cathode chambers represent concentric annuli, their equivalent hydraulic diameters are given by:

$$d_{hA} = d_{DA} - d_{AD} \text{ and } d_{hC} = d_{CD} - d_{DC},$$

where d_{DA} and d_{DC} are the inner and outer diaphragm diameter, d_{AD} and d_{CD} are the outer and inner diameters of the anode and cathode, respectively.

Ohmic electrical resistance inside the cylindrical diaphragmic electrolyzer: The equation for the ohmic electrical resistance is useful for describing the distribution of electric potential and thermal balance in the reactor. The electrical resistance of the diaphragm filled with electrolyte and ohmic (i.e. without polarization of the electrodes) resistance of the anode and cathode chambers are determined by their geometry. For the medium with ohmic conductance situated between the two concentric cylindrical ideally conducting electrodes, the Gauss law in the differential form and cylindrical coordinates is given by [74]:

$$div\,\vec{E} = \frac{1}{r}\frac{\partial}{\partial r}(rE_r) + \frac{1}{r}\frac{\partial E_\theta}{\partial \theta} + \frac{\partial E_z}{\partial z} = 0 \tag{8.4}$$

where E is the electric field, r is the radial coordinate, θ is the azimuth, and z is the height. Since the electric field is perpendicular to the electrodes, Eq. 8.4 and its solution can be written as:

$$div\,\vec{E} = \frac{1}{r}\frac{\partial}{\partial r}(rE_r) = 0 \quad \text{and} \quad E_r = \frac{c}{r} \tag{8.5}$$

where c is the integration constant, which has different values for the anode chamber (c_A), diaphragm (c_D) and cathode chamber (c_C). The integration constants are determined using the equations connecting the electric potentials with electric fields inside the corresponding chambers:

$$\phi_A = \int_{r_{AD}}^{r_{DA}} E_r dr = c_A \int_{r_{AD}}^{r_{DA}} \frac{dr}{r} = c_A \ln\left(a_{AD}\right)^{-1}, \quad \phi_D = \int_{r_{DA}}^{r_{DC}} E_r dr = c_D \ln\left(a_D\right)^{-1},$$

$$\phi_C = \int_{r_{DC}}^{r_{CD}} E_r dr = c_C \ln\left(a_{CD}\right)^{-1} \tag{8.6}$$

where ϕ_A, ϕ_C, and ϕ_D are the voltages of the anode and cathode chambers and diaphragm, respectively, and $a_D = r_{DA}/r_{DC}$ is the diaphragm aspect ratio. From Eqs. 8.5 and 8.6, one can obtain:

$$E_{rA} = \frac{\phi_A}{r\ln\left(a_{AD}\right)^{-1}}, \quad E_{rD} = \frac{\phi_D}{r\ln\left(a_D\right)^{-1}}, \quad E_{rC} = \frac{\phi_C}{r\ln\left(a_{CD}\right)^{-1}}$$

From the Ohm's law in differential forms $J_r = \sigma E_r$, where J_r is the current density in the radial direction and σ is the specific electroconductance, one can find for the different chambers:

$$J_{rA} = \frac{\sigma_A\phi_A}{r\ln\left(a_{AD}\right)^{-1}}, \quad J_{rD} = \frac{\sigma_D\phi_D}{r\ln\left(a_D\right)^{-1}}, \quad J_{rC} = \frac{\sigma_C\phi_C}{r\ln\left(a_{CD}\right)^{-1}} \tag{8.7}$$

where σ_A, σ_C, and σ_D are the specific electroconductances of the anode and cathode chambers, and of the diaphragm, respectively. Noteworthy, the specific electroconductance of the diaphragm is defined by the properties of electrolyte filling the porous space and by geometry of this space [11]. Since the anode and cathode chambers and diaphragm could be presented as conductors connected in series, for which the electric current is constant for any given radius, one can write, taking into consideration Eq. 8.7:

$$I = J_r \times 2\pi r L = \frac{2\pi L\sigma_A \phi_A}{\ln\left(a_{AD}\right)^{-1}}, \quad I = \frac{2\pi L\sigma_D \phi_D}{\ln\left(a_D\right)^{-1}}, \quad I = \frac{2\pi L\sigma_C \phi_C}{\ln\left(a_{CD}\right)^{-1}} \tag{8.8}$$

where $2\pi rL$ represents the area of cylindrical surface. From the Eq. 8.8, the voltage between the electrodes ϕ_{tot} is written as:

$$\varphi_{tot} = \varphi_A + \varphi_D + \varphi_C = \frac{I}{2\pi L}[\rho_A \ln\left(a_{AD}\right)^{-1} + \rho_D \ln\left(a_D\right)^{-1} + \rho_C \ln\left(a_{CD}\right)^{-1}],$$

where $\rho = 1/\sigma$ is the specific electrical resistance. Finally, the expression for the total electrical resistance of the CCFE is written as:

$$R_{tot} = \frac{\phi_{tot}}{I} = \frac{1}{2\pi L}[\rho_A \ln\left(a_{AD}\right)^{-1} + \rho_D \ln\left(a_D\right)^{-1} + \rho_C \ln\left(a_{CD}\right)^{-1}]$$

8.5 Concluding Remarks

We have described an emerging technology of electrochemical treatment of aqueous solutions dubbed electrochemical activation. The technology has already been extensively employed in numerous scientific studies and practical applications. However, the further implementation of the technology could be expedited by the development of the scientific basis for the comparative structure-functional analysis of the existing electrochemical reactors. Here, we presented the constructional figures-of-merit for the prototypical concentric cylindrical electrolyzers. However, the formulation of these characteristics is applicable to CCFE of any dimensions and proportions. The influence of increasing of the structural parts' dimensions onto constructional figures-of-merit was established. It was shown that simple scaling, i.e., increasing the dimensions without changing proportions, is not possible under conditions of constant specific areas of electrodes. Obtained figures-of-merit are useful for analysis of electrolyzers having various designs.

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Chapter 9
Environmental and Human Health Issues of Silver Nanoparticles Applications

Renat R. Khaydarov, Rashid A. Khaydarov, Svetlana Evgrafova, Stefanie Wagner, and Seung Y. Cho

Abstract The significant growth in applications of silver nanoparticles across various branches of industry as well as in consumer products has caused concerns that nanosilver may have a toxic effect on the environment and human health and may have implications for eco-terorism. This paper presents research on antimicrobial effects of silver nanoparticles. We studied the cytotoxicity of silver nanoparticles via an MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-tetrazolium-bromid) assay that measures cell activity through the mitochondrial cleavage of a molecule that exhibits a change of colour that can be measured spectrophotometrically. NIH-3T3 (Swiss mouse embryo), HEP-G2 (human hepatocellular carcinoma), A-549 (human lung carcinoma), PC-12 (rat adrenal pheochromocytoma), and Colo-320 (human colon adenocarcinoma) cells were chosen in order to study different possible absorption paths of nanoparticles into the organism and various areas of particle accumulation in the body. The obtained MTT test results have shown that silver nanoparticles with concentrations of ~1–10 ppm entering the body from air or liquid suspensions can present a potential risk to human health.

Keywords Silver • Nanoparticle • Bacteria • Fungi • Nanosilver • Cytotoxicity • Consumer product • Nanomaterial • Environment • Human health

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R.R. Khaydarov (✉) and R.A. Khaydarov
Institute of Nuclear Physics, Tashkent, Uzbekistan
e-mail: renat2@gmail.com

S. Evgrafova
V.N. Sukachev Institute of Forest SB RAS, Krasnoyarsk, Russia

S. Wagner
Institute of Technical Chemistry, Gottfried-Wilhelm-Leibniz University, Hannover, Germany

S.Y. Cho
Department of Environmental Engineering, Yonsei University, Wonju, South Korea

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9.1 Introduction

Over the last decades silver nanoparticles, defined as structures up to 100 nanometers (nm) in size, have been investigated extensively and applied in various areas of science and technology [20] due to their unique size-dependent optical, electrical, and magnetic properties. Although according to a recent market research report (http://www.bourneresearch.com), nanosilver is "one of the fastest growing product categories in the nanotechnology industry", most present-day applications are related to antibacterial/antifungal uses [4]. For example, there is a growing interest in preparation of bactericidal cotton fibers containing silver nanoparticles for the textile industry [15]. There is also a promising trend to impregnate commercially available paints with silver nanoparticles [8]. Furthermore, silver nanoparticles are widely used as antimicrobial agents in a diverse range of consumer products: air sanitizer sprays, pillows, slippers, respirators, wet wipes, detergents, soaps, shampoos, toothpastes, air filters, coatings of refrigerators, vacuum cleaners, washing machines, food storage containers, cellular phones, and others [4].

The rapid growth in nanotechnology activity all over the world has generated concerns that nano-sized particles can potentially be used in acts of eco-terrorism aimed at destroying parts of environment. Ecologists have warned that silver nanoparticles being released in waste streams could lead to serious negative consequences for bacteria in natural systems, algae, some plants and fish. There is also growing evidence that as well as being toxic to bacteria, nanosilver is also very toxic to mammalian cells [3, 6, 9, 10, 22, 26]. A recent review cautioned: "these are questions that need to be imperatively answered before people rush to indulge into the nanosilver boom" [5].

The purpose of our study was (a) to estimate antimicrobial effect of silver nanoparticles by comparing it with that of silver ions and known antibiotics, and (b) to quantify cytotoxicity of silver nanoparticles using standard colorimetric MTT assays.

9.2 Materials and Methods

9.2.1 Preparation of Ag Ions and Nanoparticles

The silver ions used in the bacterial susceptibility tests were released from pure silver electrodes via 12 V battery-operated constant current generators. The apparatus used for silver ions generation was described previously [11]. The water-based silver colloidal solution was obtained by recently reported techniques based on (a) the use of the cellulose fibers [14], and (b) electrochemical processes [12]. The concentration of silver nanoparticles and ions in solutions was determined by neutron activation analysis (NAA) [25]. Samples were irradiated in the nuclear reactor of the Institute of Nuclear Physics (Tashkent, Uzbekistan). The product of nuclear reaction $^{109}Ag(n,\gamma)\ ^{110m}Ag$ has a half-life of $T_{1/2}=253$ days. The silver concentration was determined through measurements of the intensity of gamma radiation with an energy of 0.657 and 0.884 MeV emitted by ^{110m}Ag. A Ge(Li) detector with a resolution of about 1.9 keV at 1.33 MeV and a 6144-channel analyser were used for recording gamma-ray quanta. The size and shape of the nanoparticles in solution were determined by transmission electron microscopy (TEM) (LEO-912-OMEGA, Carl Zeiss, Germany).

9.2.2 Antimicrobial Activity Assay

The agar disk diffusion method was used to assay the antimicrobial activity of silver nanoparticles in aqueous solution against *E. coli* on solid media. Bacteria inocula were prepared from a log-phase culture of *E. coli* K12 grown in LB-media on a rotary shaker (120 rpm) at 37°C. The inocula were diluted with 0.9% NaCl to the 0.5 McFarland standard and 100 μL were applied onto 9 cm Mueller-Hinton agar plates with a depth of approximately 5 mm. Disks of absorbent paper (5 mm in diameter) were impregnated with 10 μL of silver nanoparticle solutions (47.5, 42.5, 22.6 and 11.3 ppm). For comparison, disks of the same diameter with 10 μL Tetracycline, Penicillin G and Ampicillin (1 g/L each) were used, leading to a concentration of the respective substance of 10 μg/disk. The freshly-prepared disks were placed on the surface of the inoculated agar plates. After incubation at 37°C for 18 h, the zones of bacterial inhibition were measured optically.

To evaluate the antibacterial and fungicidal properties of silver particles *Escherichia coli* was used as a representative Gram-negative bacterium; *Staphylococcus aureus* and *Bacillus subtilis* were used as Gram-positive bacteria; *Aspergillus niger*, *Aureobasidium pullulans*, and *Penicillium phoeniceum* were used to represent cosmopolitan saprotrophic fungi. The minimum inhibitory concentrations (MICs) of solutions for various microbes were determined using the macrodilution broth susceptibility test. Nutrient broth used in the macrodilution method contained a peptic digest of animal tissue 50.00 g/L; beef extract 1.5 g/L; sodium chloride 5.00 g/L; glucose 5 g/L; pH 7.4 ± 0.2. A standardized suspension of approximately 10^6 CFU/mL density was obtained by inoculating the culture in nutrient broth (Hi-Media) and incubating the tubes at 37°C for 3 h. A serial dilution of the dispersion of Ag ions and the dispersion of silver nanoparticles were prepared within a desired range. Then 10 mL of the standardized culture suspension was inoculated and tubes were incubated at 37°C for 24 h. MIC was defined as the lowest concentration of the inhibiting agent that completely inhibited bacterial growth, the unit for MIC was chosen as mg(Ag)/L. MIC was examined visually, by checking the turbidity of the tubes.

9.2.3 Materials for Cytotoxicity Assay

All solutions were prepared with deionised water (Arium, SARTORIUS, Göttingen, Germany). Dulbecco's Modified Eagles Medium (DMEM) was purchased from Sigma-Aldrich (Steinheim, Germany) and foetal calf serum (FCS) and newborn calf serum (NCS) from PAA (Cölbe, Germany). Horse serum (HOS) was purchased from Invitrogen (Karlsruhe, Germany). Buffers, salts, antibiotics, and other reagents were purchased from Fluka (Buchs, Switzerland) and Sigma-Aldrich (Steinheim, Germany) and are of *per analysi* quality. The NIH-3 T3 cells (Swiss mouse embryo) were cultivated in DMEM containing 10% NCS and antibiotics (penicillin and streptomycin) at 37°C/5% CO_2. The HEP-G2 (human hepatocellular carcinoma) cells were cultivated in DMEM containing 10% FCS and antibiotics (penicillin and streptomycin) at 37°C/5% CO_2. The A-549 (human lung carcinoma) cells were cultivated in DMEM containing 10% FCS and antibiotics (penicillin and streptomycin) at 37°C/5% CO_2. The PC-12 cells (rat adrenal pheochromocytoma) were cultivated in a PLL coated T-75-flask in DMEM containing 10% HOS, 5% NCS, 1% sodiumpyruvate, 1% L-glutamine and antibiotics (penicillin and streptomycin) at 37°C/5% CO_2. The Colo-320 cells (human colon adenocarcinoma) were cultivated in Roswell Park Memorial Institute 1640 medium (RPMI 1640) containing 10% FCS and antibiotics (penicillin and streptomycin) at 37°C/5% CO_2. All cell lines had grown to confluence after 3–4 days and were then detached with trypsin and cultured in a new flask.

9.2.4 Cultivation and Cell Viability

To test the effect of silver nanoparticles, 96-well plates were seeded with a defined number of cells (see Table 9.1). The plates were incubated for 4 days (37°C/5% CO_2). On day 5 the suspensions of particles in the culture medium in different concentrations or just water in the highest concentration in the medium were added to the cells. On day 7 the viability of the cells was determined via a MTT-test.

The viability of the cells was analysed by the MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-tetrazolium-bromid) test (Sigma-Aldrich, Steinheim, Germany). This assay is based on the hydrolysis of a tetrazoium ring by mitochondrial dehydrogenase enzymes to an insoluble blue reaction product. To perform the MTT test the medium of each well was removed and 100 μL of fresh medium and 10 μL of MTT solution (5 mg/mL PBS, sterile) were added to each well, followed by incubation for 4 h at 37°C/ 5% CO_2. Subsequently, 100 μL of 10% SDS in 0.01 M HCl was added and the plates were further incubated for 24 h. The absorbance of solutions at the wavelengths of 570–630 nm was determined using a microplate reader (Bio-Rad, München, Germany).

Table 9.1 Number of cells per well for NIH-3T3, HEP-G2, A-549, PC-12 and Colo-320

	NIH-3T3	HEP-G2	A-549	PC-12	Colo-320
Number of cells per well	6,000	10,000	8,000	10,000	10,000

9.3 Results and Discussion

9.3.1 Silver Nanoparticles vis-a-vis Some Antibiotics

We have compared the antibacterial effect of silver colloids (with concentrations of 47.5, 42.5, 22.6 and 11.3 ppm) and that of known antibiotics. The concentrations of silver were selected in such a way as to correspond to maximum Ag concentrations used in consumer nanoproducts that are currently available on the market [8]. Comparing zones of growth inhibition around the disks impregnated with various antibiotics and Ag nanoparticles (cf. Fig. 9.1), silver nanoparticle solution demonstrated a certain antimicrobial effect. The intensity of the effect is increased with the concentration of the solution.

Figure 9.2 demonstrates zones of growth inhibition around the disks impregnated with various antibiotics and the disk with the largest Ag nanoparticles concentrations that we have used. Considering that the Ag concentration used in the experiment was approximately 20 times lower than that of the antibiotics, it was expect that silver nanoparticles would outperform Ampicillin, Penicillin and Tetracycline antibiotics of the same concentration [13].

