ENVIRONMENTAL FORENSICS FUNDAMENTALS

A Practical Guide

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Ioana Gloria Petrisor

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“Our fingerprints don’t fade from the lives we touch!”

(“Remember Me” movie, 2010)

To my husband Adrian and to my parents Maria-Viorica and Ioan

… whose fingerprints touched my life and have shaped me into who I am!

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Foreword

Lorne G. Everett, Ph.D., D.Sc.

Rarely does one have the opportunity to see, much less participate in, a stellar environmental career in America that begins in a far-off country such as Romania. I am reminded of my career, which began in Canada and was dependent upon highly successful technical books that catapulted my career. This book, which grew out of the intense passion of Dr. Ioana Petrisor for environmental forensics, is destined to be a best seller not only for its technical merit but also for the sheer enjoyment of how the book was crafted.

Parts of this highly detailed and highly referenced textbook were derived from Dr. Petrisor's initial research when she was a post-doctoral biochemist working on projects for the United States Department of Energy through the Institute for International Cooperative Environmental Research at Florida State University (FSU). It was at that location, while I was a member of the United States Navy's, Naval Facilities Engineering Service Center, National Hydrocarbon Test Site Program, that I first met Dr. Petrisor. I was asked to participate in and provide training at the International Containment Technology Conferences sponsored by the United States Department of Energy at FSU. Her work on phytoremediation and phytoextraction of heavy metals was of great interest to the research community within the US Department of Energy and formed the underpinnings for her thorough discussion of the tree-ring fingerprinting topic in the book.

My impressions of Dr. Petrisor were so strong that I enthusiastically provided a recommendation for her to join Dr. Teh Fu Yen, arguably America's "finest hydrocarbon chemist" at the University of Southern California in Los Angeles. Working in Dr. Yen's state-of-the-art research laboratory, Dr. Petrisor was able to further develop her innovative remedial approaches and deepen her understanding of fate and transport of contaminants in subsurface environments. She has also gained useful insights into fingerprinting petroleum and chlorinated hydrocarbons. The sophisticated technologies on which she worked with Dr. Yen provide the bases for her hydrocarbon fingerprinting and chiral fingerprinting chapters within the book. Subsequently, Dr. Petrisor worked on developing her forensic skills at DPRA, Cardno ENTRIX, and Haley & Aldrich, wherein I had the pleasure of working directly with her on several high-visibility environmental forensic cases. While working with Dr. Petrisor on several cases, I saw her develop exceptional deposition and trial skills. One jury consultant noted she was the finest expert he had seen on the stand. In court Dr. Petrisor learned which forensic technologies made the largest impressions on lay juries. She has refined her courtroom experience and biochemical insights into an understanding of successful forensic techniques and forensic strategies, which are clearly evident in the book.

Perhaps of greatest importance to this forensic book is the in-depth experience Dr. Petrisor has gained as editor-in-chief of the *Environmental Forensics Journal*, an international, quarterly, peer-reviewed publication offering scientific studies that explore source, fate, transport, and ecological effects of environmental contamination, with contamination being delineated in terms of chemical characterization, biological influence, responsible parties, and legal consequences. Serving in this capacity, Dr. Petrisor has seen, on a weekly basis, the evolution of environmental forensics at the international level. Her professional paper reviews and editorials have garnered a stellar place in environmental forensics technologies. Her familiarity with this international journal on environmental forensics has allowed her to populate each forensics technique with not only the classic references on each technique but also the latest references which continually are improving and solidifying the forensic techniques that she presents. This book is derived from the passion of Dr. Petrisor for her science but, more importantly, this book represents the current state of the art in environmental forensics at the international level.

I would be remiss if I did not comment that Dr. Petrisor is driven. She can voraciously evaluate enormous numbers of documents and data and can derive technical interpretations and defendable solutions faster than anyone I have ever met. The structure upon which she has based this book perhaps identifies how she can maintain this intensity. Just as the *CSI* (Crime Scene Investigation) TV series has been ranked the Number 1 International Television Drama Series three times, Dr. Petrisor approaches each case and each technology in her book with the same fascination and enthusiasm to arrive at a defendable case.

The reference to Agatha Christie's work in the Preface is highly symbolic not only for Dr. Petrisor but for all of those readers who have enjoyed exquisite mystery stories solved through forensic techniques. This coupling of sophisticated techniques, which is woven together like a *CSI* plot in an Agatha Christie novel, gives the reader an opportunity to enthusiastically and with great anticipation work their way through this book on environmental forensics.

It is my distinct honor and pleasure to highly endorse this state-of-the-art book on environmental forensics.

Disclaimer

Throughout the book, site names and specifics are not revealed as they are not relevant for the demonstrative purposes for which the case studies are presented. The information presented from various case studies should not be used by anyone for any purposes other than learning and acquiring a strategic understanding of challenges and solutions in the field of environmental forensics.

The information and the presented lines of evidence strictly relate to the opinion of the author based on her interpretations and do not necessarily imply that legal or regulatory acceptance of these opinions/lines of evidence has taken place.

Any interpretations, opinions, and advice in this book reflect the views of the author (based on personal experience, knowledge, and/or cited publications) and are given here for illustrative purposes.

The solutions and interpretations related to various case studies presented in this book may not be directly applicable to other sites/case studies, even if they seem similar or seem to belong to the same type of challenges. Every site should be evaluated individually and within its historical context. It is the role and the responsibility of each forensic investigator to develop his or her personal interpretations and conclusions based on knowledge, experience, and a thorough evaluation of historical and analytical data available for any given site.

Note that the interpretations and opinions included throughout this book were reached after a detailed study of historical files and other available data and lines of evidence (for each individual case). That level of detail is not presented within the limited pages of this book as the book is designed to serve as a practical guide for fast learning.

The summary description of each case study presented in Part III of the book is simply meant to convey the main concepts and findings relevant to the forensic purposes and is not meant to be comprehensive. Since each case study has many specific aspects and details, it is not possible to depict here every feature/characteristic related to each site. The purpose of the book is to provide selected relevant information (snapshots of the forensic investigation) with the author's interpretations based on her knowledge and understanding of the "big picture." The final goal is to point out and equip the reader with adequate knowledge and strategy-building skills to tackle difficult environmental forensic challenges on their own.

Preface

Why Read This Book?

I believe that anyone who becomes excited by the *CSI* (Crime Scene Investigation) TV series and who values our environment would be interested in reading this book.

Likewise, if you are an environmental professional who wants to specialize in environmental forensics, to apply certain forensic tools (e.g., isotopic testing or tree coring and analysis), or simply to understand the opportunities that come with using forensic techniques, this book provides you all the information you need.

I truly believe that the information included in this book will enable any professional (whether scientist, engineer, lawyer, regulator, or industrial site operator) to acquire the knowledge and understanding for practicing in the exciting field of environmental forensics without spending a lot of time going through the many thousands of pages available on this topic. The book provides principles and just enough detail, examples, real and hypothetical case studies, and hints to guide the reader through the challenging field of environmental forensics. It also equips the reader with key knowledge and strategy-building skills that I have reached after many years of research and practice in this field.

I remember that when I started working in environmental forensics I was given several bulky textbooks and many articles. In the passing years, I succeeded in reading all that and many additional materials. I now realize how useful it would have been if I had a guide-type book consistently addressing the main forensic techniques to date and providing key applications and selective references that would enable the reader to learn the basics from a single source. I believe this volume achieves exactly this objective.

Moreover, as a journal editor and an instructor in the field, I realized how important it is to teach your readers and students the principles and concepts needed for strategy building. With this in mind, I noticed that many common forensic challenges can be grouped together in certain main types that require certain strategies. Typically, professionals publish case studies but do not generalize their cases by type of challenge. This book goes beyond presenting case studies by introducing some common types of forensic challenges and strategies to be followed. There are, of course, other types of challenges that are not included here, but I believe that some of the most common ones are.

It is my firm belief that environmental forensics is not only exciting but also needed to ensure the health of our planet and of all of us.

What Is Environmental Forensics?

Environmental forensics is a growing scientific field that combines the excitement of detective stories with the rigor of the court of law and the innovation of cutting-edge science to solve “environmental crimes.” The crimes against our environment sometimes go unnoticed and are perceived as less interesting and important compared to human crimes, yet they may affect all of us without our realization. It is not only the esthetics of our natural environment that is affected but also potentially our health, natural resources, and ultimately, the legacy we leave to future generations. After all, there is only one Earth, and until humans find alternative homes in space, we should strive to preserve our Earth the best we can. Environmental crimes are among the most stringent problems of modern human society, and environmental forensics plays a key role in identifying and preventing such crimes, as well as ensuring that the responsible parties contribute their fair share to the required environmental restoration.

I hope that by now the reader shares my excitement related to this growing field of science. But, what exactly is environmental forensics? Generally, *forensics* means reconstruction of past events based on the traces that are left behind. Specifically, environmental forensics focuses on reconstruction of past contamination (pollution) events and related fate and transport of contaminants (pollutants) through the environment in which they were released. Hence, the environmental forensics “mystery” can be described by a few basic questions routinely asked at contaminated sites:

- Who has contaminated the environment?
- When did the contamination happen and how?
- If additional responsible parties are identified, how much has each of them contributed?

To answer such questions, environmental forensics makes use of a variety of scientific investigative techniques, usually referred to as “fingerprinting” techniques. Thus, environmental forensics uses fingerprinting techniques to reveal how the existent contamination got to the place where it is detected, what the source(s) is, or when the contamination was released. The forensic investigation may point out multiple releases of the same or different chemicals at the same site, which usually triggers the need for allocation of contributions for each identified release. Allocation of contributions becomes especially relevant when different parties (potentially responsible parties, PRPs) may be responsible for a distinct release in time at the same site or when multiple parties from neighboring sites may have released contamination that finally commingled within the studied contaminated plume. In other words, multiple releases from various sources in time and space may contribute to a detected contamination plume. It is the role of the environmental forensic investigator to solve such intricate environmental puzzles to provide adequate evidence for litigated and nonlitigated situations.

What Are Specific Applications of Environmental Forensics?

When one talks about *forensics*, inevitably a crime scene comes to mind. This also applies to environmental forensics. Based on a common perception, environmental forensics is perceived as using scientific methods to resolve legal disputes resulting from environmental crimes. The *environmental crimes* term generally refers to any intentional or accidental release of contaminants in the environment.

Apart from its "classic" application to resolve environmental disputes (e.g., litigation support), environmental forensics provides value and should be applied beyond the court of law, in regular environmental site investigations. This is because environmental forensic techniques are valuable tools for many environment-related issues, such as contaminated site characterization and remedial design. Incorporating environmental forensics into regular site assessment and remedial investigation could bring myriad benefits, such as the following:

- Potential substantial cost savings in site remediation by using adequate cleanup limits. Environmental forensics has a proven record of successful use in defining and obtaining regulatory acceptance of site-specific cleanup limits (see also Case Study 7.1 from Section III of this book), which should take into account background contamination values and potential off-site contributions.
- Effective long-term remediation by enabling better remedial design tailored for specific sources and release types. This should come as no surprise since the goal of the forensic investigations is to find the "culprit" or source, which is not always obvious; there are reported cases

of contamination suddenly increasing after years of remediation due to an additional or ongoing source uncovered by routine site testing.

- Elimination of futile costly active remediation alternatives by providing convincing straightforward evidence for the acceptance of "green" remedial alternatives such as natural attenuation (e.g., isotopic evidence is decisive in proving that monitored natural attenuation [MNA] is a viable remedial alternative at a site).
- Reaching/developing reliable site conceptual models by using the most accurate site characterization and understanding of contaminant fate and transport mechanisms.
- Potentially reducing the time to achieve site closure by using adequate remedial design.
- Elimination or minimization of future vulnerability to legal claims by collecting adequate evidence before it is too late (evidence is lost or substantially transformed). Environmental forensic investigations provide valuable information that can be used in any future disputes to disprove unsubstantiated claims.
- Providing reliable evidence for insurance claims by age-dating contamination at sites with multiple insurance carriers through the years. Reliable age-dating of contamination is needed for insurance claims to address the right insurance carrier.
- Loss prevention associated with property transactions by early identification of potential future liability types of issues.

What to Expect from This Book

This book provides an easy-to-follow and well-organized guide for anyone (basic scientific knowledge may be required, particularly in the fields of chemistry, biology, and geology) interested in learning environmental forensics or simply becoming informed on what forensics means when applied to the environment, what the *CSI*-type of environmental story problems are, and how we can solve them. This book also aims to raise awareness and interest in the emerging field of environmental forensics.

The book was written for the busy individuals of modern society and was intentionally kept brief and to the point. The intent is to provide concepts and principles to enable the reader not only to understand the large variety of forensic techniques and applications but also to practice in this field without the need to consult a large volume of material from many sources. From this point of view, I truly believe this book fills a gap in spite of the growing scientific literature (including textbooks and articles) in this field. Note that I have intentionally included selected key references only to provide more in-depth information on certain topics in the most efficient way.

The book contains relevant information related to environmental forensics evidence, techniques, and practical applications. Both general and specific information are provided in an easy-to-understand and easy-to-use way. The presented information is organized in three main parts:

- *Section I* covers the evidence. Forensic investigations look for key evidence to solve environmental puzzles. It is the evidence—that small unusual trace left unnoticed—that provides clues and helps reveal the truth. This is why this book emphasizes the evidence and its role in the forensic investigations and court proceedings. General forensic concepts and hints for obtaining defensible evidence are also provided.
- *Section II* covers the state of the art in environmental forensic investigative techniques. The information for each presented technique has been carefully selected and organized for easy understanding and learning. In addition, a step-by-step practical guide (generally in a "Method Steps" section) is included to enable the reader to apply the technique in practice. Main limitations and subsequent recommendations and hints are also included along with application examples (hypothetical examples as well as examples from the literature or from my cases). The emphasis was to provide the information in an organized way without getting into much scientific detail. Selected key references are given for those interested in acquiring more details on any given matter or technique.
- *Section III* covers strategy building. Several common types of environmental forensic challenges are strategically discussed and exemplified through real case studies in which I was involved. Each case study is presented in the form of a "story." The cases have been selected to cover a large array of forensic scenarios and contaminants, as well as a variety of forensic approaches. This part of the book illustrates how "real-world" forensic puzzles are approached and ultimately solved using the techniques described in Section II of the book. Key remarks are included to provide useful information for similar cases and communicate the "lessons learned" from each story.

Ultimately, the presented information is meant as a guide to help the reader understand and choose the appropriate forensic techniques for solving environmental and legal puzzles and obtaining defensible evidence.

Why Is Environmental Forensics Fascinating?

> Our environment today is the result of a complex overlay of human activities through time.
>
> **Ebert, 2007**

I was always fascinated by mystery and detective stories. It started when I first read a novel by Agatha Christie, which happened to be *And Then There Were None*, the world's best-selling mystery and the seventh-most-popular novel of all time. The story describes the perfect crime. It is the story of a crime that remains unsolved and yet preserved in a message from a bottle floating ashore … a message written by the criminal himself, who wanted the world to marvel at his crime. The story is intriguing, culminating with a dramatic switch of criminal-victim positions. To me, this first mystery novel not only created an intense passion to read and watch mystery stories but also ignited an acute desire to solve them.

I realized that for any mystery there are clues, and that any action leaves traces, usually referred to as evidence. Even in the ideal case of the perfect unsolvable crime from Christie's story, a trace does exist: the message in the bottle floating ashore, which made it possible to unravel the whole intriguing story.

With all these in mind, I began organizing my thoughts and identifying tools, which I then tested, applied, and improved to solve more and more mystery stories. The more I practiced, the better I became in identifying clues and solving mysteries. I also noticed that if I imagined my own short mystery stories, I created the framework to experiment with the efficiency of my mystery-solving tools. The principle is that of testing a new product (such as a new medicine or remedial agent for a contaminated environment) in the lab before field application. For example, I created my own mental algorithm for tackling complex mysteries involving 10 steps, which I still remember and value today. I am now happy to share those steps with you, my reader, since to me they proved so useful in mystery solving and may be applicable to any type of crimes—human or environment related.

Mystery-Solving Steps

1. Gather available information from
    a. *The story*—careful reading of the story;
    b. *Other related information*—acquiring useful information from sources other than the story itself;

2. Double-check acquired information for accuracy and details;
3. Create and understand the "big picture"—map (write down and organize) the acquired information (*evidence*), including
    a. *Objective information*—discern and write down all the undisputable facts;
    b. *Subjective information*—identify and synthesize any "speculative" information;
4. Identify clues and gaps, for example:
    a. *Relevant* information;
    b. "Unfitting details"—data that *do NOT match* the general facts;
    c. *Unusual, unexpected* data/details/human reactions, which provide *hints*;
    d. Missing information and data;
5. Establish "suspects" and hypotheses:
    a. Link the facts and clues to reach the story's end;
    b. Always consider alternative scenarios;
6. Fill data gaps (if needed):
    a. Collect additional evidence (samples, analyses, data processing, etc.);
    b. Conduct interviews with suspects and relevant people;
    c. Acquire additional relevant information (triggered by identified suspects/hypotheses);
7. Test various hypotheses relative to clues and all acquired data/information:
    a. Consider theoretical cases: "If I were … , what would I have done?" approach;
    b. Consider other similar cases and lessons learned from past cases;
    c. Interpret the unfitting detail within the big picture;
8. Solve the mystery—select the "more-likely-than-not" hypothesis;
9. Record lessons learned and "solving strategies" to help solve future mysteries;
10. Document and organize the information (case and findings) for quick future reference.

These steps were not only useful for solving mysteries but also made me understand that:

> "Learning is organized knowledge!"

Years have passed. My attraction to mystery stories along with my profound admiration for my parents and the desire to learn and discover new things every day like my parents (both scientists) inspired me to become a scientist. Yet, little did I know then that, beyond research and discoveries, I would—one day—become a "detective" investigating real "environmental mysteries." In other words, I am fortunate to apply my mystery-solving skills along with my scientific knowledge and experience to solve real-world environmental mysteries that relate to the biggest environmental crime: pollution.

It is probably clear to you by now that I am proud to be a scientist who investigates environmental contamination events with the main purpose of identifying who did it and when and how it happened. And, since the knowledge acquired during the "forensic" investigation enables better site rehabilitation, I see what I do as ultimately contributing toward a cleaner and greener environment.

If, at this point, you are still wondering what really makes what I do so exciting, here is my answer: Similar to classic detective stories, environmental forensic investigations start with a crime (intentional or accidental pollution event) and many suspects (potentially responsible parties). The investigation uses clues and advanced scientific techniques to identify responsible parties (sources) and provide the evidence. In other words, it is the forensic investigation that sets things right by unraveling events that occurred in the past (sometimes decades or even centuries ago). This is possible due to advancements in various scientific fields that provide cutting-edge techniques that enable us to go back in time and reconstruct environmental contamination events based on the evidence that is left.

Overall, this is how I see environmental forensics, and this is why I am proud and enthusiastic to refer to myself as an environmental forensic scientist or simply a "detective of the environment." The mystery-solving satisfaction, associated with the opportunity to apply cutting-edge science and discover new things, ultimately leading to a greener and more sustainable tomorrow, constitute the basis of my fascination with environmental forensics. It is my hope that after reading this book you will also become fascinated by environmental forensics.