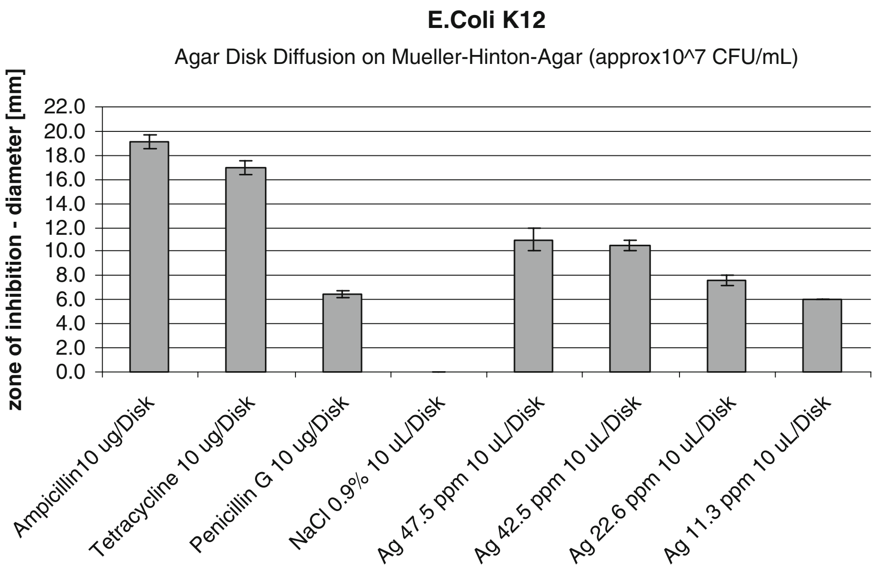

Fig. 9.1 Antibacterial activity of silver nanoparticles in aqueous solution against *E. coli* K12 determined by the agar disk diffusion method

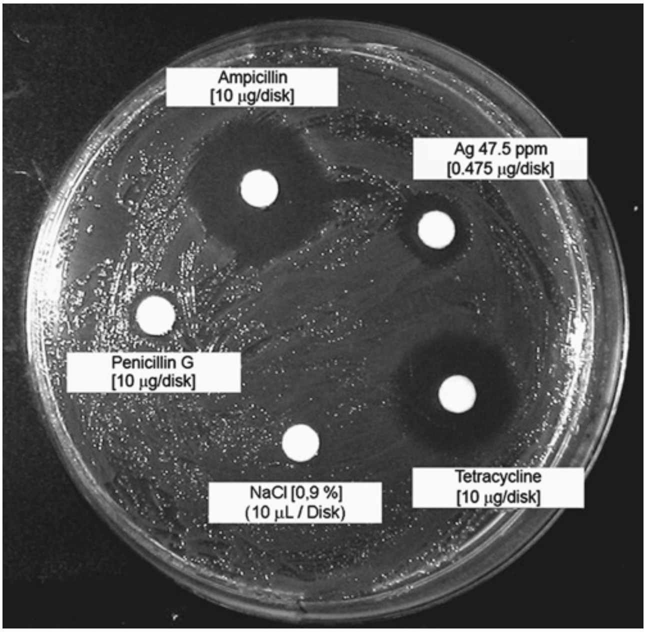

Fig. 9.2 Zones of growth inhibition around disks impregnated with silver nanoparticles and various antibiotics

Table 9.2 Results of minimum inhibitory concentration (MIC) assay for silver nanoparticles and silver ions for some microbial species

Microbe	Electrically generated silver ions MIC (mg(Ag)/L)	Silver nanoparticles (average particle size of 4 nm) MIC (mg(Ag)/L)
E. coli	1	3
S. aureus	0.6	2
P. phoeniceum	0.5	1.5
B. subtilis	2.4	22

9.3.2 MIC Assays

The minimum inhibitory concentration (MIC) assays were conducted for electrically generated silver ions and silver nanoparticles using Gram-negative bacterium *E. coli*, Gram-positive bacteria *S. aureus* and *B. subtilis* and fungus *P. phoeniceum* [14]. As seen from Table 9.2, in order to inhibit the growth of representatives of gram-positive and gram-negative bacteria and fungi it was necessary to apply higher concentrations of nanosilver as compared to the concentration of electrically generated silver ions.

9.3.3 Risks of Nanosilver Applications

Silver-based materials have been widely used over the last decades in medical organizations, photographic laboratories, etc. Recently, the annual silver released into the environment from industrial wastes and emissions was estimated at approximately 2,500 ton, of which 150 ton ended up in the sludge of wastewater treatment plants with 80 ton being released into surface waters [23, 24]. The maximum concentrations of silver released into the environment are regulated at various levels in different countries by their appropriate environmental protection agencies. It was well documented in studies conducted in the twentieth century that the toxicity of silver in the environment occurred mainly in the aqueous phase and depended on the concentration of active, free Ag^+ ions. [23]. As for the impact on human health, the scientific literature of the last century cited mainly cases of permanent bluish-gray discoloration of the skin (argyria) or eyes (argyrosis) occurring when the accepted threshold values for silver and its compounds were exceeded [1].

Although the toxicity of silver particles in the μm size range has been established reliably [7], there is still a lack of information on the toxicity of nano-size silver particles. The mechanism of the bactericidal effect of silver nanoparticles is not well understood as yet. Lok et al. [18] have recently reported that "Nanosilver represents a special physicochemical system which confers their antimicrobial activities via Ag^+". If this conclusion is verified then most bioaccumulation and toxicity issues relating to silver nanoparticles can be considered from the point of view of the toxic potential of ionic silver, which is well-documented. As the ionic silver is readily transformed to nonreactive compounds [23] under natural environmental conditions, this would mean that the environmental risks of nanosilver toxicity is not as severe as popular perception may suggest. In contrast, according to Morones et al. [19] the bactericidal effect of silver nanoparticles on microorganisms is connected not merely with the release of silver ions in solution. Following their report, silver nanoparticles can also be attached to the surface of the cell membrane and disturb its proper function drastically. They are also able to penetrate inside the bacteria and cause further damage by possibly interacting with sulfur- and phosphorus-containing compounds such as DNA. It is interesting to note that silver nanoparticles have also demonstrated synergistic effects with known antibiotics, such as amoxicillin [17].

There is a public perception that silver nanoparticles do not discriminate between different strains of bacteria and are likely to destroy microbes beneficial to other organisms and ecological processes [2]. The wide usage of silver nanoparticles in technical areas and consumer products will definitely cause environmental releases of silver over the lifetime of the product. The unrestrained release of silver nanoparticles into wastewater will potentially have a negative impact on ecosystems by damaging beneficial microbes in the environment and adversely affecting complex food webs.

We also do not know much currently on biological interactions of nanosilver with cells including cellular proteins. Nanomaterials can enter human tissues through several ports: via the lungs after inhalation, through the digestive system, and possibly through the skin [21]. The major toxicological concern derives from the fact that nanoparticles can penetrate the cell membranes and interact with the mitochondria [3].

We have studied the cytotoxicity of silver nanoparticles by the MTT test that measures cell activity through the mitochondrial cleavage of a molecule that exhibits a change of color that can be measured spectrophotometrically. NIH-3T3, HEP-G2, A-549, PC-12, and Colo-320 cells have been chosen in order to study different possible absorption paths of silver nanoparticles into the organism and various areas of particle accumulation in the body. Figure 9.3 shows the effect of silver nanoparticles on the aforementioned cells. The results of the MTT tests presented in the bar diagrams in Fig. 9.3 reveal a significant decrease of the viability of the Colo-320 cells and the NIH-3T3 cells when exposed to 5 ppm nanosilver.

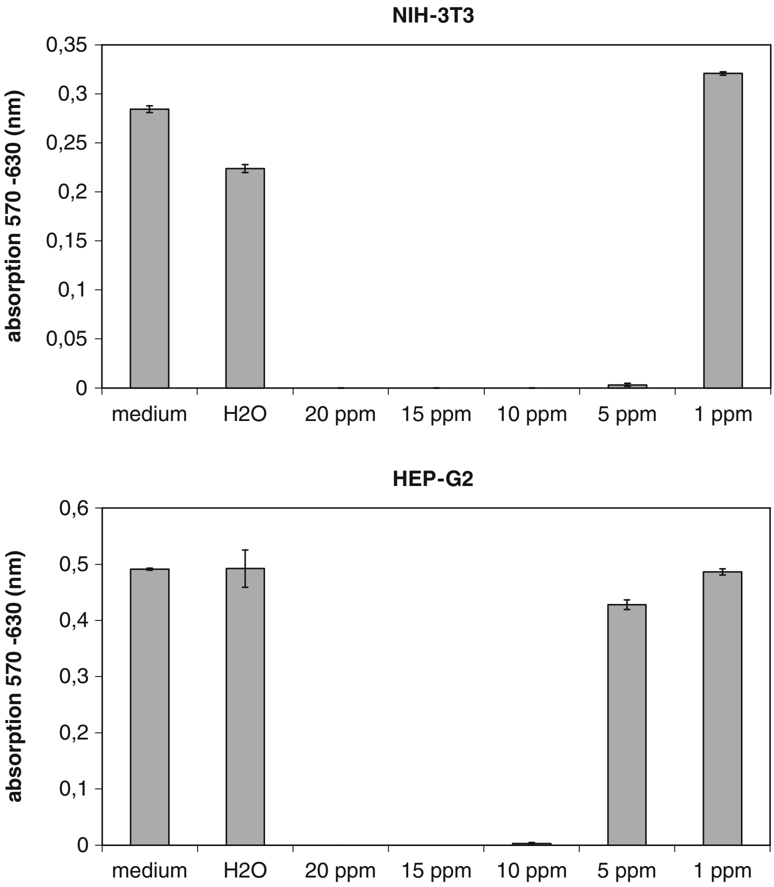

Fig. 9.3 Results of MTT test for NIH-3T3, HEP-G2, A-549, PC-12, and Colo-320 cells

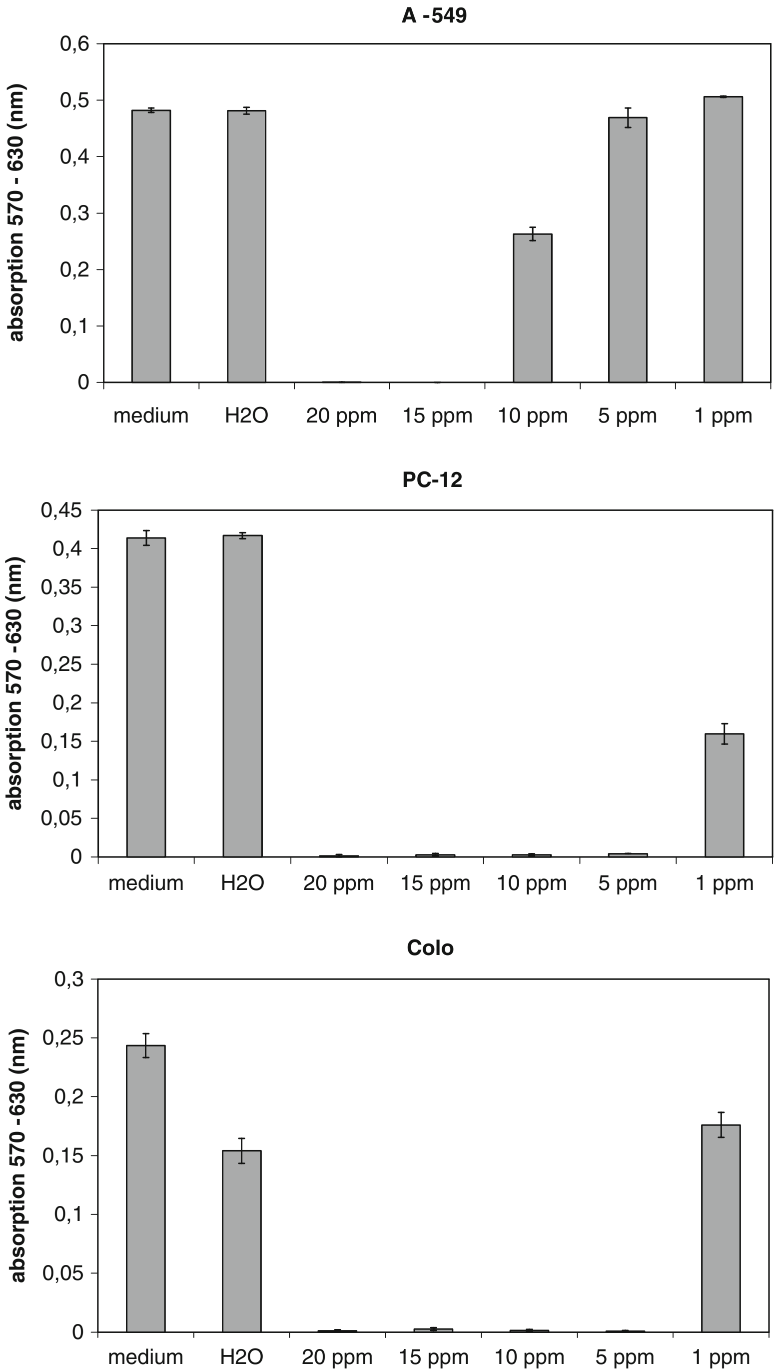

Fig. 9.3 (continued)

A-549 and HEP-G2 showed more resistance, with a significant decrease of the viability being observed for higher concentrations ~10 ppm. As for PC-12 cells, even 1 ppm nanosilver caused a certain decrease in their viability.

The present MTT test results suggest that silver nanoparticles with concentrations of ~1–10 ppm entering the body from air or liquid suspensions can present a potential risk to human health.

There is still an urgent need for further studies on the bactericidal mechanism of silver nanoparticles, which will be a step forward to a better understanding of their environmental and human health impacts. As nanosilver-based materials have a great commercialization potential, we anticipate a large number of reports from various scientific groups in the field of nanosilver toxicity in the near future. To quote a recent review: "A full understanding of the hazards of nanoparticles will make a major contribution to the risk assessment that is so urgently needed to ensure that products that utilize nanoparticles are made safely, are exploited to their full potential and then disposed of safely" [16].

9.4 Conclusions

Silver nanoparticles have been proven to be very promising as antimicrobial agents. Low MIC values for *Escherichia coli* (5 mg/L), *Staphylococcus aureus* (2 mg/L), *P. phoeniceum* (3 mg/L) and *Bacillus subtilis* (22 mg/L) cultures for 4-nm silver nanoparticle aqueous dispersions have been obtained. However, the MTT test results conducted with NIH-3T3 (Swiss mouse embryo), HEP-G2 (human hepatocellular carcinoma), A-549 (human lung carcinoma), PC-12 (rat adrenal pheochromocytoma), and Colo-320 (human colon adenocarcinoma) cells showed that silver nanoparticles with concentrations of ~1–10 ppm entering the body from air or liquid suspensions can present a potential health hazard. A brief review of the scientific literature on recent studies into the impact of silver nanoparticles on environment and human health has been also provided.

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Chapter 10
Environmental Security of Solid Wastes in the Western Donbas Coal Mining Region, Ukraine

Mykola M. Kharytonov and Anna A. Kroik

Abstract The chemical reactions of hydrolysis, oxidation, ion exchange, and carbonization, which accompany the weathering of rock from coal mines, are presented. The environmental safety of the wastes that are exposed during storage on the surface is defined by the processes of leaching and pollutant transfer. Data were obtained related to the contents and changes of the water-soluble form of heavy metals in the rock heaps after weathering on the surface. It was established that, unlike rock freshly taken to the surface that is rated as class IV hazardous material, weathered rock is rated as class II and III hazardous material. The rock heaps in the Western Donbas coal mining region become environmentally hazardous during weathering. Land reclamation technology can be applied to these mining sites as a preventive measure to decrease weathering and leaching processes.

Keywords Coal-mine heaps • Hazard • Weathering • Leaching • Heavy metals • Land reclamation

10.1 Introduction

Ukraine's rich endowment of mineral reserves and its intellectual advancements in the earth sciences have combined to make substantive contributions to the nation's economic development. Presently 111 species of mineral products are known to be distributed across 20,000 known sites. Of these, 96 species are suitable for

M.M. Kharytonov (✉)
Dnipropetrovsk State Agrarian University, Voroshilova St., 25,
Dnipropetrovsk 49027, Ukraine
e-mail: mykola_kh@yahoo.com

A.A. Kroik
Dnipropetrovsk National University, Gagarina Av., 44, Dnipropetrovsk 49600, Ukraine

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industrial use and are counted in the state's reserve balance. These resources are mined at 7,667 sites and include: coal—766 sites, metal minerals—358 sites, non-metallic minerals—3,907 sites, and groundwater—1,067 sites [5]. However, extreme technogenic loadings and long-term, large-scale mining operations have resulted in significant environmental challenges. The accumulated wastes from all kinds of industry in the form of terraces, terricones, different kinds of dumps, and slurry depositories are spread over 160,000 ha. The most visible examples of negative impacts are associated with coal and iron ore mining. Up to 14 billion tons of these materials and approximately an equal amount of overburden have been removed from the ground over the last century. In recent years, the annual mass of waste produced ranges between 150 and 200 million tons. Rapid restructuring of the mineral industries complex under conditions of economic crisis has contributed to the poor utilization of rock that is regarded as mining waste. Only about 12% of the waste from these sites is put to productive use in other areas of the economy, such as for construction materials (roads, dams, embankments, etc.). In comparison, up to 65% is utilized in others parts of the world.