Ioana G. Petrisor, PhD

Acknowledgments

I would like to acknowledge all my great colleagues and mentors, with whom I enjoyed working and learning with every single project during the years at Cardno ENTRIX, Haley & Aldrich, DPRA/Zymax Forensics, University of Southern California, Florida State University, University of Queensland, National Technical University of Athens, and the Institute of Biology of the Romanian Academy of Sciences.

I would like to express my thanks and appreciation to my colleagues from Haley & Aldrich and from DPRA/Zymax Forensics, with whom I have collaborated on some of the presented case studies from this book.

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I express my gratitude to many of my colleagues and peers who have encouraged me and provided useful comments for the improvement of the book. In particular, I would like to acknowledge and convey my most sincere appreciation to Dr. Lorne Everett of L. Everett & Associates; Dr. Anna Knox of Savannah River National Laboratory; Helder Costa of Haley & Aldrich; Dr. Manuel Dekermanjian of ENVIRON; Dr. Ashok Katyal of Resources & Systems International; Dr. Zhendi Wang of Environment Canada; Dr. Cristina Barazzetti Barbieri of Instituto Geral de Pericias, Brazil; Prof. G. C. Fang of Hungkuang University, Taiwan; and Prof. Kostas Komnitsas of Technical University Crete, Greece. All these individuals kindly agreed to review parts of this book.

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Introduction: Environmental Forensics—Science in Legal Disputes and Beyond

> Too much mercy … often resulted in further crimes which were fatal to innocent victims who need not have been victims if justice had been put first and mercy second.
>
> **Agatha Christie**

I.1 Environmental Forensics in the Realm of Forensic and Environmental Sciences

Environmental forensics focuses on reconstruction of past contamination (pollution) events based on the evidence that is left (e.g., identifying the source and age of environmental contaminants and allocating responsibility for contamination). The forensic evidence is acquired through a series of techniques, starting with historical file review and potentially ending with application of cutting-edge scientific testing techniques. The environmental forensic testing techniques are generally referred to using the generic term *fingerprinting*. Similar to fingerprints used in homicides or other crimes to identify a criminal, contaminant fingerprints are used to identify the contamination source or responsible party who is ultimately going to pay for the damages. As in the case of criminal forensics, the justice and legal systems play a major role in the process. Typically, a lawsuit is filed, and evidence acquired through environmental forensic studies is used in litigation support. However, distinct from criminal forensics, environmental forensics also has many useful applications that do not involve legal proceedings or disputes, such as those in contaminated site investigation and remediation (see discussion in the Preface). While these nonlegal applications are growing, the link between criminal and environmental forensics is obvious and will continue to influence environmental forensics science and make it unique.

It is clear that environmental forensics should be integrated within both environmental and forensic sciences. Yet, environmental forensic investigations have some distinct specific objectives and particularities. This is why it is important to establish up front the position of environmental forensic investigations in the bigger realm of environmental and forensic studies. For further information on forensic science, a comprehensive review of Brettell et al. (2009) is recommended.

To summarize, environmental forensics has both similar and district traits compared to environmental and forensic sciences. These traits are presented in Table I.1. For example, compared to environmental sciences, environmental forensics goes one step further by investigating not only what and how much contamination is present at a site, but also how any contamination found got there.

Usually, a forensic investigator takes advantage of the entire body of existing information related to a site, starting with site history, aerial photography, and interviews with site operators/workers, while using any existent site operation and environmental monitoring data to build independent lines of evidence. In some cases, additional fingerprinting-type testing may be conducted.

I.2 Criminal versus Environmental Forensics

Although criminal and environmental forensics are distinct fields, they have some main common elements. They are both triggered by "crimes"; they both use scientific investigative methods to identify and confirm responsible parties, and ultimately, they both ensure that justice occurs in order to compensate the damaged parties and restore order.

The distinction between the two forensic fields resides basically in the type of "crime," including the criminal means. While criminal forensics applies to human crimes, environmental forensics refers to "environmental crimes," in other words, environmental contamination episodes.

Thus, the direct and primary receptor of an environmental crime is the environment (including land, air, surface water, and groundwater). Yet, in many cases, the environment is neither the only nor the final receptor. That is because the ecosystem and humans may ultimately become affected while in contact with the contaminated environment. It is this potential to affect human health and ecosystems that makes environmental crimes of equal, if not higher, "long-term" importance than any other crimes. It is the potential for devastating long-term effects on humans, ecosystems, and natural resources that may threaten our future. Hence, the importance of understanding and dealing with environmental crime and the need for adequate environmental forensic tools and approaches are acute.

A common element between various forensics and environmental fields is the *evidence*—the ultimate target of any of these studies.

Evidence is needed to investigate anything. Evidence is the core of both forensic and environmental sciences. While evidence is a common trait, the type of evidence and the investigated details are distinct between forensic and environmental studies. Environmental science generally investigates what is out there now and how what is out there affects us and the environment.

TABLE I.1

Forensic and Environmental Sciences: Similarities and Distinctions

Topic	Definition/Goal	Similar Traits (Means of Investigations)	Distinct Traits (Object of Investigation/ Questions to Be Answered)
General forensic sciences	Reconstruction of past events based on the evidence that is left. The ultimate goal is to resolve legal disputes and provide scientific evidence.		Investigates a variety of past events based on current evidence. What happened? When and how did it happen? Who is responsible?
Archeological forensics	Reconstruction of historical events, behavioral patterns, dating historical sites and events. The ultimate goal is to obtain evidence that helps re-create the history of civilizations that no longer exist.		Investigates ancient civilizations. What happened? When and how did it happen? Why did it happen? What does that mean?
Criminal forensics	Reconstruction of a human crime and identification of the criminal based on the study of evidence found at the crime scene. The ultimate goal is to obtain defensible evidence to be used in the court of law to bring the criminal to justice.	Use of scientific TECHNIQUES and PRINCIPLES to study and obtain the EVIDENCE	Investigates human crimes/criminals and usually does not involve pollutants but may involve DNA and other fingerprinting techniques. Who did it? When and how did it happen?
Environmental forensics	Reconstruction of contamination events and identification of the source(s) and age of contaminants, as well as of contaminant fate and transport based on the study of available evidence (historical and experimental). The ultimate goal is to obtain defensible evidence to resolve environmental disputes and allocate responsibilities.	Are all based on EVIDENCE	Investigates: • source of contamination • age of contamination • allocation between multiple PRPs Who caused it? When and how did it happen? How did it get there?
General environmental sciences	Study of environmental contaminants and their effects on nature, ecological habitat, and humans. The ultimate goal is to design efficient and cost-effective preventive and remediation systems for environmental rehabilitation and human health protection.	Are all based on EVIDENCE	Investigates existing pattern of environmental contaminants (e.g., contaminant types, concentrations, locations) to define risks to humans and environment and to design effective remediation. What is out there, and how does it behave?

Forensic science investigates not only what is out there but also how and when what is out there got there. Environmental forensics may be seen as a "bridge" linking environmental and forensic sciences.

I.3 Why Care about Environmental Contamination?

Although the direct target of environmental crime is the environment, major collateral damage may be triggered with potentially serious consequences for humans and other living beings. Thus, one should not be deceived into thinking that environmental crimes are somehow less important or have less impact for us than other crimes. On the contrary, depending on their severity and magnitude, environmental crimes could encompass a variety of short- and long-term negative effects on humans and ecological systems. Such negative effects may trigger serious impairment and even death of humans and animals, apart from possibly long-term environmental damages involving serious economic impacts in affected areas.

Mass poisoning episodes due to consumption of polluted food (e.g., contaminated fish) resulting in the death of humans constitute "classic" examples of the complex acute effects of environmental crimes. However, as spectacular and publicized as these acute exposure episodes may be, they are not common. There are also the chronic exposure episodes (to low contamination levels for a longer time) during day-to-day activities that may be more commonly encountered, potentially affecting more people with potentially serious health consequences on a long-term basis. The trickiest part is that such consequences are many times not linked to environmental pollution, which usually remains a "hidden and unthought-of issue." For example, prolonged exposure to even a low concentration of some chemicals or contaminants may cause or contribute to the development of various cancers later in life. Day-to-day exposure may be through simple mechanisms, such as breathing contaminated air or drinking contaminated water without knowing it. This may happen, for example, while in our homes if a polluted plume resides below the home (at shallow depths) and the pollutants are volatile (will become gases and travel upward through soil pores and a house foundation, intruding into the home indoor air). What is quite dangerous in these mechanisms of exposure is that they may be left unnoticed and may affect people routinely while in homes or offices. Depending on the type of contamination, even low levels—unnoticeable by our tastes/senses—may cause harm to humans on a long-term basis.

In addition, contamination may deplete Earth's limited natural resources (e.g., potable water sources, agricultural land, and residential areas) and may impair our ability to exploit and enjoy the beautiful natural wonders that our blue planet provides at no costs.

For all these reasons, it is important to prevent environmental contamination and treat already-contaminated environments. Also, we need to be prepared for any new accidental release. Environmental forensics provides the tools needed to understand what happens to contaminants once they are released and therefore design adequate remedial solutions. Moreover, environmental forensic tools are capable of identifying responsible parties to ensure adequate funding for costly remediation programs.

I.4 Who May Benefit from This Book?

While the book may appeal to anyone interested in solving "environmental mysteries" and moving toward a greener and more sustainable future, some readers may find the information particularly useful in their activities. Specific professions that could benefit from the information described in this book are given in Table I.2.

In addition, both professors in academia and students (studying science or law) are strongly encouraged to consult this book. Environmental forensics is both exciting and rewarding; it is hoped the book will provide incentive to develop environmental forensics teaching programs worldwide.

Table I.2

Environmental Forensic Main Applications and Associated Professions

Main Applications	Examples	Main Associated Profession/Interested Parties
Legal disputes involving environmental contamination or people exposed to contamination	Provide evidence on the source identity, contamination extent, or allocation in environmental litigation cases, which may involve, for example: • lawsuits with multiple PRPs; • toxic torts (exposed citizens suing PRPs); • natural resource damages (usually state authorities and municipalities may sue for damages to natural resources); • maritime oil spills of unknown or disputed source; • national or international air pollution issues.	Environmental lawyers and judges Environmental managers from potentially liable parties (e.g., manufacturing companies, mining and smelting, foundries, chemical companies, petrochemical companies and refineries, waste disposal and transport, landfills, dry cleaners, developers, construction companies) Regulatory agency employees Environmental consultants and university professors, who may provide expert witness testimony or litigation support
Insurance coverage claims and insurance litigation	• Provide evidence related to timing of contamination release event(s) to recover cleanup costs from an insurance agency at sites where multiple insurance contracts/policies are recorded along the years; usually, this applies in the case of policies triggered by a release. • Provide evidence related to the characteristics of contamination release for sites with insurance contracts specifying coverage for certain types of releases or contaminants. • Evaluate the imminence for off-site migration of contaminated groundwater plume. • Determine if the damage was "expected and intended" (e.g., by comparison of facility practices with historical waste disposal practices). • Ensure equitable cost sharing when multiple PRPs contribute to remedial costs; otherwise, the policy coverage may be disputed.	Insurance carrier employees Environmental consultants Environmental lawyers Environmental managers from the insured companies

Property transactions	Environmental forensic studies commissioned by the buyer: • Provide valuable tools for site characterization during due diligence investigation and ensure appropriate evidence minimizing future liabilities; • Provide appropriate evidence to estimate site remedial costs for transactions of contaminated properties. Environmental forensic studies commissioned by the seller: • When contamination is found, forensic investigations may reveal potentially other responsible parties.	Environmental lawyers Developers/contractors Buyers/sellers Environmental consultants (conducting the due diligence investigations)
Site characterization for remedial design	• Provide accurate tools for identification of all contaminated sources, pathways, and specific contributions that should be targeted by remediation → developing of site conceptual models.	Environmental consultants Engineers Environmental managers from site operator/owners, as well as from vendors of remedial products
Establish site-specific cleanup values	• Provide right investigative tools to establish background values (e.g., in the case of metal remediation at sites located in mining areas or areas with naturally high metal levels ; the background values of metals should serve as site cleanup limits, regardless if they are higher than regulatory health limits).	Environmental consultants Environmental lawyers Scientists and managers from regulatory agencies and municipalities Environmental managers from industrial site operators
Prevent or minimize future liabilities	• Acquire forensic monitoring data (e.g., in selected relevant samples). • Forensic characterization of products handled at a site providing specific associated fingerprints, which may enable easy identification and settlement of potential future claims. • Thorough documentation of practices and accidental spills.	Environmental consultants Environmental managers from industrial site operators Environmental lawyers Industrial site owners/operators

About the Author

Dr. Ioana G. Petrisor is a biochemist with over 20 years of experience (in both academia and industry), specializing in environmental forensics and litigation support. She has applied a large variety of forensic techniques to track the source and age–date environmental contaminants. Dr. Petrisor has served as an expert witness in California courts in several cases to testify on the fate and transport as well as sources and age of environmental contamination. She provides services as an environmental consultant based in San Diego, California.

Dr. Petrisor is editor-in-chief of the *Environmental Forensics Journal*. In this capacity, she provides the scientific lead of the journal and is up to date with leading-edge research. She has extensive publication experience, including an invention patent, six book chapters, over 70 research and review articles, 12 editorials, and three technical guidelines. Dr. Petrisor is often an invited speaker at national and international conferences and scientific meetings and regularly presents professional seminars and workshops.

As an instructor with the AEHS (Association for Environmental Health and Sciences) Foundation and EOS (Environmental, Outreach, and Stewardship) Alliance, Dr. Petrisor teaches both online and in-class environmental forensic courses. She is developing an environmental forensics certification program.

Dr. Petrisor has managed and conducted innovative research for the U.S. Department of Energy (DOE), U.S. Department of Defense (DOD), and the European Community on environmental characterization, as well as the development of innovative remedial technologies for a variety of contaminants in soil, aquatic sediments, and water. She designed and conducted successful field applications based on laboratory and pilot-scale data.

Dr. Petrisor has a PhD in biochemistry (environmental biotechnology) from the Romanian Academy of Sciences and a bachelor's in chemistry (biochemistry major) from Bucharest University, Romania. Her PhD focused on environmental characterization, assessment, and development of innovative remedial biotechnologies for heavy metals from mining operations, in the framework of an E.U.-funded project (with research conducted at the Institute of Biology of the Romanian Academy and National Technical University of Athens). In 1999, she completed a UNESCO (United Nations Educational, Scientific, and Cultural Organization) training program in plant molecular genetics at the University of Queensland, Brisbane, Australia.

Section I

Evidence

1

Environmental Forensic Evidence

> Crime is terribly revealing. Try and vary your methods as you will, your tastes, your habits, your attitude of mind, and your soul is revealed by your actions.
>
> **—Agatha Christie**
> *And Then There Were None*

1.1 "Traces" Provide Evidence

Every contact leaves a trace. As Agatha Christie pointed out, a crime is revealed by the various actions leading to the crime itself. This is because any action involves some type of contact that leaves traces. In other words, we all have heard that "there is no perfect crime." It is all a matter of finding that revealing "trace," which in legal terms is referred to as *evidence*. So, the generated traces provide the actual evidence that is absolutely required in legal proceedings and without which a criminal may never be charged with the crime, even if guilty. This is why it is essential to define the traces used to generate crime evidence.

Moreover, since it may be generalized that at least a trace is produced as a result of the actions leading to crime, the key to solving a crime is finding revealing traces. However, as the name suggests, a trace is not easily noticed since it involves something in a small amount, usually hidden or less obvious. Thus, finding and revealing the trace usually requires careful examination of the crime scene, consultation of comprehensive documentation, and application of experimental "fingerprinting" techniques.

Types of traces: For most crimes, the traces may be classified in the following main categories:

1. **Physical entities:** Generally refers to objects belonging or linked to the criminal (e.g., small fabric pieces from the criminal clothes, fallen hair strings, bloodstains, partially smoked cigarettes, fallen personal objects such as a shirt button, etc.);
2. **Alterations of the crime environment** due to the presence and actions of the criminal (such as the fingerprints left on a glass or table, footprints in garden soil, scratches on a surface or wall, etc.);

3. **Behavioral changes** related to specific revealing behavioral traits of the criminal or, in other words, what Agatha Christie referred to as "tastes, habits, attitude of mind, and soul." Such particular traits may influence the type of actions leading to a crime. The reconstructed actions may be used backward to reveal the character of a criminal. This may be essential in identifying the criminal in relation to many suspects.

In brief, evidence plays a central role in solving crimes. Evidence not only helps to reconstruct past events that led to the crime itself but also is absolutely needed to bring the criminal to justice and recover damages. Without it, everything remains at the speculation level.

Obtaining reliable and relevant evidence is key and is the ultimate goal of any forensic investigation. This is why the evidence plays a central role.

The discussion of trace/evidence and its role applies to any type of forensic investigation, including environmental forensics—the object of the current book. The discussion has been kept general so far because it is easier to start with the familiar human criminal investigation scheme and understand how various principles and common concepts expand over the environmental side.

Now, let us concentrate further specifically on environmental forensic-associated evidence and revealing investigative techniques.

1.2 Environmental Forensic Evidence

> The present is the key to the past.
>
> **—James Hutton**
> **Scottish geologist (1726–1797)**

In principle, the key for solving any mystery consists of identifying and following the evidence. Such evidence might have been produced years, decades, or centuries ago and, if still present, may be difficult to find. This is where testing and experimenting could help reveal what happened long ago. In addition, understanding how things behave could be used to unravel what happened in the past in a similar setting according to the quotation above by the "parent" of modern geology, James Hutton.

Environmental forensics tracks contaminants in the environment to investigate who has caused the contaminant release and when and how the release happened. Thus, in the case of environmental forensics, the main types of evidence usually refer to the first two types listed previously (physical entities and environmental alterations). While behavioral evidence may also play an important role in solving environmental mysteries or "crimes," especially when intentional contamination is suspected, this type of evidence is less used in common environmental forensic investigations and does not fall within the scope of the current book. The documentary and fingerprinting techniques described here refer to tracking the first two main categories of traces/evidence.

Table 1.1 indicates the two main types of scientific evidence (represented by traces) applicable to environmental forensic case studies, along with the main forensic techniques that may be used to reveal various traces and obtain defensible evidence.

The following are hints for efficient use of Table 1.1:

- The examples of revealing trace comprise things to look for when using a certain investigative technique.
- While a forensic study may be solved by only one investigative technique, it is generally recommended to use at least two distinct techniques and compare the results. This will provide independent lines of evidence. The independent lines of evidence should lead toward the same conclusion for a defensible case. If this does not happen, further investigations should be carried out using other forensic techniques, and the conclusions or working hypotheses should be revised. Note that individual forensic techniques may not always be used as independent lines of evidence. In some cases, they should be used interdependently as will be discussed later in this book.
- The traces or effects left by contaminants may be preserved over long periods of time, while the contaminants themselves start changing from the moment of their release.
- Tree-ring fingerprinting may extend as far back in time as the age of the studied tree (e.g., even thousands of years).
- Historical and aerial photography reviews are generally applicable to any case and should constitute the first step of environmental forensic investigations. In some cases, the evidence provided by these techniques may be sufficient to solve the case without the need of further testing by various fingerprinting and other forensic techniques.
- Successive releases of the same type of contamination at the same site (same general area) may be resolved by the historical review or by the tree-ring fingerprinting techniques. No other forensic technique can provide evidence and distinguish between releases of the same type of contaminants at the same site which occurred at distinct times.
- Apart from the source, age, and allocation of environmental contamination, details related to the type of release (e.g., sudden vs. progressive) may be useful in some cases.