Beyond the unused (or underused) volume of waste generated through mining operations, there are concerns about the toxicity of the rock. Spoil dumps and mine waters may be long-term sources of environmental pollution and several publications are devoted to the various aspects of mine-complex impact assessment [2, 7]. In most cases, previous studies have focused on estimating stocks of valuable components found in the mining dumps [8]. The environment impact of the heaps during storage on the surface remains little-studied. In particular, the potential change in the waste's hazard class as a result of weathering has not been estimated. Furthermore, the mobile forms of toxic elements of different hazard classes in the rocks have not been defined [1]. Finally, there are no data concerning the transfer of toxic elements through water.

Remediating toxic sites mined in the past and providing environmental safety for the future requires not only new technologies for resource extraction but also new landscape restoration technologies. Such technologies should provide the maximum possible protection of surface and groundwater at the locations of rock storage. Land cover preservation is a related concern. In particular, these technologies should protect the landscape from saliferous components and heavy metals pollution. Considerable attention must be paid to heavy metals because they do not biodegrade and can migrate to humans through trophic chains.

Over the last 40 years, the Dnipropetrovsk State Agrarian University has been responsible for investigating the efficiency of land reclamation technologies in the southeast of Ukraine. Studies were carried out within the network of mining regions. The objective of this research is to decrease heavy metals technogenic flow resulting from weathering processes in the Western Donbas coal mining region.

In a broad sense, the coal mining enterprise activity can be considered as a latent case of ecological terrorism where potentially toxic wastes accumulate without land reclamation technologies. This viewpoint is strengthened becomes when industry ignores principles of environmental safety with minimal financial input for restoration measures.

The fast restructuring of raw mineral mining under the economic crisis conditions has inhibited the complete utilization of mine rocks. New strategies should tackle the problems of handling waste heaps such as utilization within agricultural and (or) forest land reclamation (for the creation of the recreation zones with the use of tree plantations), industrial and civil construction (the tops and platforms of high waste heaps), summer-cottage community building, etc.

10.2 Geo-Environmental Approach

This case study was carried out in the Western Donbas in the Dnipropetrovsk province of southeastern Ukraine. Coal mining in this area occurs at 11 sites. The wastes are stored in spoil dumps (19 million tons), used for the land reclamation (2,464 ha), and for the construction of dams protecting the new bed of the Samara River (36.6 ha) and artificial reservoirs (700 ha). We studied the lithologic, mineralogical, and chemical composition of the mining heaps and the coal washing products.

Environmental problems of the region are in places where mine processing produces tailings. The arrangement of used mine fields under the Samara River bottomland leads to surface sinking.

The qualitative and quantitative assessment of trace elements within the waste rock during weathering was assessed by laboratory experiments. Samples were taken of rock recently deposited on the surface at mine dumps and reclaimed sites. The samples were selected on the basis of their depth and the duration over which they were stored on the surface. The water-soluble mobile forms of trace elements were studied in the weathering processes. The method of aquatic fractions was used to estimate the contents of trace elements in several variants. The process of estimation consisted of a sample treatment by distilled water with the ratio of solid and liquid phase 1:5. The geochemical assessment was carried out in the land reclamation station situated near the Pavlogradskaya coal mine. The land reclamation scheme consisted of several trials with and without a shielding screen of loess-like loam:

1. Mine rock MR + 30 cm of chernozem [4] or black soil (30BS);
2. MR + 50 BS;
3. MR + 70 BS;
4. MR + 50 cm of loess – like loam (50LLL) + 30BS;
5. MR + 50 LLL + 50 BS;
6. MR + 50 LLL + 70 BS.

The concentration of mobile forms of heavy metals at the samples of rock and soil was determined with atomic absorption spectrophotometry.

10.3 Leaching Process Intensity Assessment in the Weathered Rocks

The lithological and mineral composition of the mine rocks of Western Donbas consists of sandstones, aleurolites, clay rocks, carbonates, and sulfides. It is necessary to note the presence of iron in aleurolites and sulfides as they cause a higher concentration of FeO (5.7–7.8%) and SO_3 (0.5–1.3%). The data on heavy metals content in the mine rocks samples, which were taken from conveyor strips, are presented in Table 10.1.

It was established that highest metal content corresponds with rock that has an acidic reaction. It was possible to mark some leading types of chemical reactions accompanying the weathering of mine rocks during their storage in the form of heaps and terricones. These reactions are present with hydrolysis, oxidation, ion exchange, and carbonatization. The environmental safety of the wastes, which are exposed during the storage on the surface, is exactly defined by the processes of leaching and pollutant transfer. The pollution from heaps, tailing dumps, and waste depositories enters the surface and groundwater mainly from atmospheric precipitation. The concentration rate of the atmospheric precipitation by pollutants is defined by filtering properties of the waste material composing heaps, as well as by the material stability to weathering. Environmental pollution caused by solid waste weathering is closely associated with dissolution and leaching processes. Dissolution is the geological process of the transition from solid to liquid phase accompanied by the destruction of the crystalline texture of the solid phase. Leaching represents a selective extraction of any component from a solid, preserving the crystalline texture.

The dissolution of a substance occurs in several stages. The first stage is the diffusion transfer of components to the interaction surface, the transition of ingredients from the solid phase to the dissolved condition occurring at the participation

Table 10.1 Heavy metals content in the mining rocks of Western Donbas

	Metal content, mg/kg						
Coal mine name	Pb	Cd	Zn	Mn	Cu	Cr	Ni
Zapadno-donbasskaya	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1	62.0 / < 0.1	717.0 / 10.2	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1
Stepnaya	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1	140.0 / 24.0	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1	16.3 / < 0.1
Samarskaya	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1	16.0 / < 0.1	125.0 / 3.2	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1
Stashkova	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1	28.0 / 1.2	38.0 / < 0.1	56.4 / 9.0	≤ 0.1 / < 0.1	54.0 / 3.0
Blagodatnaya	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1	42.4 / 0.8	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1	≤ 0.1 / < 0.1

Nominator: total content; denominator: mobile form content

Table 10.2 Heavy metals water soluble forms content in the weathered rocks

	Heavy metals								
pH	Fe	Mn	Zn	Ni	Co	Cr	Cu	Pb	Cd
2.85–3.95	17.56	15.75	4.25	18.5	5.50	0.84	2.33	0.47	6.0
4.2–5.2	7.75	6.35	2.40	1.22	1.90	0.50	0.34	0.30	3.5
6.5–7.7	2.26	0.33	0.39	0.04	0.05	0.001	0.05	0.01	0.01

of physical and chemical reactions, and the retraction of components to the solution mass. In the second stage, the processes of hydrolysis and complex formation, as well as other chemical reactions, are of most importance. It was established that the enclosing rock of the coal deposit in Western Donbas contains trace elements of the first hazard class; lead, cadmium, zinc, copper, chrome, nickel. The rocks also contain manganese and iron, which belong to the second hazard class. The greatest concentrations of metals correspond to rocks with acidic reaction of the aquatic fraction (Table 10.2).

This finding is in accordance with the mechanism of weathering described by Kroik [5], who posits two types of processes. The first type includes the congruous solution of chloride and sulphate salts of alkaline, alkaline-earth elements and heavy metals, the hydrolysis of aluminum silicates and carbonates, and the replacement in the exchange of the absorbing complex of rocks. The second type of weathering concerns pyrite oxidation, sulfuric solution of silicates, and carbonates. The contents of heavy metals mobile forms for two types of weathering of rock differ considerably. There is a significant amount of Fe, Mn, Zn, Ni, Co, Cr, and Pb in rocks with the acidic reaction of water fraction. This finding is also in accordance with Kroik's description of weathering. Weathering of the second type from rocks (aqueous extract with pH <5) produces a multiplying effect of the release of heavy metals into the environment: nickel 21.9 times, copper 15.5 times, cobalt 12.2 times, chrome 9.3 times, iron 7.5 times, manganese 12 times, zinc 6.9 times, lead 6.7 times, and cadmium 3.5 times.

The results of the laboratory experiments permit estimates to be made of the leaching of single elements. The variations are associated with the occurrence forms in rock and the types of rock weathering. Manganese, cobalt, nickel, and chrome give high values of the correlation coefficient (0.64–0.80) with the salinity value and the amount of sulphate-ion (first type of weathering). Components such as manganese, cobalt, zinc, and iron (second type of weathering) are associated with the sulphate-ion. This indicates that the mobile form of metals in this rock heaps is found in the form of sulphate salts. The estimation of a potential stock of trace elements, which can be transferred to the environment from the rock during the weathering, was carried out using the results from laboratory experimentation using a method of consequent leaching from one sample.

According to the results, a potential stock of heavy metals, which can leach out from rocks, differs greatly depending on the weathering type and ranges from 20 to 63 mg/kg for iron, from 18 to 52 mg/kg for manganese, from 0.3 to 1.5 mg/kg for zinc and nickel, from 0.1 to 0.2 mg/kg for cobalt and copper, from

0.03 to 0.06 mg/kg for lead, from 0.02 to 0.1 mg/kg for chrome, and from 0.05 to 0.1 mg/kg for cadmium. The migration process of metal ions in aquatic fraction occurs most intensively in the area of average and maximal concentrations. This distinction is maximal for manganese 40%, for copper 50%, for cobalt 35%, and for iron, zinc, nickel, chrome and lead 15–20%. Thus a single aqueous extract in its standard variant allows the determination of about 60–70% of the general contents of water-soluble metals association in rock. The coefficients of rock leaching are calculated for comparative assessment according to the formula:

$$C_{\text{leaching}}\left(C_n - C_k\right)/C_k \tag{10.1}$$

where C_n and C_k is the concentration of trace elements in the first and in the last fractions. The leaching coefficients may be placed in the following decreasing order: manganese (6.2) > copper (4.6) > zinc (3.7) > nickel (2.4) > iron (1.3) > lead (1.0) > chrome (0.6) > cadmium (0.5) > cobalt (0.2). Thus the leaching coefficient, which has been defined experimentally, provides a generalized characteristic of differences in leaching rates of readily soluble trace elements from rock on the basis of salts solubility. The latter is associated with the chemical properties (ionic radius, charge, ionic mass, ionization potential), as well as with the amount of solvent interacting with the rock.

The amount of trace elements leachable from the rock should be defined, first of all, by the type of weathering process. The intensity of leaching will be defined by the chemical properties of the components, and can be characterized with the leaching coefficients derived from the laboratory experiments. The larger the element's atomic weight, the stronger the bond with the rock and the lower the ability to leach out. The leaching and mass transfer processes intensity is more considerable for components with low ion weight. This dependence is consistent in mine rock for such elements as manganese, iron, copper, and zinc [6].

Thus for the first stage data were obtained regarding contents and changes of the water-soluble forms of heavy metals in the rock heaps after weathering on the surface. Then it was established that while rocks newly taken to the surface were classified as a IV class of hazard, those rocks that were weathered were classified as class of hazard II and III. The most toxic elements were lead and cadmium. Taking into account the maximum allowable concentration (MAC) of these elements, and the fact that their leaching process proceeds quickly and completely, it is possible to conclude that the rock heaps in Western Donbas become environmentally more hazardous during weathering. The black soil and loess-like loam sorption capacity with respect to zinc, copper, lead, and cadmium has been estimated in laboratory tests to study the impacts of using black soil and loess-like loam as a geochemical screen (Table 10.3).

Table 10.3 Soil and rock sorption capacity estimation to heavy metals, mg/g

Substratum	Pb	Cu	Zn	Cd
Black soil	135	45	70	65
Loess-like loam	310	115	107	75

The capacity of loess-like loam to absorb the studied heavy metals also varied. These data suggest the necessity to create favorable hydrogeological and soil-reclamation conditions towards environmentally-safe agricultural products.

10.4 Land Reclamation as a Preventive Measure to Decrease Coal-Mine Heaps Weathering

Based on field data, it is possible to say that the weathering of rock heaps of Western Donbas results in significant damage (see Fig. 10.1). Manganese differs with greatest chemical activity while Zinc and Nickel take second place. The mine heaps were covered with soil and rock mass for the purpose of decreasing weathering processes. The comparison of the contents of heavy metals in the soil and mine heaps at the contacting area in the variant MR+70BS affirmed the presence of a chemical weathering process of the mine rocks [3].

Applying a 120 cm stratum of black soil and loam produces appropriate changes in the distribution of heavy metals. One extract of the results of the heavy metals profile distribution study according to the land reclamation scheme in Western Donbas is given for the variant MR+50 LLL+70BS in Fig. 10.2.

The addition of 50 cm of a loess-like loam layer causes considerable suppression of heavy metals migration. Figure 10.3 is an illustration of the positive impact of a geochemical barrier based on the data of alfalfa hay harvested in third land reclamation variants.

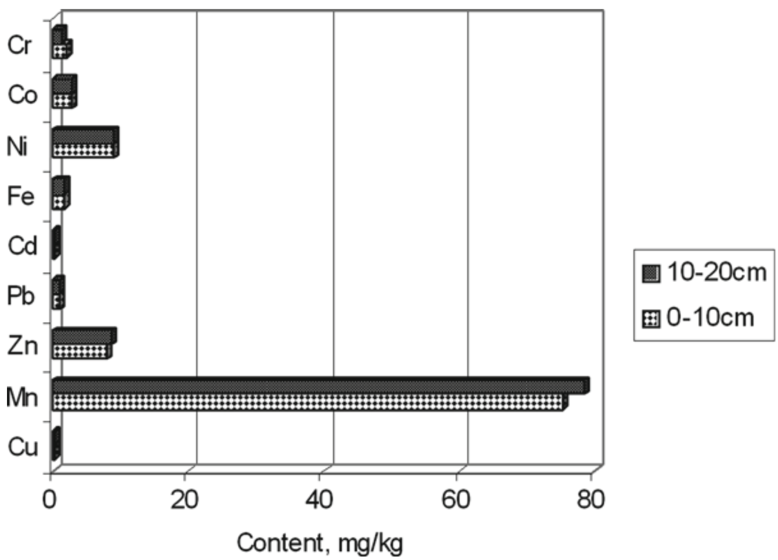

Fig. 10.1 The distribution of heavy metals in a non-reclaimed mine heap

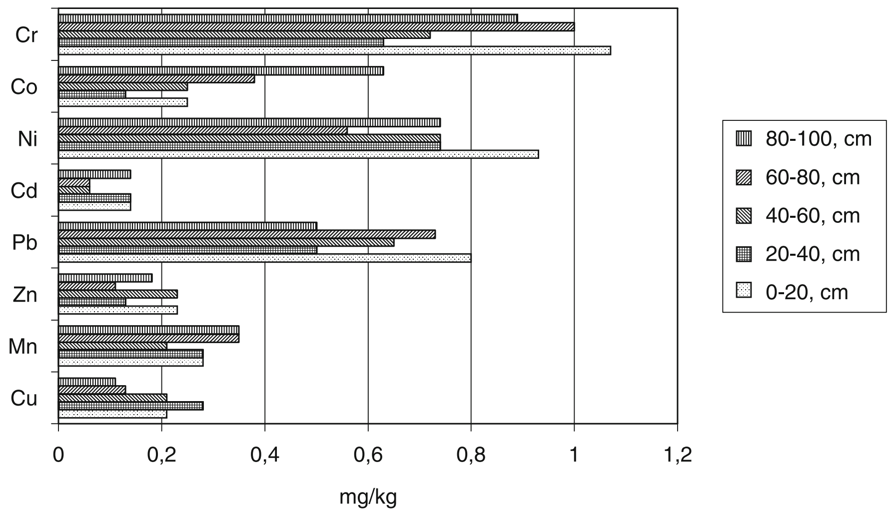

Fig. 10.2 The distribution of heavy metals by depth at reclaimed variant MR +50LLL+70BS, mg/kg

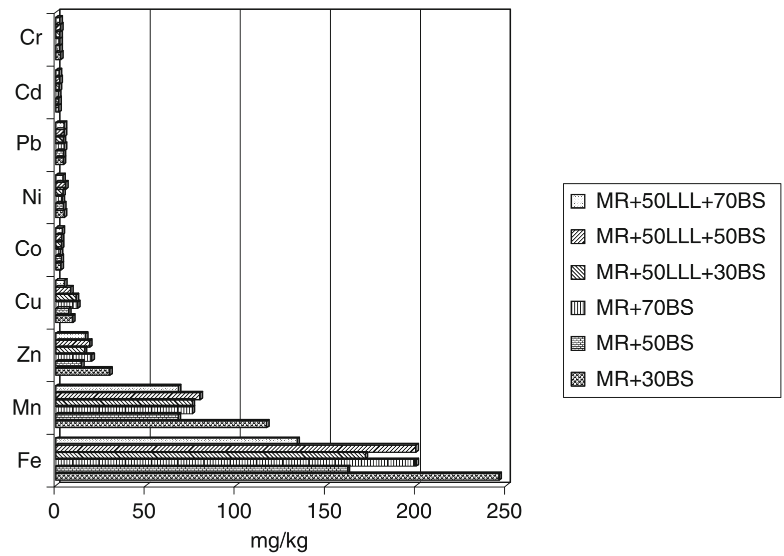

Fig. 10.3 The heavy metals content in alfalfa hay harvested in different land reclamation variants

The greatest amount of manganese, zinc, and copper has been defined at variant MR+30BS. Better geochemical indexes were fixed for two variants: MR+50LLL+50BS and MR+50LLL+70BS.