TABLE 1.1

Main Types of Environmental Forensic Evidence and Investigative Techniques

Main Type of Evidence	Examples of the Revealing Trace/Evidence	Applicable Environmental Forensic Techniques	Forensic Principle
"Physical" evidence	Documented release/spill Raw materials used Waste streams Site features and operations Incidents (e.g., explosions, fires, renovation, repairs, spills, construction) Surrounding sites and operations	Historical document review	Looking for and investigating the *cause* of contamination events as the revealing trace *Key notes:* • Usually, the cause is represented by the released contaminant itself, a mixture of contaminants, chemicals released along with contaminants of concern, as well as degradation products formed in the environment after the release occurred. • Documented releases or indications of potential releases may also be seen as "physical" evidence.
	Discolored or impacted soil Leaking drums Contamination sheens Site features and operations Storage of chemicals Off-site potential sources Historical monitoring data Buildings/construction	Historical aerial photography review/photo interpretation, digital imaging, and mapping Historical document review	
	Contaminants (type and amount) characteristic of original sources and persistent in environment	Chemical fingerprinting (e.g., comprehensive chemical and chiral fingerprinting techniques) such as biomarkers, PCB (polychlorinated biphenyl) congeners	
	Patterns (type and amount) and correlations of contaminants in mixtures as well as contaminants and their degradation products	Chemical fingerprinting: ratio analysis/correlations Statistical analysis	

	Presence of chemicals associated with main contaminants and unique to a certain source (help track the source of the main pollutant)	Signature chemicals	
	Isotopic composition of contaminants composed of elements with more than one (stable) isotope	Isotopic fingerprinting (bulk, compound-specific, or position-specific isotopic fingerprinting)	
	Size, shape, and chemical composition of particles and minerals associated with targeted contaminants in soil or dust	Mineralogical fingerprinting	
	Spatial and temporal contaminant concentration distribution patterns in soil, water, or air (ambient, indoor, soil gas)	Geochemical fingerprinting Data visualization Transport modeling	
"Alteration" evidence	Trace atmospheric contaminants present in groundwater	Atmospheric tracers (e.g., for groundwater age-dating)	Looking for and investigating the *effect* of contamination as the revealing trace *Key note:* • The effect could be on microorganisms, plants/trees, or the contaminated media itself.
	Changes in the width and/or the chemical composition of tree growth rings due to uptake of contaminants in exposed trees	Tree-ring fingerprinting (dendroecology)	
	Changes of the DNA composition of microbial communities from contaminated environment (soil or water)	DNA fingerprinting	

- In all forensic investigations, a detailed analysis of contaminant fate and transport is useful to interpret both historical and experimental data and to reach reliable conclusions. Thus, such an analysis should be conducted in the initial stage of the forensic investigation. Interpretation of relevant information should be done keeping in mind how the contaminant physical-chemical characteristics influence its transport through a certain environment.

1.3 "Ideal" Evidence in Environmental Forensics

The "ideal" evidence should not only solve the environmental mystery but also be defensible (relevant and reliable) in the trial court, easy to explain, and obtained through inexpensive, easy-to-apply, and largely accepted techniques. In addition, especially for court-related applications, the evidence should be easy to communicate using visual aids.

Table 1.2 reveals the main traits of the ideal evidence (except the easy-to-be-communicated trait since that applies mainly to applications in the court of law). While true ideal evidence may never be acquired in practice, the higher the number of ideal traits there are, the better and more defensible the evidence is considered. The ideal traits mentioned in Table 1.2 may help select the best available and applicable forensic techniques for a certain case.

As seen in Table 1.2, some traits are shared by many forensic techniques and generated evidence, while others are rare. Although most forensic techniques may reveal contamination characteristics specific to original sources, relatively few techniques can be applied to age-date old releases, and even fewer have the ability to provide relevant evidence when multiple releases occurred at a site in time.

Any technique investigating the "cause of pollution" relies on the existence of the pollutant itself or any other associated chemical (e.g., degradation products, signature chemicals) and thus is subjected to alteration in time. Yet, the other types of techniques based on looking at the "effect of pollution" rather than the cause are independent of various environmental transformations and ultimate pollutant degradation and therefore are more sensitive and may be used over longer periods of time, including for multiple releases at a site in time. In fact, of all environmental forensic techniques, only those investigating the effect of contamination may be applicable after the contamination is gone from the study area (degraded or transformed).

Table 1.2 generally reflects the current state of the art associated with the various experimental techniques. Note that there are some unique advantages related to the evidence capturing contaminants within their environmental matrix (e.g., mineralogical fingerprints, geochemical fingerprints) that are not captured in this table. Refer to Chapter 5 for a more complete picture related to this type of evidence and associated forensic techniques.

TABLE 1.2

Traits of Ideal Evidence in Environmental Forensics (Testing Evidence)

Ideal Trait	Explanation	Relevance	Examples of Complying Evidence
Specific to original sources—highly versatile	The evidence should reveal the "signature" of the original sources and should be unequivocally linked to specific sources.	Accurate defensible evidence for source identification	Isotopic fingerprints Some chemical fingerprints (e.g., Biomarkers/Chiral fingerprints) Signature chemicals Mineralogical fingerprints/DNA fingerprints
Persistent and consistent in time	The evidence should not change or have little change in time (after contaminant release).	Increased applicability and defensibility	Tree-ring fingerprints Signature chemicals Some chemical fingerprints (e.g., biomarkers)
Ubiquitously applicable	The evidence should be traceable in any environment (water, soil, air) and under any conditions (e.g., extreme conditions).	Increased applicability	Chemical fingerprints (including chiral fingerprints and signature chemicals) Isotopic fingerprints DNA fingerprints Contaminant transport models
Unrelated to pollutant presence	The evidence may be recovered even when original contaminants are gone.	Increased applicability	DNA fingerprints Tree-ring fingerprints
Simply to monitor by standardized methods	Standard methods published and accepted by the scientific community (and with a known rate of error) should be used to provide defensible evidence acceptable in the court of law.	Reduced costs and improved forensic representativeness and defensibility	Chemical fingerprints Isotopic fingerprints/Geochemical fingerprints Tree-ring fingerprints

continued

TABLE 1.2 (continued)

Traits of Ideal Evidence in Environmental Forensics (Testing Evidence)

Ideal Trait	Explanation	Relevance	Examples of Complying Evidence
Changing in a predictable way	Ideal evidence should not change; yet, when change occurs, the evidence may still be forensically used if the change is predictable.	Increased accuracy and application in age-dating	Chemical fingerprints Isotopic fingerprints/Geochemical fingerprints Atmospheric tracers
Distinguishable in mixtures	The evidence should be accurately identified when commingled contamination from multiple sources exists at a site.	Increased applicability for source tracking and allocation	Isotopic fingerprints Signature chemicals Mineralogical fingerprints/Tree-ring fingerprints
Detectable in tiny amounts	The evidence should be easily measurable even when only tiny amounts of contaminants are present.	Increased applicability (in both time and space)	Chemical fingerprints/signature chemicals Mineralogical fingerprints/Geochemical fingerprints Tree-ring fingerprints/Atmospheric tracers DNA fingerprints
Sustainable/ "green"	The evidence should be obtained with minimal disturbance and energy consumption.	Moving toward a green sustainable future	Tree-ring fingerprints
Easy to explain	The forensic principles should be easy to explain.	Increased acceptance	Tree-ring fingerprints/Signature chemicals Geochemical fingerprints

2

Obtaining Defensible Evidence

2.1 Principles and Hints for Obtaining Defensible Evidence

General forensic principles and hints that should be understood and applied for effective environmental forensic investigations and acquisition of defensible evidence are given below. Illustrative comparisons are included to prove such concepts:

- **Use multiple independent "lines of evidence"/forensic techniques:** Unless a case can be conclusively solved by some obvious historical evidence (e.g., a reported release or dumping) or straightforward evidence, more than one forensic technique is recommended to be used independently to obtain defensible evidence. It is important to specify that this general concept should not be used with the idea of simply providing stronger evidence but rather to verify and guide the forensic investigation.
- If evidence from multiple techniques conflicts, two main solutions are envisioned:
    1. **More information should be gathered and the forensic investigation restarted**. This is similar to realizing that a wrong turn has been made on a road trip. In such a situation, the best solution is simply to go back to the starting point or as far back as necessary until intersecting the right road. Similarly, when two lines of evidence provide conflicting evidence, one should restart the case and the experimental testing to gather more information. As with a missed turn on a road trip, one should not continue on a wrong road with the hope that it may eventually lead to the correct destination. Rather, the sooner one returns to the departure point, the sooner the correct road can be reached that will end at the desired destination. Usually, if two lines of evidence give conflicting conclusions, it is not recommended to try a third approach or line of evidence and go with the "majority conclusion" but rather a detailed analysis of possible flaws

within the two lines of evidence should be attempted. If no flaws are detected, then one should rethink the case. Maybe the assumptions are not correct, or maybe the data are insufficient. This means going back to the starting point but with the gained experience of what not to do or where not to go.

2. If the lines of evidence may have different levels of specificity, priorities may be assigned, and the evidence with higher priority should prevail in generating the final conclusion as long as the technique was applied correctly on representative samples. That would be what I like to refer to as interdependent use of lines of evidence. An example would be when comparing evidence obtained through chemical and isotopic fingerprinting related to source identification. If the chemical fingerprints of contaminants (e.g., crude oil) in two samples are similar while their isotopic fingerprints are distinct, it should not be concluded that something might be wrong with any one of these lines of evidence, but rather one should assign higher priority to isotopic fingerprints as usually these can attain a higher level of source specificity. In other words, it is not uncommon for two sources to generate the same chemical fingerprints and distinct isotopic ones at the same time. One needs to understand the techniques and their level of source specificity before generating interpretations. Chapter 4 of this book contains relevant information for both of these techniques/evidence that justifies assigning higher priority on source specificity to isotopic fingerprints. Note that isotopic fingerprints may also change in time, so distinct fingerprints due to changes of isotopic composition in time should also be considered. Since isotopic changes (fractionation) are predictable, one may evaluate if the changes in the two sample fingerprints may be due to different degrees of weathering or to distinct sources.

- **Read and understand all available information** (including historical documents, aerial and other photographs, and existing environmental reports/data**) before starting any specific forensic testing.** This will help design better sampling, decide which techniques are more feasible for a certain case, and interpret the results. Planning experiments and interpreting results having a thorough knowledge of available information is similar to understanding the behavior of a person after knowing something about that person. In contrast, planning experimental testing without good knowledge of the available information is like interpreting a photograph without knowing where it was taken. To illustrate further, let us consider a hypothetical example: If one knows a photo was taken during summer, any white coverage of the land that is not due to photographic artifacts may indicate some sort of dust and possible contamination rather than snow. Reading and understanding all available information will ensure you are on the "right path" from the beginning and that you will not have to turn back and start over. This means spending more time up front with a higher potential of overall success and saving a client's money in the long run.

- **Always start with the simplest straightforward evidence you may be able to gather**. While there are many sophisticated forensic techniques, it is always desirable to start with the most straightforward ones. This is also important when the evidence has to go through jury scrutiny, as the successful evidence also needs to be successfully communicated. For example, it is much easier to explain the "signature chemical" forensic concept (having a chemical associated with the contaminant of concern and with only one suspected source) than to explain isotopic testing and how isotopes can be interpreted. It is simpler to explain the data from tree growth rings (everyone is aware that trees have annual rings) than to explain data from DNA fingerprinting. In addition, keep in mind that clearly recorded historical evidence (through depositions or documents) is always the simplest and the most accurate type of evidence one can use. The ideal evidence may involve documented information (e.g., documented release) and concurring experimental testing (which proves the release actually had an impact on the environment). In conclusion, it is recommended to leave the sophisticated testing for when such straightforward evidence is not achievable.
- **Look at the "big picture" without disregarding details**. This is the difficult role of the expert, who needs to come up with answers using data that are rarely homogeneous. Many times, the data may be conflicting, and even when trends are revealed, there may always be one or more particular samples that conflict with the rest. Unlike a computer program that may simply disregard the minority data, an expert should consider such data but always interpret the data within the "big picture." While the trends are useful for defining an expert opinion, minor conflicting data may sometimes cancel the trends. It is the role of the forensic expert to interpret and decide when such conflicting minority data are relevant. Sometimes, small signals indicate you are on a wrong road. T**he strength of forensic investigations lies in mastering the use of details within the "big picture."**
- **Avoid preestablished patterns.** Knowledge is rapidly evolving, and what was considered accurate a few years back may be proven less accurate now. We all think in patterns that are influenced by the general well-established knowledge at one point. While patterns are useful to connect things and reach conclusions, we should not be restricted to them. We should always "think outside the box"

and be open to new possibilities and explanations. Forensic means investigating, and the accurate solution may only be revealed to the open minded.

- **Avoid biased investigation and "preestablished conclusions."** Regardless of whom one is representing, the forensic investigator always seeks the truth. When the facts are against one's client, it is better to reveal this to the client as soon as possible and build the right strategy for moving forward. Sometimes, settling a case sooner could be the right strategy. If an expert tries to prove a preestablished conclusion that is not supported by the weight of the evidence, the expert will first hurt his or her reputation and second hurt the case, which will probably be lost. In a "lost case," the goal should be to minimize the loss rather than desperately try to win. If a "blind" review of documents is not possible, one may benefit from a third independent opinion from a colleague or peer who is not aware of the client's identification.
- The power of successful use and communication of evidence relies in two main traits:
    1. **Detail:** The successful evidence should be based on the detail interpreted with in-depth knowledge of the big picture.
    2. **Visual communication:** The successful evidence should be visually communicated to clients, jury, judges, regulators, and so on.
- **Use combined forensic techniques in a "symbiotic" way,** when feasible. While no single forensic technique will lead to evidence displaying all "ideal" traits (see Table 1.2), some techniques may complement each other in this respect. This leads to the potential for the combined (interrelated) use of two or more techniques to obtain ideal evidence. In theory, any two or more techniques may be combined for better, more accurate, and more defensible evidence. Please note the difference between independent use of techniques to provide independent evidence, which is distinct from the proposed "symbiotic" use of techniques to complement each other and provide stronger evidence. A theoretical example of such symbiotic use is combining tree-ring fingerprinting with isotopic fingerprinting. This may provide stronger and more specific evidence linked to both the sources and the age of contamination found in trees. By itself, tree-ring fingerprinting can accurately reveal the year when contamination got into the tree, but it is less accurate to identify the specific contaminant and its source. When combined with isotopic fingerprinting (which could be performed within the rings of interest), not only accurate age-dating is achieved but also accurate source identification could be attempted. By "symbiotic" use of two

or more forensic techniques, the ideal evidence may be within our reach, and this likely represents one future path for environmental forensic investigations. With so many techniques and fast advancement in knowledge, this should offer infinite possibilities.

2.2 Basic Recommendations for Further Reading

Acquiring defensible evidence requires being up to date with progress in the forensic field. One needs to be aware of the existing body of knowledge and of any new method, principle, or discovery in the field. This book provides an up-to-date review of the major environmental forensic techniques and applications in Sections II and III. In addition to the information presented here, several basic environmental forensic textbooks, reviews, journal articles, and editorials are recommended for those interested in acquiring more in-depth information on the selected topics:

Murphy and Morrison (2002, 2007): *Introduction to Environmental Forensics* (first and second editions, respectively), including information on the following forensic techniques/investigations:

- Historical document review—site history—the first tool of environmental forensics team/photogrammetry, photointerpretation, and digital imaging and mapping;
- Forensic review of soil gas, soil, and groundwater data/the measurement process;
- Application of stable isotopes and radioisotopes in environmental forensics;
- Chemical fingerprinting/laser ablation inductively coupled plasma mass spectrometry;
- Environmental forensic microscopy;
- Source identification and age-dating of chlorinated solvents;
- Subsurface models/forensic air dispersion modeling and analysis;
- Statistical tools for ratio data;
- Principal component analysis and receptor models in environmental forensics;
- Emerging forensic techniques, including the use of atmospheric contaminants to age-date contaminants in groundwater; tree-ring fingerprinting (dendroecology); DNA fingerprinting/microbiological techniques.

Morrison and Murphy (2006): *Environmental Forensics—Contaminant Specific Guide*, including information on the following common contaminants:

- Metals: mercury (Hg), lead (Pb), arsenic (As), chromium (Cr);
- Chlorinated solvents;
- Crude oil and refined products/polycyclic aromatic hydrocarbons (PAHs);
- Polychlorinated biphenyls (PCBs)/dioxins and furans;
- Perchlorate/methane (CH_4)/radioactive compounds/pesticides;
- Asbestos/sewage;
- Microbial contamination/DNA fingerprinting.

Wang and Stout (2007): *Oil Spill Environmental Forensics—Fingerprinting and Source Identification*, including the following specific information:

- Methods and factors affecting petroleum fingerprints in the environment;
- Spill site investigation;
- Petroleum biomarker fingerprinting;
- Characterization of polycyclic aromatic sulfur heterocycles for source identification;
- Oil spill identification by comprehensive two-dimensional gas chromatography;
- Application of stable isotope ratios in spilled oil identification;
- Multivariate approach to oil hydrocarbon fingerprinting and spill source identification;
- Biodegradation of oil hydrocarbons and its implication for source identification;
- Identification of hydrocarbons in biological samples for source determination;
- Trajectory modeling of marine oil spills;
- Oil spill remote sensing;
- Case studies, including *Exxon Valdez* experience; oil spills in the strait of Malacca, Malaysia; and hydrocarbon sources in Guanabara Bay, Brazil.

Sullivan et al. (2001): *Practical Environmental Forensics—Process and Case Histories*, including information on the following:

- Introduction to environmental law;
- Site history;

- Chemical fingerprinting;
- Contaminant transport models and use of visual evidence display;
- Allocation/risk assessment;
- Expert witness strategy and tips;
- Forensic case management;
- Alternative dispute resolution techniques;
- Communication and disclosure issues;
- Settling claims;
- Forensic cost-effectiveness.

Hester and Harrison (2008): *Environmental Forensics—Issues in Environmental Science and Technology* (Vol. 26), including information on the following:

- Microbial techniques for environmental forensics;
- Spatial considerations of stable isotope analyses;
- Diagnostic compounds for fingerprinting petroleum in the environment;
- Environmental forensics techniques for tracking chlorinated solvents;
- Perchlorate and its potential massive natural occurrence;
- Environmental forensics techniques applicable to groundwater pollution.

Morrison and O'Sullivan (2010, 2012): *Environmental Forensics—Proceedings of the INEF Conference* (for the 2009 and 2011 Conferences, respectively), including papers presented at these forensic conferences on topics such as the following:

- Fingerprinting of petroleum products;
- Mass balance calculation for retail petroleum tanks;
- Visualization and analysis of environmental forensic data;
- Isotopic fingerprinting approaches and cases including compound-specific isotopic analysis (CSIA) and position-specific isotopic analysis (PSIA);
- Forensic history of dry cleaning equipment and solvents;
- Environmental forensics and natural resource damages;
- Carbon disulfide: contaminant or biogenic compound?
- Dioxin and furan congener fingerprints during bioaccumulation in chicken and duck eggs;
- Prediction of the environmental fate of methylamphetamine waste;

- Source apportionment of industrial fugitive dusts;
- Dendroecological methods for dating petroleum releases to soil and groundwater;
- Forensic tracking of sewage waste;
- Molecular microbial forensics.