Thus, the offered land reclamation technology can be used as preventive measure to decrease the coal-mine heaps weathering and leaching.

10.5 Conclusions

We present our concluding comments in point form:

1. The amount of trace elements leachable from rock should be defined, first of all, by the type of rock weathering. The intensity of leaching defines the chemical properties of the components and can be characterized with leaching coefficients obtained in laboratory experiments on leaching processes.
2. The comparison of the contents of heavy metals in coal-mine heaps in the study area affirms the presence of the chemical weathering process of pit rocks. It was established that unlike rocks newly taken to the surface belonging to class IV hazard, weathered rocks belonged to class II and III hazard.
3. The land reclamation variants in which mine rock was overlaid with soil stratum and loess-like loam, led to a significant reduction of heavy metals migration. This result is associated with the impact of the oxidizing-reducing conditions on geochemical activity of each element as well as upon valence forms and buffer capacity of substrata.
4. The distribution of heavy metals is influenced by the activity of some geochemical barriers: mechanical, sorption, oxidizing, alkaline and others.

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Chapter 11
Urban Air Quality Management and Emergency Response

Volodymyr I. Nochvai, Angelina V. Shavrina, and Oleksandr A. Veles

Abstract Recent scientific evidence indicates that current levels of air pollution in European cities are causing significant damage to human health. Urban quality management is aimed at reaching safe levels of atmospheric pollutants. The main tasks of decision-making for air quality management and emergency response are considered. An example is provided using ozone monitoring data for environmental risk assessment and development of air quality control in Kyiv.

Keywords Decision-making • Air quality management • Surface ozone • Environmental risk assessment • Emergency response • Terror action

11.1 Introduction

Recent scientific evidence indicates that air pollution in European cities is causing significant adverse effects on human health, such as increasing mortality and morbidity, shortening life expectancy, and disturbing the normal development of children [11]. Urban air quality management is intended to keep concentrations of atmospheric pollutants at a level considered safe all year round. The purpose of emergency response systems is to reduce and rapidly respond to hazardous exposure arising as a result of man-made or natural causes. Such systems are very similar in goals and often share a common information database for decision making.

V.I. Nochvai (✉)
Pukhov Institute for Modeling in Energy Engineering, National Academy of Sciences of Ukraine, Kyiv, Ukraine
e-mail: volivn@ukr.net

A.V. Shavrina and O.A. Veles
Main Astronomical Observatory, National Academy of Sciences of Ukraine, Kyiv, Ukraine

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11.2 Air Quality Management

Proper air quality management requires an integrated approach consisting of [16]:

- Air pollution monitoring and modeling to establish an inventory and sources of key pollutants
- Use of dispersion modeling to determine the impacts of the emissions on ambient concentrations
- Use of dose–response functions and evaluation techniques to estimate the impacts of pollutants on human health
- Identification of technically feasible measures for the abatement of pollution impact and calculation of their costs
- Assessment of the consequences of these abatement measures on ambient air quality and human health
- Identification of priority measures with high benefit-cost ratios.

Air quality in urban areas is dependent on emissions from industrial enterprises, power plants, vehicles and heating. The impact can be felt not only within an urban area but down-wind, as a result of long-range transport of contaminants. To understand the relationship between health and air quality, monitoring and analysis of morbidity in the region are of paramount importance. It is also essential to discern the main pollutants and their sources and sinks.

11.3 Air Quality Management and Emergency Response Systems

From the standpoint of responding to possible emergencies, it is important to identify sources of potential hazards and to develop a mitigation action plan. Air quality management systems represent a part of the strategy of environmental management and provide a practical and scientific basis for building effective emergency response systems. In addition to achieving long-term safe pollution levels, air quality management should aim at preventing, monitoring and informing residents about dangerous episodes of air pollution due to adverse weather conditions (for example, high surface ozone concentration) and unauthorized emissions as in the case of accidents or terrorist attacks. In such situations, reaction time is imperative. Due to limited decision-making time in a critical situation, it is necessary to prepare in advance basic mitigation plans as a set of alternatives to choose from when a particular situation arises.

The task of decision making relating to air quality management is to minimize the environmental and health damage and the monetary cost of possible measures and actions. The set of variables for decision making depends on the characteristics of the target functions. To reduce dangerous concentrations under adverse weather conditions, emission parameters are considered [4, 6, 9] as decision variables. In parallel, decision-making during emergencies or terrorist attacks requires evacuation options (areas, routes, etc.) and public awareness of such options. Typical responses during emergencies include finding shelter, evacuation, public information and relocation [7]. However, decision-making in both cases requires assessing the risk of harmful effects by air pollution using modeling and spatial analysis to identify potential risk sources and receptors.

The process of decision-making is based on predicting the dispersal of pollution, environmental risk assessment and consideration of technical and economic actions to prevent and respond to the emergency. Pollutant dispersion prediction and modeling of photochemical transformation require meteorological data which are the main source of uncertainty in urban-scale models. For such tasks, reliable urban air quality information and forecasting systems play a key role. The availability of such systems with weather and pollution forecasts could be of relevant support for emergency management [1]:

- accidental radioactive or toxic emissions,
- potential terrorist attacks,
- fires, etc.

The main possible threats and risks of a terror action in urban areas include: chemical harmful releases, radioactive releases [2, 3] and bioterror actions [15].

When the terror action occurs, one must calculate the impact zone and quickly develop the correspondent mitigation action plan. The situation is the same with accidental release response but, in this case, there is usually less information available about release parameters: location, time period, and strength. If the region has proper air quality information and a forecasting system, the deliberate release parameters can be estimated on the basis of monitoring and combining the forward and inverse modeling [1]. In addition, it is important not only to quickly identify deliberate releases but assess risks of it affecting people and to develop a plan of information and evacuation options using regional emergency response systems.

Thus response to terrorist attacks and other possible emergencies is considerably enhanced when relevant air quality and emergency response systems are available.

11.4 Risk Assessment for Dangerous Elevated Ozone Concentration for Kyiv

A risk assessment of elevated ozone concentrations for Kyiv is presented here. Ozone, together with particulate matter (PM_{10} and $PM_{2.5}$), NO_x and SO_2, comprise the key pollutants for local monitoring and control [11]. The results of surface ozone observations in two points are local and cannot serve as a basis for forecasting ozone content over the entire city of Kyiv. However, such points can serve to develop a method of control of ozone concentrations using mathematical modeling confirmed by observed data [14].

To model the surface ozone distribution in Kyiv, the model UAM-V was employed which combines calculations of emission flows of ozone forming substances, their transport and turbulent motions, formation of urban plume of primary pollutants, their photochemical transformations and production of secondary pollutants, including surface ozone [13]. A typical episode of elevated ozone concentration (August 19–20, 2000) with cloud-free weather, negligible diurnal variations of pressure, weak transfer of air mass and lack of precipitation was selected for modeling. The modeled ozone distribution demonstrated that the areas hosting the observation stations are possibly not the most polluted (maximal 1-h average ozone concentration of about 60 ppb). For example, the northeast part of Kyiv is characterized by more elevated predicted ozone concentrations (up to 104 ppb), which exceed the European threshold (90 ppb averaged over 1 h) [5]. The Prognostic Meteorological Model [12] was used as a preprocessor for meteorological data needed for modeling the ozone concentrations. The measurements of temperature, pressure, humidity and wind parameters, such as velocities and directions at ground level, conducted at six weather stations and balloon measurements (up to 10 km of altitude) at one station performed twice per day were used for simulation of wind and temperature fields. A set of key meteorological situations corresponding to possible emission scenarios in the region should be simulated for the purpose of air quality management and prevention of dangerous incidents of elevated ozone levels.

For the residents, a wide variety of physiological responses to ozone should be considered. The responses are both individually peculiar and similar in some population groups. It is important to identify different categories of the population on the basis of their sensitivity to elevated exposures to ozone. Such categories usually include younger children, child and adult asthmatics, exercising individuals or individuals exposed to higher temperatures and/or humidity. The map of Kyiv and its nearest surroundings using a Geographic Information System (GIS) could be used for estimation of exposures of the city population to ozone. The map of Kyiv, with calculated 8-h (from 10:00 to 18:00) mean ozone concentrations exceeding 60 ppb (European target value for protection of human health), is shown in Fig. 11.1.

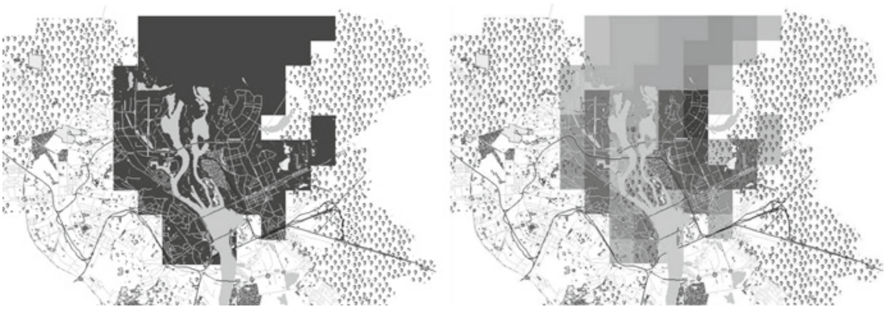

Fig. 11.1 Map of calculated ozone concentration during 8 h exceeded 60 ppb shown in black (*left panel*) and the local risk levels of surface ozone exposure estimated for the population of the city during a modeling episode (*right panel*). The levels of higher risk correspond in the right panel to the darker shades

The risk analysis approach was applied to estimate the possibility of harm for various population groups. The ecological risk, R, is assessed using the formula [10]:

$$R = Y \times p$$

where Y is the risk level representing the value of damage proportional to exceeding the threshold averaged over an 8-h exposure, and p is the risk factor as a probability of damage for a given period.

It is necessary to estimate risk from exposure to ozone for different population groups and ecosystems. This can be done by conducting epidemiological and toxicological studies that, together with modeling and measurements of exposure to ozone, may provide information concerning of exposure and risk reduction. The value of damage is determined by the concentration and toxicity of the pollutant:

$$Y = \left(\sum_{1}^{N} M_i \times K_i \right) \times K_L$$

where N is the number of exceedances of threshold value, M_i is the concentration of pollutant for i-case of exceedance, K_i is the coefficient of relative ecological and economical danger of air pollution, K_L is the local coefficient of ecological situation and ecological consequences for the area.

The value of K_i is linked to parameters such as population density, type of area (residential, recreational, etc.) and concentrations of other pollutants. The value of K_L depends on exposure time. The risk levels for the population of Kyiv estimated for an ozone exposure episode are presented in Fig. 11.1 (*right panel*). The risk level in each cell was calculated related to population exposure. The higher risk levels were found in the central part of the city.

There are two ways to reduce the risk level; by limiting exposure by informing and relocating the population, and by reducing the ozone concentration by controlling anthropogenic emissions.

Notably, urban ozone is produced from NO_x emission by solar UV radiation (<410 nm) in the presence of VOCs (volatile organic compounds). Since the dependence of ozone concentration on NO_x and VOCs concentrations is not linear, modeling is needed for ozone abatement for each modeling cell of the Kyiv area. The aim of the policy-making process is to base any regulatory measures on real-time modeling of surface ozone that estimates, together with stationary sources, the traffic loads and thus the emissions on each street segment.

GIS can be used to assess spatial risk characteristics that should be supplied to the public when an alert threshold is exceeded or predicted. This includes [5]:

1. Information on observed exceedance(s):
   - location or area of the exceedance,
   - type of threshold exceeded (informational or alert),
   - start time and duration of the exceedance,
   - the highest 1-h and 8-h mean concentrations;

2. Forecast for the following afternoon/day(s):
    - geographical extent of expected exceedances and/or alert threshold,
    - expected change in pollution (improvement, stabilization or deterioration);
3. Information on type of population concerned, possible health effects and recommended actions:
    - information on population groups at risk,
    - description of likely symptoms,
    - recommended precautions to be taken by the population concerned,
    - where to find further information;
4. Information on preventive action to reduce pollution and/or exposure to: indication of main source(s) of exposure; recommendations for actions to reduce emissions.

11.5 Conclusions

Urban air quality management is moving towards providing citizen-centered services for improving the quality of life. Internet-based systems for public information used by many city authorities can be employed in air quality management systems, for example, for disseminating information to the public via mobile phone SMS messages [8].

It is important to develop national and regional air quality management systems and integrate them into emergency response systems. Emergency situations, either man-made or natural, can differ considerably. A matrix of natural conditions can be filled by calculating typical meteorological situations resulting in a high level of urban pollution (for example, a surface ozone episode). Ecological risks estimated for each condition and emission scenarios provide information needed to construct the decision matrix.

A Decision Support System, including observation data management, GIS, a pollution modeling system, and a set of simulation and optimization models should be installed centrally and all authorities involved in the decision-making process should have access to the results provided by the system. It is also important to develop environmental information services, such as forecasting modules, for near-real time or real time environmental information and visualization modules.

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Chapter 12
Processing of Hyperspectral Imagery for Contamination Detection in Urban Areas

Mikhail A. Popov, Sergey A. Stankevich, Ludmila P. Lischenko, Vladimir V. Lukin, and Nikolay N. Ponomarenko

Abstract The application of hyperspectral imaging to detect soil contaminations is considered with respect to contamination assessment within urban areas. An optimal selection of hyperspectral imagery spectral bands is proposed. There is no reason to process all spectral bands as usually the 10–30 most informative ones are sufficient. A new criterion is introduced that incorporates such fundamental properties of hyperspectral imagery such as spatial resolution, mutual spectral information and signal-to-noise ratio. Algorithms for hyperspectral imagery processing and analysis were adapted for geochemical contamination detection. EO-1/Hyperion hyperspectral imagery was applied to central Kiev, Ukraine, and estimations of geochemical contamination of this area were mapped.

Keywords Urban area • Geochemical contamination • Hyperspectral imagery

12.1 Introduction

The threats to environmental security in the modern world now have a new component in the form of ecological terrorism. Ecoterrorism is the use or threatened use of violence of a criminal nature against innocent victims or property by an environmentally-oriented, sub-national group for environmental-political reasons, or aimed at an audience beyond the target, often of a symbolic nature [6]. There is a growing necessity to develop quantitative estimations of potential environmental harm for both prediction and rapid response [4].

One goal of ecological terrorism is to intimidate people by means of environmental impacts, such as ecocatastrophes. This can include attacks damaging or destroying

M.A. Popov, S.A. Stankevich (✉), and L.P. Lischenko
Scientific Centre for Aerospace Research of the Earth, Kiev, Ukraine
e-mail: st@casre.kiev.ua

V.V. Lukin and N.N. Ponomarenko
National Aerospace University, Kharkov, Ukraine

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power plants, large dams, nuclear, chemical, petroleum-refining, metallurgical and bioengineering works, raw materials and products storages, oil, gas and ammonia pipelines, military bases, and radioactive and toxic waste dumps. In many cases, attractive targets are located in or near ports and industrial zones within densely populated urban areas.

It is known that the soil can be a repository for a wide range of environmental pollutants. Soil contamination can occur through deposition from the atmosphere (e.g. acid rain), deliberate application (e.g. fertilizer), spillage, leakage or illegal deliberate hazardous waste dumping [3]. Deliberate contamination of soil can also be regarded as a method of ecoterrorism.

In Iraq deliberate spills of chemicals (acids and solvents) will impact soils and, potentially, groundwater [27]. Deliberate acts of sabotage causing extensive contamination of soil and water have occurred in Nigeria [28].

Factors that affect soil reflectance include moisture, chemical agents, and organic matter content [5].

An objective and reliable estimation of local contamination from a release is needed for planning and countermeasures. Recent developments in model assimilation, data processing, electronic reporting, compliance information integration, and sharing results of environmental research has facilitated new and improved approaches to handle ecological problems in industrial zones and urban areas. The same technologies offer the opportunity to develop more effective efforts to target the most egregious violators and international traffickers of ecoterrorism [16]. The utilization of remote sensing and associated technologies can help track environmental conditions and violations and support environmental protection and security at a global basis, particularly for developing nations.