Mudge (2009): *Methods in Environmental Forensics*, including the following selected topics:

- Chemical fingerprinting of petroleum hydrocarbons;
- Biomarkers and stable isotopes in environmental forensic studies;
- Molecular biology application to environmental forensics;
- Biological communities as forensic tool in marine environments;
- Multivariate and geostatistical methods;
- Modeling techniques for identification of air pollution sources.

Comprehensive environmental forensics reviews:

- Age dating of organic residues (Kaplan, 2003);
- "Application of Forensic Techniques for Age-Dating and Source Identification" and "Critical Review of Environmental Forensic Techniques" (Morrison, 2000a,b,c);
- Environmental multimedia models (Zhang et al., 2012);
- Related to chlorinated solvents and perchlorate forensic investigations (Petrisor and Wells, 2008a,b);
- Age of hydrocarbon fuel releases (Kaplan and Galperin, 1996).

Papers reviewing source allocation methods (note that while specific source allocation methods are not discussed in detail being out of the scope of this book, these recommended papers may provide some good examples of useful practical means for source allocation at contaminated groundwater sites):

- Liability theories in contaminated groundwater litigation (Aronovsky, 2000);
- Allocating responsibility for groundwater remediation costs (Graves et al., 2000);
- Apportioning costs among potentially responsible parties with allocation formulas (Ram et al., 2005).

Papers discussing useful atypical potential applications of environmental forensics related to

- Sustainable drought management (Katyal and Petrisor, 2012);
- Sustainable flood management (Katyal and Petrisor, 2011);
- Site investigation (Bica et al., 2009);
- Defective Chinese drywall evaluation (Petrisor and Kanner, 2010).

Publications from *Environmental Forensics Journal* (published since 2000) (http://www.informaworld.com/smpp/title~db=all~content=t713770863), including the following selected topics:

- Editorials (e.g., Petrisor and Kitts, 2004, 2005a,b, 2006a,b,c, 2007, 2012; Petrisor and Westerfield, 2008; Petrisor and Lazar, 2008);
- Articles related to petroleum hydrocarbons:
    - Distinguishing crude oils from heavy fuel oils using PAH fingerprints (Liu et al., 2013);
    - Allocation of hydrocarbon mixtures based on chemical ratios (Lundegard and Surgi, 2012);
    - Application of light petroleum biomarkers for source identification of spilled light refined oils (Yang et al., 2012);
    - Differentiation of pyrogenic and petrogenic PAHs using criteria of relative abundance of alkyl PAHs (Saha et al., 2012);
- Stable isotopic fingerprinting for identification of MTBE (methyl tertiary-butyl ether) manufacturer (Shin et al., 2013);
- CSIA (compound specific isotope analysis) for identification of nitrate-contaminated waters (Bronders et al., 2012);
- Detection of possible chemicals related to terrorism in the water distribution network (Cho et al., 2013);
- Incorporating incremental sampling into environmental forensic investigations (Hadley and Petrisor, 2013);
- Tracking environmental contamination using advanced aerial platforms and infrared thermography (Lega et al., 2012);
- A special issue dedicated to petroleum fingerprinting published in December 2013 (Vol. 14, No. 4).

Section II

Techniques

MOTTO: KNOWLEDGE IS ORGANIZED INFORMATION!

The chapters comprising Section II review the main up-to-date techniques used in environmental forensic investigations. The review is meant to transmit general principles and provide organized information and hints for successful forensic use of each technique.

It is not the aim of this book to provide a comprehensive literature review and detailed scientific information related to various forensic techniques, evidence, or other aspects of environmental forensics. Rather, the intent is to select and organize relevant environmental forensic information and literature references in an easy-to-understand and easy-to-use manner. Apart from the general reading recommendations provided in Chapter 2, basic reading suggestions for each technique are provided for those interested in learning more. The main aim of the book consists of raising the interest and providing general knowledge and guidance for learning and practicing in the emerging field of environmental forensics.

Knowledge is, after all, organized information. Thus, the information is organized consistently for each presented technique, including method principles, steps, applications, limitations, and recommendations. Selected useful references are inserted. In addition, hints for effective applications of the presented techniques are included. Examples using both hypothetical and published cases are also inserted when talking about technique applications. A particular emphasis is placed on chemical fingerprinting of crude oil and petroleum products considering the complexity of chemical composition of oils and the large amount of available useful forensic information related to oil (petroleum) fingerprinting.

3

Nontesting Techniques: The First Forensic Tools

3.1 Historical Document Review

Every environmental forensic investigation should start with historical document review. This is the first forensics tool (Bookspan et al., 2007) and consists of gathering and reviewing historical information related to a site, including any recorded environmental data. Usually, this step does not require help from historians; however, if such help is provided, the historian should closely work with the forensic scientist. This section includes information related to the main sources for historical documents along with guidance on what to look for and how to conduct efficient historical research.

Document review could be a tedious, time-consuming step as it generally involves thousands or tens of thousands of pages of documents that the forensic scientist has to read and become familiar with. In many cases, these documents are not immediately available, and the scientist may be required to spend some time researching for documents at public agencies, libraries, and many other potential document sources to reveal the site history. Historical site research may look like a boring part of the investigation and a job for a historian, but it is nonetheless a critical step in forensic investigations. Conducting a forensic investigation without or after a superficial historical document review is like participating in a car race with a dirty windshield.

There is no bypass or shortcut when it comes to historical document review. Even if a historian is hired to do the research, the forensic scientist always has to become involved and become familiar with the content of the acquired documents. If the forensic scientist relies solely on the historian to provide relevant site data, important scientific-relevant details may remain unrevealed, and the case is less likely to be solved effectively. You can never “a priori” establish all the relevant criteria to look for in solving a case. New criteria may be revealed once you better understand site history during the document review phase. For example, a certain chemical may not pose a health risk and thus not be reported as a contaminant of concern but could nonetheless be linked to the original contaminant (e.g., as an additive or stored and released from the same source) and may influence the fate and transport of the original contaminant as well as have the potential to provide source-specific signatures. A historian may not distinguish or look for such peculiar information.

A useful review of the specific investigation tools for acquisition and use of site historical documents was provided by Bookspan et al. (2007). In this section, practical guidance and hints are provided for conducting effective document review. A theoretical example related to dry cleaners is also provided.

3.1.1 What to Look For

Efficient historical research should collect two types of information:

- General information and
- Site-specific information

3.1.1.1 General Information

General information relates to the type of industry/business that is investigated (e.g., suspected to have caused the pollution or with a historical presence at the investigated site). This information should be generally applicable to each investigated type of business/industry regardless of the specific conditions of the investigated site. Such key information could be quite useful in forensic investigations as it may help establish the following up front:

- What are the usual contaminants associated with the investigated business type/industry?
- What are the typical release mechanisms reported from operations associated with the investigated business type/industry?
- How often are contamination issues reported at sites associated to the investigated business type/industry?
- Are there any patterns related to contamination occurrence (e.g., type and amount along with location of contaminants) at sites associated with the investigated business type/industry?
- Are there any typical historical practices associated with the investigated business type/industry that would have resulted in voluntary or involuntary release of contaminants?

Subsequently, the general information to be acquired includes:

- **Understanding the business type/industry:**
  - Manufacturing processes, materials, and wastes
  - Equipment: typical use and failure mechanisms
  - Reported practices with environmental impact (e.g., waste management issues, permitted or unpermitted discharges)

- **Understanding the context** in which the business type/industry operates and has operated in the past (i.e., during the timeframe the investigated business has operated):
  - Historical
  - Regulatory
  - Scientific
  - Legal
- **Understanding common contamination issues (if any)** reported at sites with similar operations as the investigated business type/industry.
- **Evaluating contaminant distribution patterns (if any)** at sites with similar operations as the investigated business type or industry.
- **Evaluating contaminant release patterns (if any)** at sites with similar operations as the investigated business type or industry.

Such general information may be largely available on the Internet, in trade and scientific literature, as well as in other publications. Typically, searches for reported case studies from certain industry/business types provide the needed information and may help establish patterns and typical contaminants and issues associated with the investigated business type/industry.

3.1.1.1.1 Theoretical Examples: Utility of General Information Review in Forensic Investigations

Acquiring general information is many times overlooked by the forensic investigator due to the lack of time or funding or simply underevaluation of its benefits. However, such information may be critical in guiding or even solving environmental puzzles. Some hypothetical examples are given next.

HYPOTHETICAL CASE STUDY 3.1

Evaluating the Source(s) of a Chlorinated Solvent Plume at a Historical Junkyard

Let us consider a hypothetical site historically used as a junkyard where a variety of chlorinated solvents (e.g., PCE—perchloroethylene, TCE—trichloroethylene, 1,1,1-TCA—1,1,1-trichloroethylene, CCl_4—carbon tetrachloride, $CHCl_3$—chloroform) are reported in shallow groundwater to exceed regulatory limits. No inorganic contaminants (e.g., metals) are reported to be of concern for this site. Very limited specific information exists related to the site history and operations, and no historical soil data were ever reported at this site. In this context, the forensic investigation of the chlorinated solvent sources is challenging. The groundwater monitoring data for the past decade indicates no other obvious source in the area. The location of the plume incriminates the site's past operations even in the absence of historical site-specific data. In addition, an EDR (Environmental Data Resources; see more at http://www.edrnet.com) survey does not identify other potential sources in the immediate site vicinity.

At this point, without documenting general information on junkyard operations, the historical site use (as a junkyard) seems the likely source of the chlorinated solvent groundwater plume. However, after reviewing general information related to similar junkyard sites and operations, a different forensic conclusion may be reached as described here. Gathering general information for this business type (junkyards) would reveal that chlorinated solvents are not typically associated with operations and materials related to this business type, and they are not reported as detected for many of the published case studies involving junkyards in other areas. Once this general information is established with strong literature support, the forensic investigator realizes that the chlorinated solvent plume is likely not directly associated with the site's historical operation as a junkyard; therefore, the chlorinated solvent source(s) may be either (1) exclusively coming from off-site location(s) or (2) the result of illegal dumping on the site property. However, as mentioned, both the groundwater monitoring data and the off-site survey do not indicate the possibility of any major off-site source(s), so the only logical forensic conclusion would be that some sort of illegal dumping might have occurred at the property.