Hyperspectral remote sensing is a powerful tool for mineral and soil mapping. The spectral signatures derived from hyperspectral imagery can be used to identify mineralogical ingredients. For example, hyperspectral remote sensing data can provide the mapping and monitoring of red dust polluted areas [15]. The possibility of hyperspectral imaging to perform rapid and reliable tests to identify and quantify specific contaminated soil characteristics is explained in Bonifazi [2]. The hyperspectral signature of soil can be applied with a processing algorithm to identify soil-contaminated areas [22], oil-polluted soil and water on ponds [23].

12.2 Geo-Information Approach

Environmental contamination is a serious problem in cities and urban areas. The main contamination agents are carbon monoxide/dioxide, sulphur oxides, nitrogen compounds, hydrocarbons, fluorides, potassium derivatives, synthetic organic substances, and industrial dust and heavy metals. Immediate contamination of road pavements and open soils, water bodies and water flows by liquid and solid wastes often occurs in cities. Urban wastes tend to accumulate in terrain lowlands. Strong spatial differentiation of contamination density is observed under such conditions. Atmospheric precipitation stimulates contamination of aeration zones and groundwater.

The contamination load inside urban areas depends on lithological/facial composition and subsurface aquifer structure. As a result, significant technogenic geochemical anomalies are found in release sites of long-term and intensive industrial pollution.

Spatial distribution data of contaminants inside urban area are commonly stored and analyzed using a municipal geoinformation system (MGIS). MGIS includes such information layers such as urban landscape type, geology, terrain elevation, wind roses, transportation contamination sources and stream layer and a general ecological layer (parks, water bodies, open space, etc.) [8].

The Kiev MGIS contains ecological, geological, geoecological and tectonic plot maps, and a transportation diagram. In addition, MGIS contains spatial distribution data of technogenic load on city territories (Fig. 12.1).

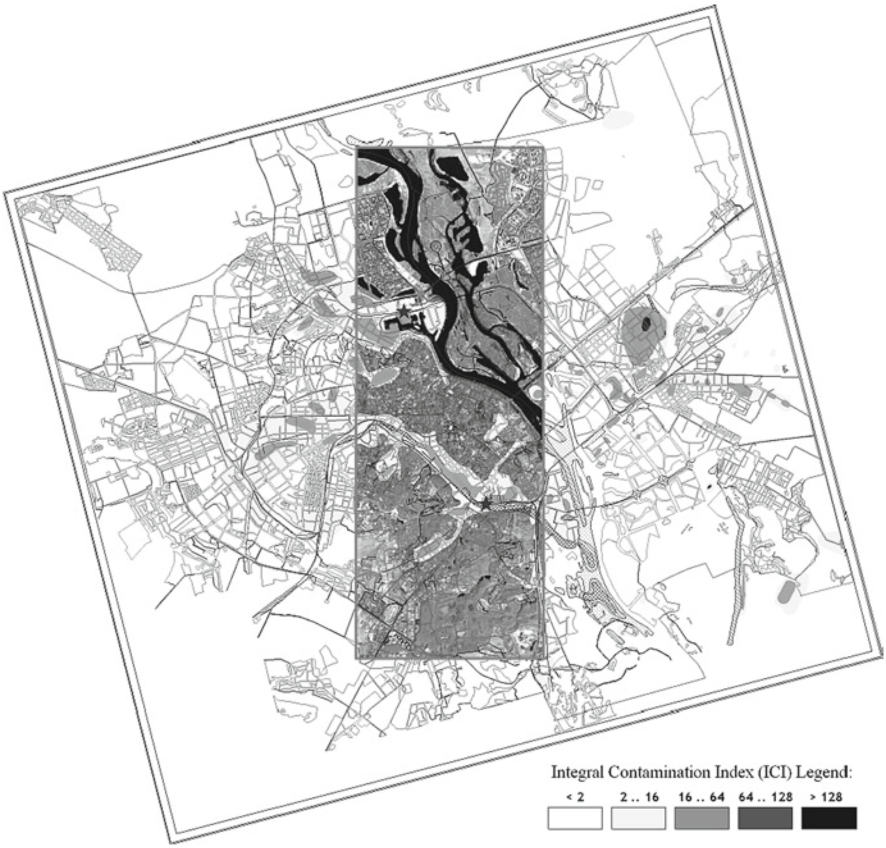

Fig. 12.1 Geochemical contamination map within Kiev [13]. Increasing shading indicates a higher background level of contamination. (⋆ – ground test sites, □ – satellite image outline)

12.3 Hyperspectral Imagery Information

Airborne/spaceborne remote sensing can be an efficient tool for monitoring urban areas. Its main advantages are efficiency and relatively low cost, especially for mapping of large areas. However, information extraction for monitoring ecological conditions of a region from ordinary remote sensing data is usually difficult or impossible because land cover recognition features have fine spectra differences. Therefore, both environmental monitoring and contamination detection in urban areas require hyperspectral imaging data.

Hyperspectral remote sensing data, as a rule, are information redundant for specific tasks and useful information extraction from these data is a rather difficult problem. Its solution starts with hyperspectral imagery information estimation and successive spectral bands subset for optimal selection for later analysis. In our paper the total information $C(\lambda)$ includes a Kullback–Leibler information divergence $D(\lambda)$, hyperspectral imagery equivalent spatial resolution $r(\lambda)$ and equivalent signal-to-noise ratio $\psi(\lambda)$ [24]:

$$C(\lambda) = \frac{D(\lambda)}{4r^2(\lambda)} \log_2 \left[1 + \psi(\lambda)\right] \tag{12.1}$$

Here $D(\lambda)$ describes spectral, $r(\lambda)$ – spatial, and $\psi(\lambda)$ – power capabilities of target detection.

Information (Eq. 12.1) defines the criterion function for optimal selection of a hyperspectral imagery spectral bands subset. The purpose of optimal bands selection is to maximize useful information retrieval for a defined task:

$$\lambda^* : C(\lambda^*) \to \max \tag{12.2}$$

Given known targets spectra, (Eq. 12.2) is an unconstrained discrete optimization problem [7]. The basic procedures of unconstrained global optimization include a local optimizer and global decision rule [1]. A local optimizer ensures finding local extremes while the global decision rule selects the best one. Various search-engine methods, method of feasible directions, slump-vector method, branch and bound method, etc. [14] can be mechanisms of local optimization.

In this paper, the multiple start pseudo-gradient search on a regular lattice in space of hyperspectral imagery spectral bands subsets is used for spectral bands optimal selection [25]. During the pseudogradient search, particular spectral bands that provide a maximum information increment are rejected sequentially. Figure 12.2 illustrates the pseudogradient search passing for EO-1/Hyperion hyperspectral image spectral bands quasi-optimal subset selection for contamination detection in the Kiev region. In total, 16 spectral bands from 160 were selected for further processing, which provided an information value of 6.23 bits per pixel (bpp) of hyperspectral imagery.

Practical experience with hyperspectral images processing shows that it is sufficient to have no more than 10–30 specially selected spectral bands for a majority of practical applications [12].

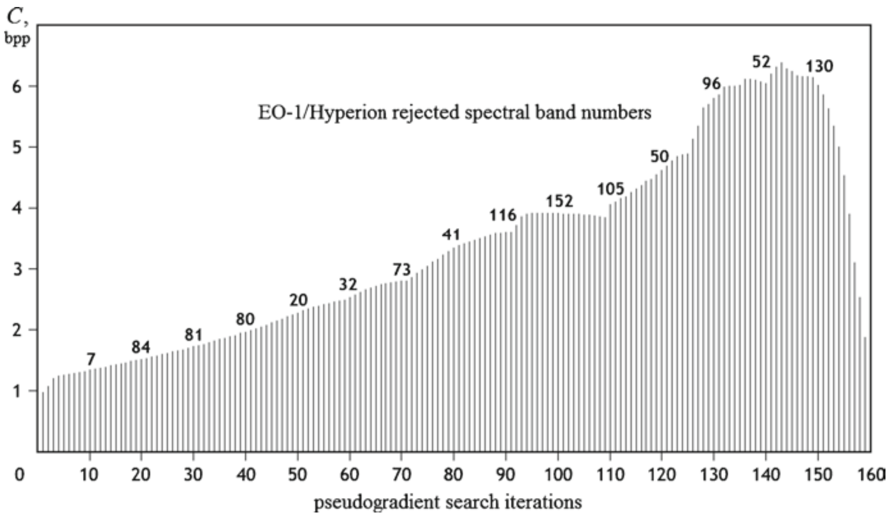

Fig. 12.2 Information propagation over spectral bands subsets of EO-1/Hyperion (Kiev, September 1, 2002) hyperspectral image

12.4 Geochemical Contamination Mapping

An estimation of total geochemical contamination by heavy metals and toxic substances for open soils was carried out using hyperspectral imaging data. EO-1/Hyperion calibrated hyperspectral satellite image of the central part of Kiev, obtained on 1 September 2002 (Fig. 12.3a) was used for this purpose. A preliminary "blind" estimation of the hyperspectral imagery noise [19] led to the selection of 160 spectral bands of Hyperion, from a total of 242, for further processing.

A preliminary landscape functional classification of city territory was then performed for the given hyperspectral image. The basic types of settlements, green belts, water bodies and other land cover classes (Fig. 12.3b) were classified by spectral/textural features [20]. A preliminary classification was necessary for further detailed analysis of geochemical contamination only within an "open natural lands" class. However the "open artificial areas" class had similar spectral/textural features and required additional post-classification separation using object-based image analysis (OBIA) (Fig. 12.3c).

The allocated open natural lands occupy a very small area within Kiev. This class occurs in patches that correspond to wastelands, construction sites, lowlands, beach sands and others. There are two ground-truth test sites (GTS) used for geochemical contaminations detection in Kiev. These GTSs were located in city industrial zones that have abnormally high concentrations of heavy metals in soil according to in-situ geochemical tests. Also, several reference GTSs with minimum contamination inside parks and beach areas were used.

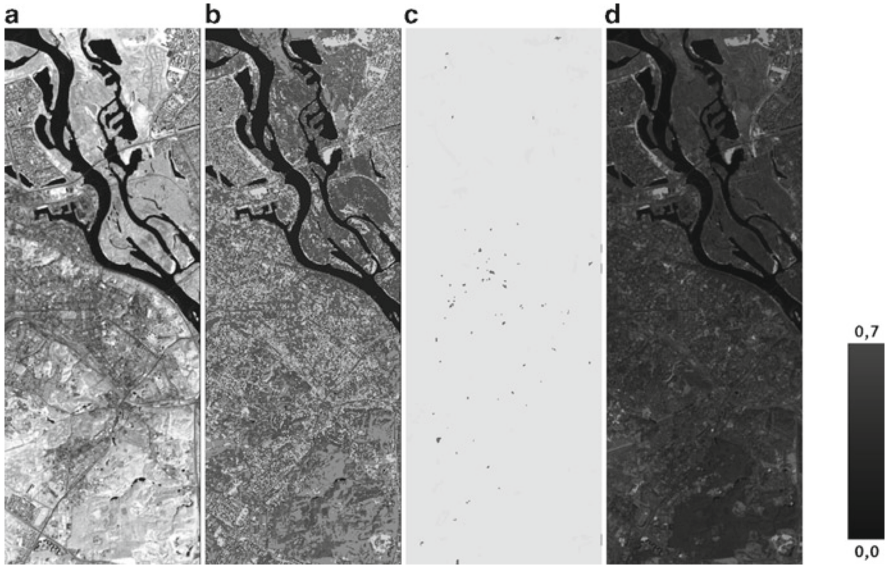

Fig. 12.3 Kiev territory estimation for contaminations within "open natural lands" class: (**a**) EO-1/Hyperion hyperspectral satellite image, September 1, 2002, spectral bands 115 (1,296 nm), 95 (1,094 nm), 36 (712 nm), 30 m spatial resolution; (**b**) – land cover classification: – high-rise districts, – industrial estates, – asphaltic roads, light roofs, – verdant yards/streets, – barren lands, sparse vegetation, – grasslands, – shrublands, – city-forests, – open natural lands, – water surfaces; (**c**) open surfaces separation using object-based image analysis between two classes: – open artificial areas, – open natural lands; (**d**) contamination spatial distribution for an "open natural lands" class

Quantitatively, the contamination level $P(x)$ was estimated by Hyperion hyperspectral imagery within the "open natural lands" class using a spectral-topological algorithm [21] with preceding optimization (Eq. 12.2) and a Bayesian decision rule:

$$P(x) = \begin{cases} \dfrac{P(x \mid A)}{P(x \mid A) + P(x \mid B)} & \text{if } x \in \text{"open natural lands"} \\ 0 \quad \text{otherwise} \end{cases} \tag{12.3}$$

where $P(x|A)$ is the conditional probability of membership of the x pixel signal in the contaminated site reference sample A, and $P(x|B)$ denotes the conditional probability of membership of the x pixel signal in the non-contaminated area reference sample B.

In Fig. 12.3d, the contamination level is shown using a continuous scale from black (contamination practically is missing) to light grey (maximum contamination). The results generally confirm the ground geochemical tests data (Fig. 12.4). Sites with the most intensive contamination (ranging from 0.3 to 0.7) are matched to the Kurenevsko-Petrovska and Lybidska industrial zones, and also to garbage dumps and a river floodplain at the intersection of highways. Isolated pixels occurred in

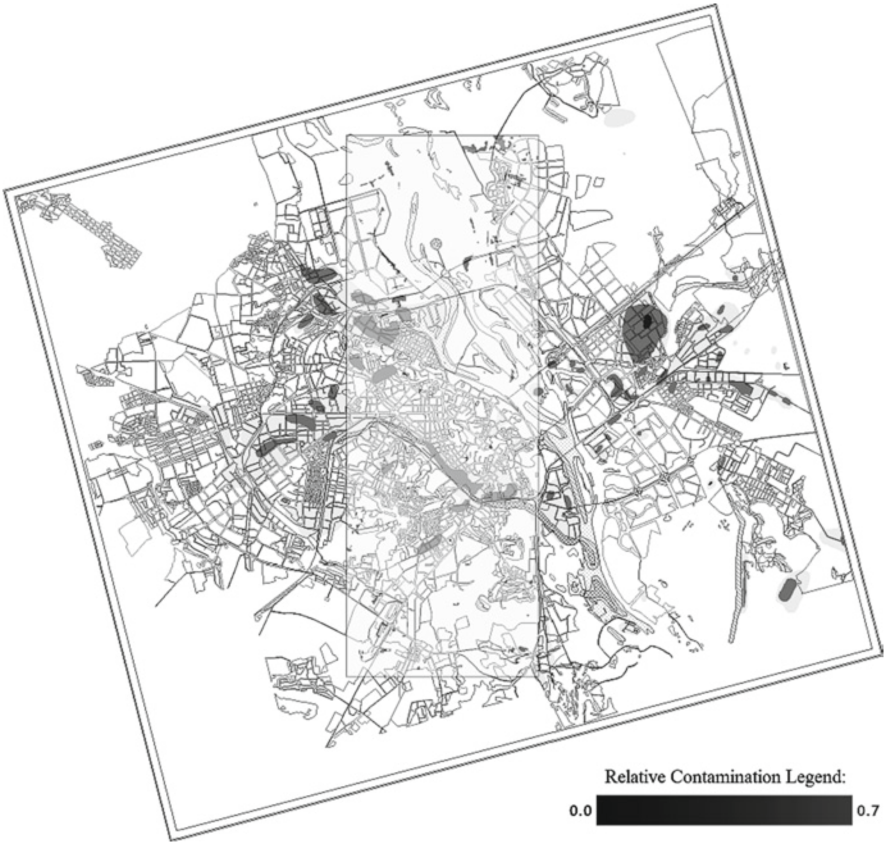

Fig. 12.4 Comparison of ground geochemical tests data and contamination of Kiev territory estimation by hyperspectral image for an “open natural lands” class

the central part of the city. They have smaller values of the contamination intensity and usually correspond to temporary construction sites.

Thus to detect technogenic contamination in urban areas, it is not necessary to process all hyperspectral imagery bands. Usually it is enough to use no more than 10–30 spectral bands that are the most informative. The advantage of the developed approach is that it improves the level of confidence for contamination detection, with a significant reduction in the required computational load.

12.5 Hyperspectral Data Compression

As the processed data quantity remains very large, remote sensing hyperspectral imagery compression is used widely. The best known lossless compression methods are not capable of providing a compression ratio larger than 3.5 times [29], which

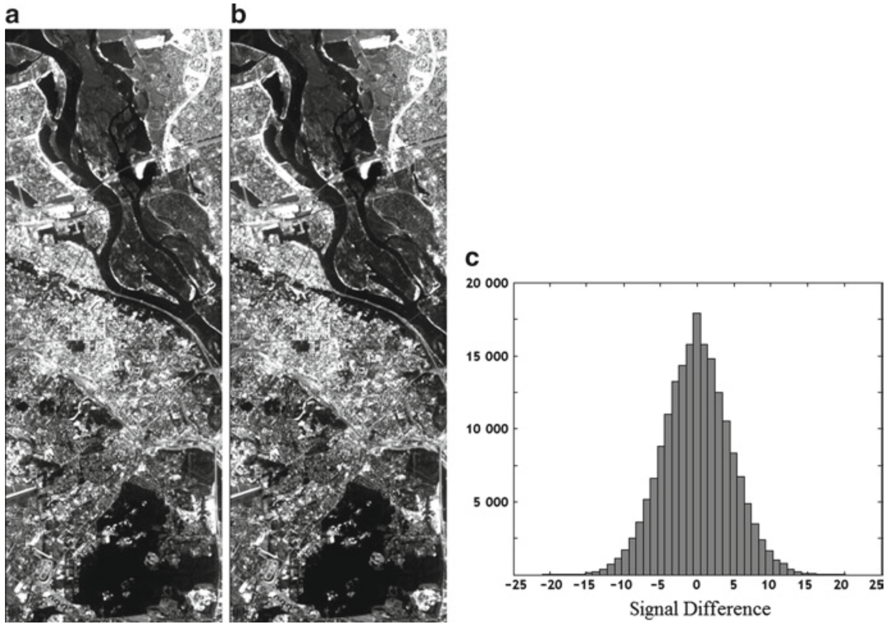

Fig. 12.5 EO-1/Hyperion hyperspectral image (Kiev, September 1, 2002, spectral bands 14 (488 nm), 22 (569 nm), 26 (610 nm), 32 (671 nm)) before (**a**) and after (**b**) 9.6 times lossy compression; (**c**) pixel deviations histogram of the compressed image

is not sufficient in many practical cases. At the same time, there are known lossy compression methods, which, in principle, can provide compression by tens and even hundreds of times [17, 26]. However, if the compression ratio is too large, introduced distortions can lead to irretrievable loss of useful information. Therefore, it is reasonable to use such lossy compression in which the quality of given data remains acceptably high [9].

Here, the quality of data compression was evaluated by the criterion of correct classification probability [11]. The decision on the permissible compression ratio was accepted in a blind manner (automatically) by the peak signal-to-noise ratio (PSNR) value [10]. It was accomplished by estimating and analyzing the PSNR-HVS-M metric for each spectral band of hyperspectral data [18]. Figure 12.5 demonstrates the possibility of the EO-1/Hyperion hyperspectral image compression without visually detectable distortions. The compression ratio in this case is of the order of 9.6 pending upon the spectral band and coder used.

12.6 Conclusions

Hyperspectral imaging can be an effective tool for contamination detection in urban areas. The obtained results are preliminary, but detection outcomes correlate well with available ground data concerning geochemical contaminations of soils/sands in Kiev. The developed dataflow specification for hyperspectral imagery processing is only applicable to "open natural lands" class areas and cannot be mechanically extended to other land cover classes. Similar research can be useful for natural vegetation areas with near biotope/phytometric performances (identical tree/herbage species, almost equal projective cover and leaf area index, crown density, age, unified habitat conditions).

The use of the most informative spectral bands subsets and their additional lossy compression allows others to pursue further interpretation and processing of about 1% of the total volume of the original hyperspectral data, on condition that this subset of spectral bands is determined in advance for a particular application.

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Chapter 13
Ukraine and Romania: Transboundary Environmental Security and Ecology of Shared Water Resources

Igor Winkler

Abstract Ukraine and Romania share a number of various water resources, such as part of the Black Sea, but the Tisza, Prut, Siret and Danube are the main shared rivers. Some of the rivers flow from Romania to Ukraine and vice versa while some smaller rivers meander within both countries or flow to adjoining countries. In the background of rather strained relations between these two nations, there are accusations of "eco-terrorism" because of regular or emergency discharges of water polluting agents into these rivers.

This work analyses the main sources of tension with regard to both small and bigger shared water resources along Ukraine-Romania border and proposes some mitigation steps. It is shown that both sides can take rather simple but effective steps to achieve a compromise.

Keywords Transboundary water resources • Water contamination • Water ecology • Pollution control and prevention

13.1 Introduction

Eco-terrorism can manifest itself in many forms and conscious water contamination or malicious regulation of river water flow can be classified as a form of terrorist activity. Transborder water flow creates many unusual problems concerning pollution sources down-river and means of regulating against such pollution. For example, an agreement regarding the Danube river was signed in 1948 when all interested parties agreed to form the Danube Commission (ICPDR), which controls most issues related to river navigation and environmental conservation in the region

I. Winkler (✉)
Yu. Fedkovych Chernivtsi National University, Kotsiubynsky St., 2, Chernivtsi 58012, Ukraine
e-mail; igorw@ukrpost.ua

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of the Danube. Unfortunately, similar legislation is lacking between rivers flowing into and out of Ukraine and Romania.

The transboundary region between Ukraine and Romania can be divided into three conditional hydrographical subregions. The Carpathian mountains divide the "upper" part of the border into the "Tisza" and "Prut-Siret" subregions and another "Danube" subregion can be identified in the "lower" part (Fig. 13.1). The "Danube" subregion also verges on the Black sea where Ukraine and Romania share a long sea border and areas of exceptional economical interests rearranged recently by the Hague International Court of Justice.

All river flow comes from Romania to Ukraine in the "Danube" subregion while the situation is reversed in the "Prut-Siret" subregion. The Tisza river starts in Ukraine and flows along the state border having its right tributaries coming from the Ukrainian side and most left tributes coming from Romania. Then the river flows to Hungary, returns to Ukraine near the town of Chop, and then again turns to Hungary.

Each sub-region has its own characteristics of water polluting agents, origin, discharge and distribution. All countries in the region use transboundary rivers to supply water for municipal and industrial needs and also to discharge wastewater, mainly to the same rivers. Accordingly, mutual accusations often appear as a result of industrial activity and/or malfunctioning of production facilities operating near

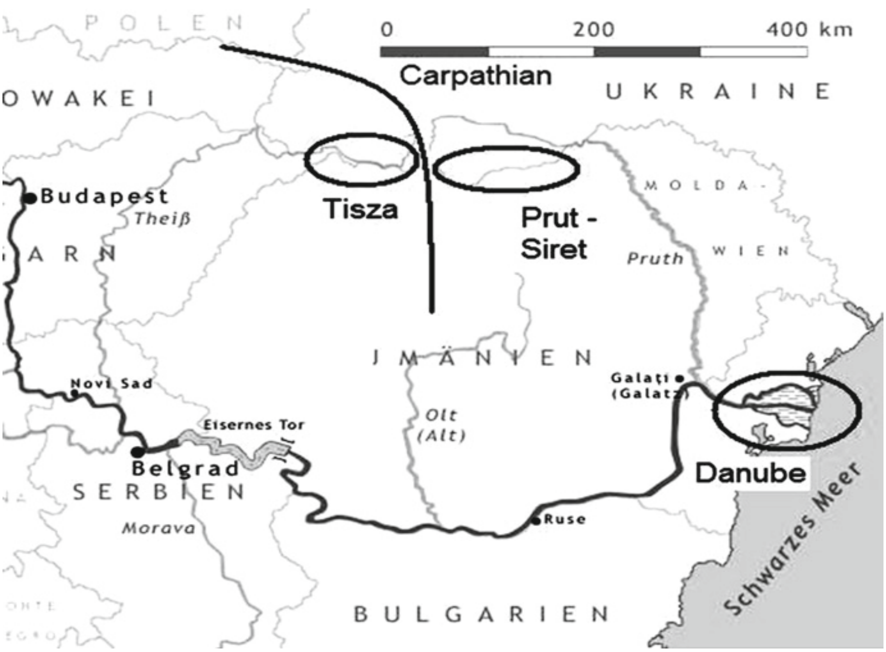

Fig. 13.1 Location of the "*upper*" (Tisza and Prut-Siret) and "*lower*" (Danube) transboundary subregions along the border between Romania and Ukraine

transboundary rivers or their tributaries and causing discharge of untreated or insufficiently treated wastewater.

This paper outlines the main issues in river flow and environment control and regulation between Ukraine and Romania and outlines possible solutions that might be used to mitigate problems.

13.2 Subregion Tisza

This area covers Ukraine–Romania borderlands along a 90 km part of the upper Tisza (Fig. 13.2). All right tributaries flow into the Tisza from the Ukrainian side and left tributaries mostly flow from Romania. There are some small towns (less than 30,000 inhabitants) near Tisza or its tributaries at the Ukrainian side: Rahiv, Tyachiv and Hust. None has heavy industry and municipal buildings are generally not connected to a centralized sewage system and thus cesspools are common. A similar situation exists in the nearby Romanian towns across the river. The municipal wastewater discharges are insignificant and thus cannot seriously influence the ecological condition of the Tisza river.

Atmospheric precipitation is very abundant and even excessive in the region, and river water is not used for agricultural melioration or artificial watering.

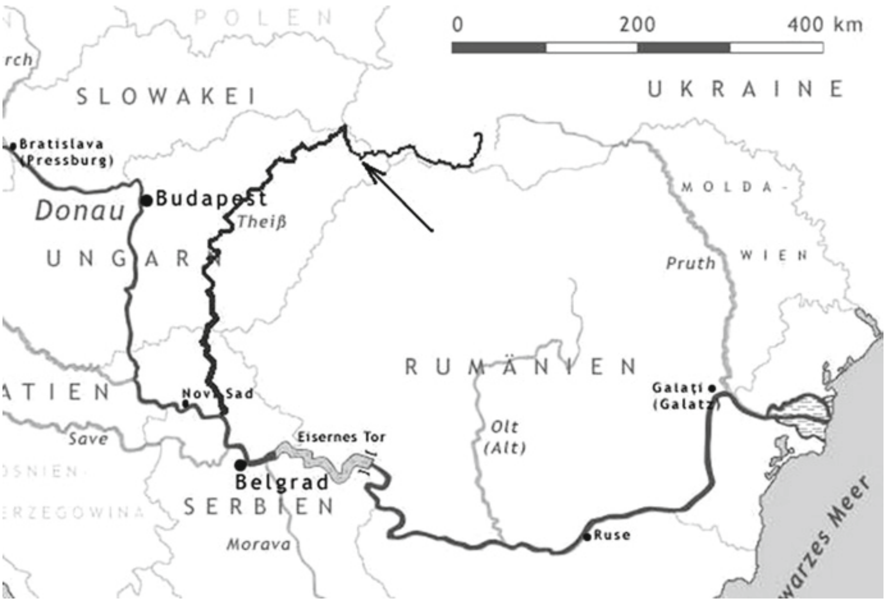

Fig. 13.2 Map of the Tisza subregion. The river is denoted with the *bold line*. An *arrow* points to the junction of the Szamos and Tisza rivers

However, the Szamos river, a left tributary of the Tisza is known as the main source of environmental threats to the Tisza ecosystem. The source of the Szamos is situated in Romania and the river flows towards Tisza, with a junction point in Hungary before it returns to Ukraine near Chop.

Two big cities, the Cluj-Napoca (320,000 population) and the Satu-Mare (120,000) stand on the Szamos. Another large city, Baia-Mare (140,000), stands within the catchment area of the Szamos. These cities have well-developed sewage systems and wastewater treatment plants, which discharge wastewaters into the Szamos. The efficiency of the wastewater treatment is adequate, which helps maintain the allowable quality of the river water.

The Baia-Mare region has numerous mining and ore refining sites that pose a very high threat to the river systems. They use intense technologies of mineral refining, extraction of gold, copper and lead from the ores and old tailings, which involve treatment with cyanides. Their technological discharges constantly bring some amount of heavy metals and cyanides to the river water in many areas downstream from the discharge points. What is much more dangerous, however, is that several major accidents at the mine refineries resulted in massive discharges of untreated solutions and wastewaters into the Szamos, which contaminated the river, damaged its ecosystem and resulted in a long-lasting ecological disturbance to the region.

A very serious spill of industrial solutions with high cyanides and heavy metals contamination happened in 2000 at the Australian-Romanian mining corporation AURUL. The corporation works with extraction of gold from old mining slurries and tailings using the cyanide method. A dam of the used solutions pond broke on January 30, 2000, and about 100,000 m^3 of highly toxic solution were discharged into the Szamos. Estimates of the cyanides indicated that about 1,000 ton [5] were discharged together with significant amounts of lead, copper and zinc. A 150 km long contaminated area traveled about 1,900 km downstream of the Szamos, Tisza and Danube rivers over 4 weeks [6]. Cyanides peak concentration in the river water exceeded maximum permissible levels (MPL, 0.05 mg/l) by 600 times at the point of discharge of contaminated water into the Szamos, 300 times at the junction of the Szamos and Tisza, 30 times in Ukraine near Chop, and 18 times where the Tisza leaves Hungary.

Another serious incident happened in the same area near Baia-Borsa in March 2000 when the dam of the Romanian mining company sediment pond broke because of intense rainfall and snowmelt. About 20,000 ton of heavy contaminated slurry were discharged in a creek and then ran into the Tisza. This accident brought to the river water mostly heavy metals: lead (about 50 ton), zinc (70 ton) and copper (20 ton) [5].

Similarly, yet not as severe, accidents became routine and occurred almost every year. The last reported accident took place on April 16, 2009 when MPL of heavy metals was exceeded by two to four times because of ruptures in the pipeline at the ore processing plant near Baia-Borsa, Romania [4].

Nevertheless serious devastation of the river ecosystems caused by the "cyanide" accident did not result in any long-lasting effect. Thousands of tons of fishes and other organisms were killed by exposure to the high cyanide concentration but they were replaced by others coming from untouched upstream areas and other tributaries. Cyanides are very unstable in the environment and the Tisza ecosystem has been found almost rehabilitated in March 2010.

On other hand, heavy metals contamination induces a long-lasting and hardly-curable effect. This contamination is very persistent and highly toxic for many living species. As a result, lowered bioproductivity of the Tisza ecosystem has been reported even several years after the accidents. Other less-severe accidents also brought additional contributions to lasting contamination of water with heavy metals.

Technological and accidental discharges of the wastewater and slurries with heavy metals and cyanides are the most dangerous threats to the environment in the Romania-Ukraine "Tisza" transboundary region.

This case also raises many questions related to the responsibility of the foreign investor, who brought a very outdated gold extraction technology, which would never be allowed to be used in Australia. Responsibility lies with local authorities who agreed to this risky activity expecting to get fast income but without proper attention to the environmental (and transboundary) issues. However, this matter is beyond the scope of this paper.

13.3 Subregion Prut-Siret

This area covers part of the near-border East Carpathian lands within a catchment of the rivers Prut and Siret (Fig. 13.3). Both rivers have their source from the Eastern side of the mountains or foothills and flow from Ukraine to Romania. All tributaries of the Siret and Prut, in their initial part, come from Ukraine. Then the Siret flows in Romania and the Prut flows along the border line between Ukraine and Romania, then to Moldova and Romania. Both rivers flow into the Danube.

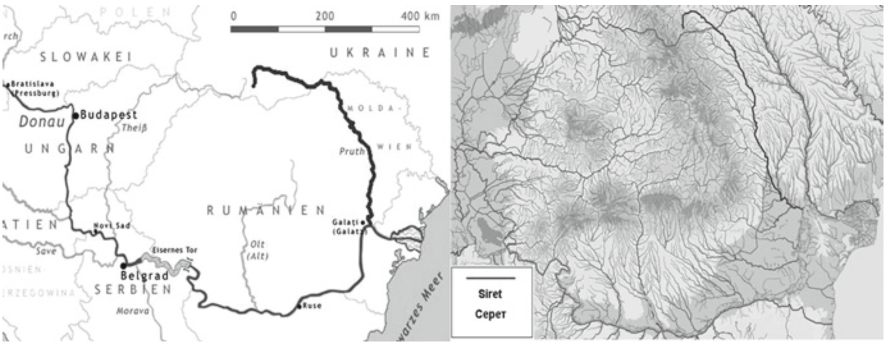

Fig. 13.3 Location of the Prut (*left*) and Siret (*right*) subregions. Rivers denoted with *bold lines*

There are no big cities in the Ukrainian part of the Siret catchment area. Storozhinets (population 14,000) is the only town in that region. Chernivtsi (population 270,000) is situated at the Prut and causes the main anthropogenic pressure on the river ecosystem.

The main environmental problems related to both rivers are:

- Excessive anthropogenic activity on the river banks;
- Gravel pits exploitation;
- Riverbed cut-off;
- Discharge of insufficiently treated wastewater.

Even though the first three issues are quite painful and can provoke (and in fact provoked) serious flooding, the discharge problem is the most acute and, due to the limited space, only this issue will be analyzed here in detail.

13.4 Prut River

Water from the Prut taken upstream of Chernivtsi is relatively clean and almost completely meets requirements for the highest, fish-production grade (Table 13.1).

All water quality parameters except for concentration of ammonium salt are under the MPL. A local wastewater treatment plant (WWTP) has been constructed for cleaning about 70–90,000 m^3 per day. The last major renovation was made in the 1980s but the municipal sewage network has now almost doubled its working area. On the other hand, an old combined sewage system still works in the downtown area and takes both residential wastewater and rainwater. As a result, the local WWTP provides more or less satisfactory treatment only during rainless periods. Any serious atmospheric precipitation causes overloading of the WWTP and partial discharge of insufficiently treated wastewater into the river. Secondary

Table 13.1 Water quality parameters for the Prut river, upstream of Chernivtsi

Parameter	Maximum permissible level (fish industry water quality), mg/l	Actual value, mg/l
Bio-oxygen demand	3.0	2.3
Chem. oxygen demand	15.0	13
NH_4^+ (salt)	0.5	**<u>0.8</u>**
NO_2^-	0.08	0.06
NO_3^-	40.0	5.1
PO_4^{3-}	3.12	0.31
Cl^-	300	34.0
SO_4^{2-}	100	40.7
Dry residue	1,000	331.5
Dredge (suspension)	12	9.2

contamination of the treated wastewater from overloaded open areas from excessive active sludge storage is another threat to the river.

All these problems contribute to the low quality of municipal wastewater discharge (Table 13.2). Half of the regularly controlled wastewater quality parameters do not meet the MPL. Bio-oxygen demand is an indicator of excessive contamination with organic pollutant and this parameter is almost eight times higher than the MPL.

Natural dilution and self-cleaning processes can improve the water quality and one of the quality parameters returns under the MPL, but levels above the MPL become less critical just 1 km downstream from the wastewater discharge point (Table 13.2).

Only two parameters exceed the MPL 30 km downstream (this point is located 10 km away from the border of Romania-Ukraine) (Table 13.3).

However, even these two parameters approach the MPL and should reach the MPL or even lower values along the next 10 km remaining till the border.

Even though most water quality parameters return to normal values within the territory of Ukraine, the river suffers from discharge of insufficiently cleaned wastewater, especially after intense rainfalls.

Table 13.2 Wastewater quality parameters at the discharge point (numerator) and 1 km downstream (denominator) (river water quality)

Parameter	Maximum permissible level, mg/l	Actual value, mg/l
Bio-oxygen demand	3.0	**22.6/5.6**
Chem. oxygen demand	15.0	**31.1/16.9**
NH_4^+ (salt)	0.5	**2.3/0.8**
NO_2^-	0.08	**0.4/0.09**
NO_3^-	40.0	17.0/6.2
PO_4^{3-}	3.12	1.4/0.62
Cl^-	300	156.0/44.4
SO_4^{2-}	100	82.3/47.8
Dry residue	1,000	432.3/357
Dredge (suspension)	12	**15.7/**11.3

Table 13.3 Water quality parameters 30 km downstream from the discharge point

Parameter	Maximum permissible level, mg/l	Actual value, mg/l
Bio-oxygen demand	3.0	**3.5**
Chem. oxygen demand	15.0	14.8
NH_4^+ (salt)	0.5	**1.0**
NO_2^-	0.08	0.06
NO_3^-	40.0	6.3
PO_4^{3-}	3.12	0.52
Cl^-	300	35.3
SO_4^{2-}	100	42.8
Dry residue	1,000	338.7
Dredge (suspension)	12	9.5

Therefore quality of the wastewater treatment at the Chernivtsi WWTP must be improved and, taking into account an eight times exceedance of the bio-oxygen demand, special attention should be paid to improvement of bio-treatment operations.

Part of this task has already been completed during a 2007–2009 reconstruction project, which resulted in a doubling of bio-treatment facilities productivity. This has not had any significant effect on the wastewater quality parameters but has seriously reduced the amount of untreated water discharges during atmospheric precipitations.

Increased efficiency of the WWTP in Chernivtsi is essential for reducing trans-boundary pollution transfer and improving ecological security in the Prut river basin.

13.5 Siret River

The Siret river originates in the foothills area of the Carpathian mountains and flows into Ukraine (about 115 km) and then into Romania until the junction with the Danube river. Storozhinets is the only relatively big settlement in the Siret catchment area on the Ukrainian side. There is no serious anthropogenic industrial activity near the Ukrainian part of Siret. Several saw-mill factories cause only moderate contamination of water from woodchips near discharge points. Water quality parameters return under MPL just in 1–2 km downstream discharge points.

River water meets all quality parameters upstream of Storozhinets. A centralized sewage system covers about 55% of the town while the rest of the residents use cesspools. Local wastewater treatment facilities provide only mechanical cleaning and short-term sedimentation. However, wastewater discharges do not result in serious contamination of the river due to the relatively small volume of the discharges.

About 40% of the wastewaters collected in Storozhinest do not reach the WWTP and are discharged directly to a small creek flowing into the Siret. This results in contamination of the creek (see Table 13.4) with ammonium content more than ten times higher than the MPL.

Table 13.4 Water quality parameters near discharge point to a creek in Storozhinets

Parameter	Maximum permissible level, mg/l	Actual value, mg/l
Bio-oxygen demand	3.0	**6.78**
Chem. oxygen demand	15.0	**26.8**
NH_4^+ (salt)	0.5	**5.8**
NO_2^-	0.08	**0.28**
NO_3^-	40.0	4.47
PO_4^{3-}	3.12	0.23
Cl^-	300	56
SO_4^{2-}	100	48
Dry residue	1,000	298
Dredge (suspension)	12	**15.3**

Contaminated water from the creek flows to the Siret and causes high bio-oxygen demand even 1 km downstream from the town. However, all water quality parameters meet the MPL just 5 km downstream, which is still far away from the point where the Siret crosses the border.

Therefore, we can conclude that water contamination in the Siret basin does not cause any transboundary effect. However, water quality can be improved by collecting all wastewater in the sewage system and ending discharge of untreated water to the creek.

13.6 Subregion Danube

The Ukrainian part of the Danube is relatively short and extends along the left bank of the Kiliya tributary – one of three main branches of the river delta. Two other tributaries (Sulina and St. George) flow into Romania. Part of the lower Danube riverside area is recognized as an important region of bio-conservation – the Danube "swampy lands". On other hand, this is a region of very intense cargo and passenger shipping to/from many European countries. Anthropogenic activity in the region is mostly directed to ensure improved navigation of ships through the Danube delta. Sand/clay banks usually endanger ship passage through the delta and Romania and Ukraine compete with each other trying to secure deeper and wider navigation channels. Millions of tons of river sand, clay and mud are excavated from the riverbed in order to keep it open for big ships. Both countries also construct artificial channels and river dams to attract more ships to pass through their territory.

Intense anthropogenic activity started in the region at the end of the nineteenth century and beginning of the twentieth century with construction of a dam (finished in 1904) at the cape of Izmail Chattal (Romania), which still seriously influences the distribution of the Danube water between its three branches. The dam extends from the riverbank at the junction point where the Kiliya and Tulcina branches towards the fairwater line, which is recognized as the state border between Romania and Ukraine (see Fig. 13.4). The dam was constructed to divert part of the Danube river flow from Kiliya towards the Tulcina tributary, which splits into two other branches: Sulina and St. George 17 km downriver. The traditional distribution of the Danube river flow was about 70% (Kiliya tributary) and 30% (Tulcina tributary). The latest hydrographical investigations showed that only about 55% of the river flow still passes through the Kiliya. Intense dredging and riverbed cut-off works resulted in increased flow through the Sulina tributary.

There are two artificial ship-passing channels built in Romania between 1949–1987. They were dug through the mainland to the southern part of the Danube about 400 km upriver from the outfall point. However, both channels are rather shallow and they cannot work with big, deeply-drafted ships and do not ensure night navigation.

In 2004 Ukraine initiated building of another deepwater channel from the Kiliya tributary. The first stage of the channel was completed in 2008 and the second

Fig. 13.4 Satellite image [1] of the dam at the Izmail Chattal cape. The *dark curve* shows the approximate position of the state border

stage of channel construction is expected to start soon. Completion of the project should ensure round-the-clock and two-directional passing of deeply-drafted ships year round.

Construction and exploitation of both Romanian and Ukrainian channels raised and are still raising intense protests mainly concerning negative influences on the environment.

The main problems related to the channels are:

- Redistribution of the river flow between its natural branches and artificial channels;
- Displacement of millions tons of river sand, clay and mud as a result of riverbed dredging works and construction of new channels;
- River bed cut-off;
- Intense navigation activity in the area of the bio-conservation Danube "swampy lands".

A Romanian channel connects the Danube and the Black Sea and was constructed between the city of Cernavoda and two suburbs of Constanta. Two branches of this channel go to the southern Harbor of Constanta and to the Harbor of Midia. The channel ensures one-direction navigation of small and medium drafted ships. In addition, it ensures the functioning of the Cernavoda nuclear power plant (total installed electric capacity 1,400 MW, producing about 20% of the national electricity supply). This results in partial diversion of water from the Danube main branch. Navigational activity influences the normal functioning of the river organisms and drives them away from the area. The power plant has another negative effect because

Fig. 13.5 Artificial navigational channels of the Danube river. *Arrows* point to the Ukrainian (*upper*) and Romanian channels

of the thermal pollution of the channel water. Warm cooling waters from both active units are discharged to the pond, which is connected with an artificial navigation channel. This facilitates rapid reproduction of algae, which often causes water blooming followed by an intense decrease of free oxygen content in the water. However, all these installation are located far from the transboundary region and these problems basically remain an internal responsibility of Romania. Big ships cannot pass through this artificial channel and should use natural branches of the river. All three branches are located in the transboundary region near bio-conservation area (Fig. 13.5).

Romania keeps dredging the riverbed and cut-off works excavating sand, clay and mud, and then discharges these materials along riverbanks or to the main channel of the Danube. This activity causes the formation of new banks and additional muddying of the river water. The Danube was considered as one of the muddiest European rivers even prior to the start of these activities and is now even muddier. This worsens living conditions of many commercially valuable species (e.g. such as the unique Danube herring), which causes commercial clashes between fish producers and authorities of both countries. In addition, new sandy banks worsen passing ship conditions.

Ukraine has completed construction of its own artificial channel “Bystroe” (“the Rapid”) by making one of the Kiliya sub-branches significantly wider and deeper. An artificial part of the channel is relatively short (~3.5 km) but anthropogenic activity also extends along all of the Kiliya tributary in order to secure passing of the big ships. No commercial ships used the "Bystroe" subchannel before construction of the channel and now about 1,360 big ships passed through the channel in 2009 [3]. This intense activity influences both river fauna and also unique species of the swampy lands. Sixteen species from the European Red Book and 58 from the Ukrainian Red Book can be found around the artificial channel. Its exploitation causes pollution of water with oil products, noise and, as a result, depopulation of the surrounding area. The Ukrainian channel requires regular dredging works to keep it passable. Finding places to store excavated soil is very problematic. All surrounding lands are protected by the status as a bio-conservation area, but riverbank dike works have been completed and some events of illegal soil discharge at the Danube islands have been reported. Ukraine claims that there is an insignificant environmental threat from channel construction and exploitation. However environmental threats monitoring is still in progress [2] and no firm conclusions about channel safety can be drawn yet.

All these factors contribute to transboundary ecological (in)security and are the cause of constant mutual economical and political conflicts between Romania and Ukraine.

13.7 Conclusions

As economical interest and expected financial gain from transboundary water resources increase, anthropogenic activity in all transboundary regions is expected to grow as well. Both countries are looking for better ways to secure their respective economic activities in these profitable regions. Hence they use environmental issues mostly as a means to accuse the other of violating international environment protection legislation as a way to hinder the opponent's activity.

This political and judicial conflict has been inherited by both countries from the end of nineteenth century when the first dredging and navigational works commenced in the mouth of the Danube. The conflict continues to grow and to involve an increasing number of participants. However, since Romania and Ukraine are the only countries controlling the Danube delta, this should be their common responsibility. Authorities of both countries should create a joint commission and authorize it to find solutions for all issues related to the regulation of anthropogenic activity in the delta.

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Chapter 14
Destruction of the Biosphere as the Result of Negative Influences of Different Factors on Living Organisms and the Environment

Irina Ermakova

Abstract Microorganisms, plants and animals play an important role in the ecological balance and in the formation of the climate on the planet. Physical, chemical and biological factors can influence living organisms negatively. It is well known that artificially created viruses and pathogenic bacteria can cause large epidemics, infecting extensive regions. Genetically modified organisms (GMOs), obtained by using of imperfect methods, are more dangerous and can cause high levels of mortality and infertility of living organisms and their subsequent disappearance. Our biosphere can be destroyed by different negative factors, produced by uncontrolled human activity. Can we stop the degradation of the biosphere, protect nature from destruction, and humans, animals and plants from their disappearing?

Keywords Biosphere • Ecology • Climate • Radiation • Chemical factors • Genetically modified • Humanity • Organisms • Environment

14.1 Introduction

The period 2007–2009 were the international years of planet Earth. Numerous activities such as resource used in pursuit of profit, absence of adequate controls for manufacturing, cutting down forests, urbanization, wide use of transport and chemical substances in everyday life, and military accidents have led to the considerable deterioration of the biosphere. The destructive processes in the biosphere have affected the climate, maintenance of oxygen in the atmosphere, the formation of ozone gaps and ozone layer exhaustion, desertification and disturbance of the

I. Ermakova (✉)
Institution of Russian Academy of Sciences, Institute of Higher Nervous Activity and Neurophysiology of RAS, Academy of Geopolitical Problems, Moscow, Russian Federation
e-mail; Ermak_i@mail.ru

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global water cycle. Sharp temperature drops and heat waves,, frequent cases of storm rains and flooding in many countries of the world, snow in Africa, Syria, Greece, Turkey, etc. confirm a changing situation on the planet. Mankind has faced global environmental problems. What are the reasons for negative ecological changes on the planet?

14.1.1 Different Negative Factors

There are three kinds of factors (physical, chemical and biological) that can destroy the environment and influence negatively living organisms, causing genetic mutations, brain disorders, tumors, infertility, etc. Among physical factors first of all are radiation, electromagnetic fields, ultraviolet and X-rays. Hazards from chemical environmental contamination are reflected shown in the direct and mediated toxic influence on living organisms [37]. It has been found that formation of complex connections of technogenic polluting substances with DNA and RNA is the reason for harsh genetic diseases. Great attention is necessary to pay to biological factors such as viruses, pathogenic bacteria, and genetically modified organisms (GMOs). It is well known that artificially created viruses and pathogenic bacteria can cause large epidemics, infecting extensive areas. GMOs, obtained by using imperfect methods, can be more dangerous and cause a high level of mortality and infertility of living organisms and their following disappearance. Genetically modified organisms (GMOs) contain genes that under natural conditions are not present in plants usually. There are several reasons for GMO hazard to the Environment. The replacement of natural plants by GMO insects and herbicides, leads to a decrease of plant diversity and to the destruction of trophic chains and disappearance of different animal species. A more dangerous GMO effect is mediated by the possibility of foreign genes to be introduced into the genome of cells of other organisms as a result of horizontal gene transfer (from species to species). This kind of introduction can lead to mutations and infertility.

14.1.2 Mental Diseases

Last years the quantity of the data specifying in dependence of some mental diseases from influence of the adverse factors and, first of all, from the toxic substances has considerably increased. It has been shown experimentally that heavy metals (mercury, lead, cadmium, etc.), polluting water and soil, can lead to the development of diseases of central nervous system, changing a metabolism of brain neurotransmitters, break synaptic transfer, influence on chromosomal reorganization. Now the syndrome of deficiency of attention with hyperactivity as the result of lead effect on organisms is often found in children. The investigation of German and Dutch scientists [31] has shown that the urbanization (the city environment) increases risk of development of a schizophrenia and other mental diseases, and it does not depend on an age, sex, a social status, a drug intake and hereditary predisposition to mental diseases.

Diseases can be caused also by mutation or destruction of genes. Now in the scientific literature the great attention is given to the destruction of genes in sexual chromosomes of the person, animals and plants. The sexual male Y-chromosome has appeared the most sensitive to influence of adverse factors of the environment. Proceeding destruction of genes in sexual chromosomes of the person can lead to the strong updating male and female, to disappearance of many kinds of animals and plants [4, 6, 11].

It has been shown experimentally that mutations and destruction of genes can be caused by the action of radiation, toxic substances, ultra-violet and X-rays. The distribution of radioactive elements, as tritium, technogenic carbon C14, plutonium and others after Chernobyl tragedy occurred divergently on the large distances. On atomic power stations isotope C14 together with atoms of carbon C12 gets into the cells of alive organisms, causing genetic and somatic damages [1]. Hazard of chemical environmental contamination, especially of pesticides, is shown in the direct and mediated toxic influence on live organisms. For example it was shown that glyphosate in microdoses (0.00001% solution) induced apoptosis and necrosis in human umbilical, embryonic, and placental cells [2].

14.2 GMO Background: Development and Current Level of GMO Use

Biological factors as viruses, pathogenic bacteria and, especially, genetically modified organisms (GMOs) could be more dangerous for the nature and living organisms than other factors. As it was mentioned earlier the artificially created organisms can infect a great amount of territories.

14.2.1 Two Types of Gene Manipulations

Two types of gene manipulations are well known: the first type is connected with the insertion of foreign genes into the host genome (genetically modified organism – GMO) and the second type – with the gene deletion.

Main sources of the hazards of GMO are accepted by scientists as those due to the new genes, and gene products introduced; unintended effects inherent to the technology; interactions between foreign genes and host genes; and those arising from the spread of the introduced genes by ordinary cross-pollination as well as by horizontal gene transfer [28].

At the same time deletions of genes can be reason of the functional disturbance, important for the natural development. Example of this kind modification is the deletion of genes in ice nucleation-active bacteria (*Pseudomonas syringae* and *Erwinia herbicola*) for protection plant crops from the frost damage.

Pathogenic changes or disappearance of bacteria, plants and animals, which play an important role in the ecological balance, could be reason of the destruction of the ecosystems, impairment of the Environment and climate change.

14.2.2 Why GMO Are Dangerous?

The term genetically modified organisms (GMOs) refers to plants, microbes and animals with genes transferred from other species in order to produce certain novel characteristics (for example, resistance to pests or herbicides), and are produced by recombinant DNA technology.

Hazard of GMO application is connected with the several reasons: (1) replacement natural plants by genetically modified plants leads to the considerable reduction of a biodiversity; (2) the destruction of trophic chains: occurrence of GM plants steady against insects, can be reason of the disappearance of many kinds of insects, then birds and small animals, then mammals and so on; (3) embedding of foreign genes into the genome of other organisms that can lead to occurrence of genetic chimeras and wide spread infertility; (4) bioterrorism, and others.

It is clear that new scientific direction as biotechnology can be future of humanity. People can solve many important problems as hunger, diseases, climate change and many others using methods of genetic engineering. From another side, if the methods are not correct the genetic engineering can cause infertility, hereditary diseases, cancer, premature death, disturbance of ecological balance, climate change.

Scientists paid a great attention to the methods of gene introduction, concluding that complication of GMO technology is combined with its imperfection that is reason of biological risks [34, 36 and others].

14.2.3 Methods of Gene Introduction

The analysis of gene introduction ways is very important for understanding of GMO hazard. Natural infectious agents exist which can transfer genes horizontally between individuals. There are *viruses* and other pieces of parasitic genetic material as *plasmids* and *transposons*, which are able to get into cells and then make use of the cell's resources to multiply many copies of themselves or to jump into (as well as out of) the cell's genome [28]. Two standard methods are used generally to introduce new DNA (genes) into a plant cell, which is going to be modified: (1) the particle acceleration, or "shot-gun" technique, and (2) agrobacterium method, or infecting the cells by the modified pathogen, with the help of *Agrobacterium tumefaciensis*. Both methods are not perfect and don't guarantee that the rest of the plant genome remains unchanged. Therefore the safety of the GM-crops created with the help of these methods cannot be guaranteed neither for human and animal health, nor for the Environment [12, 14, 34].

The "shot-gun" technique was developed in 1987. It can be used to transform all kind of plants, bacteria, moulds, algae and animals. A device was built to shoot small particles of gold or tungsten against cells. These particles can be coated with DNA material and are so small that they can penetrate the cells without lasting damage. *Agrobacterium tumefaciens* bacteria found in soil are used for agrobacterium method. This unique bacterium is able to infect the plant and transfer it's DNA to the plant with the help of plasmids (circular DNA). These plasmids are responsible for the tumor activity and are therefore called "Tumor inducing Plasmids" (Ti-plasmids).

14.3 Genetic Manipulations and Review About Negative Aspects, as a Potential Hazard for Human Health and the Environment

Widespread distribution of artificially modified organisms created by genetic manipulation that affects the environment negatively is a great ecological experiment with an unknown end. Scientists worldwide warned about hazard of GMO for the Environment repeatedly [5, 12, 14, 20, 35 and many others]. In the "Open Letter from World Scientists to all Governments concerning Genetically Modified Organisms (GMOs)" (2000) the scientists indicated that they were extremely concerned about the hazards of GMOs to biodiversity, food safety, human and animal health, and demand a moratorium on environmental releases in accordance with the precautionary principle (http://www.i-sis.org.uk/list.php). This letter was signed by 828 scientists from 84 countries.

14.3.1 Negative Influence of GMO on Soil Microorganisms and Insects

The increasing number of the reports on the ecological risks of GM plants for evaluating of the environmental impact of GM crops as soil persistence, ecosystems functioning, soil fertility causes special attention. Major environmental risks associated with GM crops include the genetic pollution [25] and influence of GMOs on non target soil microorganisms [30]. Turrini with coauthors described the negative effect of transgenic corn plants (Bt 11 and Bt 176) and their residues on soil microorganisms. Both transgenic plants suppressed fungal growth and root colonization ability.

Negative effect of GMO on insects was shown by different scientific groups. One of the most known researches, published in *Nature*, showed that larvae of the monarch butterfly, *Danaus plexippus*, reared on milkweed leaves dusted with pollen from Bt corn, ate less, grew more slowly and suffered higher mortality than larvae reared on leaves dusted with untransformed corn pollen or on leaves without pollen [16]. Adverse sub lethal effects of Bt corn incorporating event 176 on black swallowtails in the field was found by Zangerl et al. [38]. The reduction of life expectancy of ladybirds, fed by pest aphid, planted in GM-potatoes, was described in the Annual Report of the Scottish Crop Research Institute [3].

14.3.2 Hazard of GMOs for Mammals

Experiments, conducted by English scientist Arpad Pusztai showed that the potatoes modified by the insertion of the gene of the snowdrop lectin (an insecticidal protein), stunted the growth of rats, significantly affected some of their vital organs, including the kidneys, thymus, gastronomies muscle and damaged their intestine and immune system [24]. This GM-potatoes caused the proliferation of cells in the intestine [10]. Significant modifications in the cells of liver, exocrine pancreas and testis of mice, fed by diet containing Roundup Ready GM-soybean, were shown by Malatesta with co-authors [17, 18, Vecchio et al. 2004]. In another investigation the transgenic expression of non-native proteins in GM-pear led to the synthesis of structurally modified form possessing altered immunogenicity in mice [23]. Seralini with co-authors [27] observed the hepatorenal toxicity in rats after the consumption of GM-maize MON863. Austrian scientists found the pathological changes in internal organs and disturbance of reproductive functions in mice, fed by another line of GM maize NK603x MON810 [32]. Experiments with GMOs showed the hazard of Ready Roundup soy-bean modified by the transgene CP4 EPSPS (5-*enolpyruvylshikimate*-3-*phosphate synthase*, *from Agrobacterium sp*., *strain CP*4, *Monsanto*) (RR, line 40.3.2) for rats and their offspring. High mortality of newborn rats in the first generation, low body weights of some pups, pathological changes in internal organs and disturbance of reproductive functions were found [7–9, 19, 21]. In the research of [26] the plasmid containing the gene for the green fluorescent protein (pEGFP-C1) were fed to pregnant mice. Foreign DNA, orally ingested by pregnant mice, was discovered in blood (leukocytes), spleen, liver, heart, brain, testes and other organs of foetuses and newborn animals.

14.3.3 Second Type of Genetic Manipulation – Gene Deletion

Modification of the genome of ice nucleation-active bacteria (*Pseudomonas syringae* and *Erwinia herbicola*) for protection plant crops from frost damage is one of the examples of this kind of manipulation [5, 13, 15, 22, 29, 33]. Modified bacteria can cause the serious changes in the nature.

Samples of plants from California, Colorado, Florida, Louisiana, and Wisconsin were tested for the presence of ice nucleation-active bacteria: either Pseudomonas syringae or Erwinia herbicola [15]. Numbers of ice nucleation-active bacteria were large enough to suggest that plant surfaces may constitute a significant source of atmospheric ice nuclei, that necessary for freezing injury to occur. It is known that the biological substances – bacteria, viruses, seaweeds, spores of mushrooms – made about a quarter of weight of air suspensions. The smallest particles become the centres of condensation of water drops or ice crystals. Thus, clouds are formed under the influence of biological organisms also. Especially two kinds of bacteria – ice nucleation-active bacteria *Pseudomonas syringae* and *Erwinia herbicola* – play in atmosphere significant role, promoting the formation of ice crystals at temperature up to −8°, mediated by bacterial membrane ice-nucleating lipoglycoprotein complexes (ice+) [13]. Bacteria lost the possibility of ice formation after **the deletion of genes** of lipoglycoprotein complexes (ice-). What will happen if the native bacteria do not sustain competition with the modified bacteria? In this case the snow and rain lack and thawing of ice can occur and it, unfortunately, happens [5].

14.4 Conclusion

It is quite important to understand the character of influence of different factors on nature. Some of them are very danger and can destroy the environment, killing most part of alive organisms. One of the global goals is the protection of the Environment from the uncontrolled distribution of the different negative factors as radiation, toxic chemical factors, and imperfect artificially modified organisms as GMOs that as the fire grasp increasing the areas on the Earth. Genetical pollution via GM seeds and GM pollen is the great problem for the Earth. The majority of transgenic organisms become fruitless after one or more generations. Animals that eat GM-plants have problems with reproductive functions and in one–two generations disappear. Global transgenization can result in disappearance of significant part of alive organisms on the planet and lead to the destruction of biosphere and climate change. Creation of the new kind of modified organisms, safe for the Environment and humans is quite important for the safety of our Planet.

The mankind has two ways of development. The first way is following the existing way. And soon people will face the sharp deterioration of the environment; disappearance of a considerable quantity of plants and animals; increase in number of mentally abnormal people, criminality growth; military conflicts and acts of terrorism. The second way is to stop the process of destruction of biosphere by means of the strict control over a state of the environment and revealing of the reasons of its deterioration; actively to develop and introduce the safe technologies directed on restoration of broken ecological balance, recycling of a harmful and dangerous waste, biodiversity preservation. A new epoch will come. To survive, people should create the new dominant directed on balanced interaction of the person and the nature. It is necessary to pass the development of the scientifically-organized, operated, ecologic-social and economic system. Only this way will give the chance to prevent ecological accident and to rescue mankind from self-destruction.

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NATO Advanced Research Workshop
Environmental Security and Ecoterrorism
April 27–29, 2010, Hotel Izmailovo
Moscow, Russian Federation

Day 1 – Tuesday, April 27

Morning Session (20 min±10 min questions)

9.00–9.30 am **– Registration**

9.30–10.30 **–** Formal Opening of the workshop **(Chairs: Leonid Ivashov, Vladimir Krivilev, Hami Alpas, Irina Ermakova**) and Greetings: (**Leonid Ivashov,** President of Academy of geopolitical-AGP problems)

10.30–11.00 – Ecological problems of modern world: philosophical aspects **(Konstantin Sivkov, Russian Fed.)**

11.00–11.30 – Socio-technical environment: Networks and vulnerability **(Sebastien Brunet, Belgium)**

11:30–12:00 – Coffee break

12.00–12.30 **–** Destruction of biosphere as the result of negative influence of different factors on alive organisms and the environment **(Irina Ermakova, Russian Federation)**

12.30–13.00 – Research and information system for monitoring of the aggressive impact on the environment aftermath for the International situational center **(Vadim Kretov, Russian Fed.)**

13.00–13.30 – Discussion

13:30–14:40 – Lunch

Afternoon session (15 min ±5 min questions)

14.40–15.00 – Scientific basis of global earth security **(Oleg Sizov, Russian Fed.)**

15.00–15.20 – Effective environmental security policies for a sustainable future in eastern Europe **(Liviu Daniel Galatchi, Romania)**

15.20–15.40 – Methodological aspects of the assessment of earthquake impact on physical environment and exposed community **(Vasile Alcaz, Moldova)**

15.40–16.00 – Influence of human impact on climate change, air and water in the Arctic (**Fedor Pashennykh, Russian Fed.)**

16:00–16:20 – Coffee break

16.20–16.40 – Central Asia: Ecological threats and priorities of the regional cooperation **(Abduvali Isadjanov, Uzbekistan)**

16.40–17.00 – Development, implementation of regional assessment and management of land distribution in the Ukrainian steppe for environmental security **(Larysa Anisimova, Ukraine)**

17.00–17.20 – Studying antropogenic emissions impact upon atmospheric air quality over the Tashkent territory **(Tatyana Smirnova, Uzbekistan)**

17.20–17.40 – The Problems of Management and effective utilization of water and ground resources in Uzbekistan (**Suriya Turaeva, Uzbekistan**)

17.40–18.00 – Desert ecosystems, Impacts of anthropogenic factors **(Mohamed Tawfic Ahmed, Egypt)**

18.00–18.20 – Desertification of territory of Mongolia **(Khash-Erdene Sambalkhundev, Mongolia)**

18.20–19.00 – Wrap-up and conclusions

19.30 – Dinner **(hosted by Academy of Geopolitical Problems-AGP)**

Day 2 – Wednesday, April 28

Morning Session (20 min±10 min questions)

09.00-09.30 – Environmental Security and its meaning for the State **(Peter Liotta, USA)**

09.30–10.00 – Information exchange between countries at detection of the facts of ecological terrorism **(Vladimir Krivilev, Russian Fed.)**

10.00–10.30 – The concept of eco-terrorism: Anticipating the future **(Simon Berkowicz, Israel)**

10.30–11.00 – Impact of eco-terrorism on environmental security **(Hami Alpas, Turkey)**

11:00–11:30 – Coffee break

11.30–12.00 – Environmental lead contamination as a factor of eco-terrorism and a threat to ecosystem and public health (**Alexander Omelchenko, Canada)**

12.00–12.30 – Impact of pesticides and herbicides as organic micro-pollutants on environment and risk for the mankind **(Faruk Bozoglu, Turkey)**

12.30–13.30 – Discussion

13.30 – 15.00 – Lunch

Afternoon session (15 min ±5 min questions)

Short presentations on ecoterrorism by participants and debate-Part I ***(Moderator: Alexander Omelchenko, Canada)***

15.00–15.20 – Prospects of terrorism, conflicts and distribution of bio-terrorism on Northern Caucasus **(Mukhtar Gazaev, Russian Fed.)**

15:20–15:40 – Urban air quality management in information system of environmental monitoring **(Volodymyr Nochvai, Ukraine)**

15.40–16.00 **–** Ecological prospect of mankind and youth **(Engel Tagirov, Russian Fed.)**

16.00–16.20 – Ukraine and Romania: Cross-boundary environmental security and ecology of the shared water resources **(Igor Winkler, Ukraine)**

16:20–16:40 – Coffee break

Short presentations on ecoterrorism by participants and debate-Part II ***(Moderator: Sebastien Brunet, Belgium)***

16.40—17.00 – Environmental nanothreats and nanotoxicological peculiarities of nanoobjects **(Oleksii Kharlamov, Ukraine)**

17.00–17.20 – Management of Complex dynamic ecosystems:An ecological-economic modeling approach **(Ganna Kharlamova, Ukraine)**

17.20–17.40 – Environmental risks of silver nanoparticles applications **(Renat Khaydarov, Uzbekistan)**

17.40–18.30 **– General discussion**

19.30 – Dinner **(NATO-SPS)**

Day 3 – Thursday, April 29

Morning Session (15 min ±5 min questions)

Short presentations on environmental security by participants and debate- Part I ***(Moderator: Peter Liotta, USA)***

09.00–09.20 – Polyfunctional effect of pesticides on biological objects as a reason for their toxic properties (**Elena Saratovskikh, Russian Fed.)**

09.20–09.40 – Potential risks of using pesticides (**Sergei Screbec, Belarus**)

09.40–10.00 – Environment security of eroded soils and heavy metals pollution risk assessment **(Mykola Kharytonov, Ukraine)**

10.00–10.20 – Processing of hyper spectral imagery for contamination detection in urban areas, **(Sergei Stankevich, Ukraine)**

10.20–10.40 – Prospective technologies of neutralizing toxic waste and gas discharges **(Victor Grigoriev, Russian Fed.)**

10:40–11:00 – Coffee break

Short presentations on environmental security by participants and debate-Part II ***(Moderator: Simon Berkowicz, Israel)***

11.00–11.20 – Ecology and health **(Viktor Lectorov, Belarus)**

11.20 – 11.40 – Algae toxins and its danger for human health and environment **(Larisa Parshykova, Ukraine)**

11.40–12.00 – Integrated management of water basin toward flood prevention and human security **(Diana Bejko, Albenia)**

12.00–12.20 **–** Influence of novel food processing technologies on environment **(Mladen Brncic, Croatia)**

12.20–13.30 – **General discussion**

13:30–15:00 – Lunch

15.00–15.30 – Theoretical issues of food chain security and case studies **(Ales Komar, Czech Rep.)**

15.30–16.00 – Food defense and security: The new reality **(Alexandra Veiga, Portugal)**

16.00–16.30 – Food chain security **(Beyazıt Cirakoglu, Turkey)**

16.30–17.30 – General Discussion ***(Moderator: Faruk Bozoglu-Turkey)***

16.30–17.00 – Wrap-up: Summary of the results of the workshop **(co-directors).**

17.00–17.30 – Final Remarks and closing.

19:00 – Dinner + Closing Cocktail **(Closing Cocktail is hosted by Academy of Geopolitical Problems-AGP)**