This logical conclusion opens new avenues for the forensic research, which may end up finding supporting evidence for the suspected dumping (e.g., through interviews with past operators, workers, neighbors, etc.). Also, this forensic conclusion may guide further investigation to focus on any drums that could have been stored/used at this site, considering the possibility that any chemical still left in the drums could have been dumped. Thus, especially in the absence of site-specific information, a general search for the type of business can easily guide the forensic investigator toward a more plausible and defensible conclusion. Should the general information not have been gathered in this hypothetical case, the source of chlorinated solvents would have been likely attributed to historical site operations.

However, after gathering general information on junkyard sites/business and operations, a reasonable doubt is cast over the junk-yard regular operations as the likely source, and new avenues for the forensic investigations are revealed. Note that even if site-specific information would have been available and not showing the handling of any chlorinated solvent on site, without the general information support, it could always be considered that chlorinated solvents were actually used and might have been left unrecorded.

HYPOTHETICAL CASE STUDY 3.2

Evaluating Potential Contributions from a Historical Dry Cleaner to a Regional Chlorinated Solvent Plume

Let us now consider a historical dry cleaner location within a shopping mall overlying a regional PCE/TCE (perchloroethylene/trichloroethylene) groundwater plume originating from an upgradient location. The forensic question would be to evaluate any potential contributions from dry cleaner operations to the groundwater plume and, if contributions are revealed, to allocate the contributing amounts. In this hypothetical case, detailed historical information exists covering the entire period the dry cleaner operated, with no spill being recorded. In addition, no soil data exist to link the groundwater plume to the dry cleaner location. Thus, one way to evaluate the dry cleaner's potential contribution would be to identify specific potential source locations within the dry cleaner property itself and then test for any residual solvent left in soil at those suspected source locations. Any detected residual solvents in soil may be directly linked to the dry cleaner, proving that releases from the dry cleaner operations did occur and could be further potentially used to provide the chemical and isotopic "signature" of dry cleaner releases, which may help to discern contributions from the dry cleaner in the regional groundwater plume.

This particular forensic puzzle may be solved after gathering general information on dry cleaner operations, issues, and commonly reported release patterns and practices. Such information will help establish several suspected potential source areas to be sampled. For example, a review of the commonly reported equipment failure mechanisms at dry cleaners (see, e.g., the review by Lohman, 2002) will help establish potential source areas adjacent to certain parts of the dry cleaning equipment with reported failures. Also, a review of common historical practices and waste management issues at many dry cleaner locations would help identify the sewer lines as potential specific sources due to recorded practices of pouring contaminated solvent or contaminated filter sludge into the municipal sewer system, as well as water discharge from water-separating devices.

This example denotes how gathering general information of common equipment recorded failure mechanisms and waste management practices at dry cleaners can guide the forensic investigation regarding where to collect samples with a higher probability of finding residual contamination that may help prove or disprove historical dry cleaner releases and contributions to the regional groundwater plume. In addition, if any residual solvent is found near the identified "problem" areas, it could be further fingerprinted (e.g., chemically, isotopically) to provide the specific dry cleaner signature for cost allocation of the dry cleaner contributions to the commingled regional groundwater plume.

HYPOTHETICAL CASE STUDY 3.3

Investigating Historical Releases Due to Operational Procedures at a Bulk Chemical Storage and Repackaging Facility

The third hypothetical case study proving the utility of general information review in forensic investigations involves chemical storage and repackaging facilities. Such facilities will have regular operations of transferring chemicals from bigger into smaller containers. For example, the sites would receive chemicals in bulk that would be transferred, using hoses and pumps, into storage devices on site (e.g., underground or above-ground storage tanks, drums, or other specific devices). While various chemicals would be received on a daily basis, a limited number of hoses would be used for transfer purposes. So that the purity of each transferred product is not affected, a common practice of cleaning the hoses between distinct chemicals to be transferred was reported and known as "flushing." Basically, hoses were flushed with a few gallons of cleaning solvents (e.g., isopropanol) to clean them between chemical transfer operations. The few gallons of solvent used would have been stored in drums and treated as waste. However, there were reported cases when the flushing solvent (with small amounts of various chemicals that were flushed from the hoses) would be dumped on site instead of being collected as waste. Such a possibility should be investigated when dealing with historical chemical bulk storage facilities, especially those operating before the 1980s. Therefore, this type of general information may guide the forensic investigation, including interviews with past workers and operators as part of due diligence processes.

HYPOTHETICAL CASE STUDY 3.4

Source Evaluation at Former Military Bases

Consider the situation of conducting a forensic investigation at a former military base where more recent—other-than-military—uses are potential contamination sources. The forensic investigation aim will be to identify any historical contributions due to the site use as a military base. Regardless of the nature of contamination, with the lack of any specific historical information related to any spill recorded during the military operations, it becomes problematic to identify potential contributions from former military operations. However, when general information is consulted related to similar military bases and recorded/published contaminants at such sites, evidence may be gathered related to the presence of certain contaminants and contamination patterns that could be constantly reported at military bases. Also, operational procedures or common practices that may have resulted in contamination release could be identified. For example, at military bases operating during the World War II, the practice of emptying flammable contents (e.g., petroleum products) of storage tanks before a suspected bombing attack to reduce the explosion hazard was reported.

3.1.1.2 Specific Information

Specific information refers to any documents (e.g., company records, inspection reports, recorded spills or violations, discharge permits, materials, and wastes) directly related to the specific investigated site. Useful specific information to be investigated should aim to identify particular site features potentially linked to sources and typically reported impacted areas. A list of targets for the specific information gathering includes the following:

- **Site features,** such as:
    - Ditches, drains, sumps, ponds (including water ponds)
    - Sewage disposal, sewer lines

  - Piping, pumps
  - Chemical storage (areas and containers)
  - Loading-unloading areas
  - Buildings, warehouses, labs, machine shops
  - Heating system
  - USTs (underground storage tanks) and ASTs (above ground storage tanks), drum storage areas
  - Electrical components that may contain PCBs
  - Paint type and painted structures that may contain Pb
- **Handled contamination** (chemicals) related to:
  - Raw materials, solvents, and cleaning agents
  - Wastes: composition, storage, management, shipping manifests
  - Intermediate products
- **Common operation procedures:**
  - Manufacturing
  - Cleaning/repair
  - Handling of chemicals
  - Environmental permits
  - Transfer of chemicals
  - Mixing of chemicals
- **Incidents** that may have been recorded:
  - Flooding, fires, explosions, and the like
  - Violations
- **Business records:**
  - Corporate succession/ownership history
  - Selling and purchasing records
- **Other relevant information:**
  - Terrain topography
  - Climatic data
  - Surrounding sites and histories
  - Any historical environmental data

A comprehensive review of all available historical records associated with a specific site should target the features listed that could directly reveal sources or source areas and operations that resulted in contaminant releases, as well as help understand site background conditions and interpret environmental testing data.

3.1.2 Where to Look

Sources for gathering the relevant historical information are multiple. Some typical examples (of sources and type of information to be gathered) include the following:

- **Internet searches** are becoming increasingly common and should always be attempted since they are so convenient. However, Internet sources and information should be strictly scrutinized for accuracy. Useful environment-relevant information may be found online, such as in the following examples:
  - Library of Congress: http://www.loc.gov/coll/nucmc/
  - Repositories of primary sources: http://www.uiweb.uidaho.edu/special-collections/Other.Repositories.html
  - Online Archive of California: http://www.oac.cdlib.org/
  - Public records: http://publicrecords.netronline.com/
  - University of California History Digital Archives: http://sunsite.berkeley.edu/uchistory/
- **Published literature,** including journal articles, conference or other scientific meeting proceedings, books, newspapers, trade literature, and so on. The published literature should be consulted for:
  - **General information** related to similar industrial practices, sites with similar operations or contamination issues, or other generally applicable features.
  - **Site-specific information** if data from the site or site history have been published in available publications.
  - **State of the art** related to specific issues encountered at the site (e.g., if the site is contaminated with PCBs, consult the relevant literature on PCBs, such as related to properties, fate and transport, known sources, association with other chemicals based on potential sources, etc.).
  - **Climatic data** applicable to site area could be useful to interpret environmental data and reconstruct past fate and transport scenarios. Such data are also needed when information from tree rings is used.
- **Company records** should be gathered for any companies that operated at a site; usually, such records are produced when litigation occurs. While any company records should be gathered, especially useful information is provided by maps and plans; photos; operation procedure manuals; correspondence; meeting minutes; shipment and purchasing records; chemical storage and product MSDSs (Material Data Safety Sheets); permits; inspection reports; any spill

or environmental reports or sampling; past explosions/fires; transcripts from any past trials; depositions of past employees; company brochures or advertisements. Tax assessment records may also be consulted.

- **Fire insurance maps** (usually known as Sanborn maps in the United States) may provide detailed historical information on different site features and storage areas. Fire insurance maps could also display useful information on neighboring properties.
- **Regulatory agencies** (e.g., in the United States the Environmental Protection Agency [EPA], Department of Toxic Substances Control [DTSC], regional water boards, air boards, health departments) may provide:
    - Existing environmental reports
    - Correspondence/inspection reports
    - Violations/recorded spills
    - Permits, including those for industrial waste disposal, conditional use, discharges, and the like
    - Hazardous waste manifests, reports, quantities, management, and the like
- A **fire department** may provide:
    - A list of various hazardous substances stored/handled at a site over the years
    - Inspection reports
    - Fire/explosion incidents, accidental spills
- **Municipalities** may provide:
    - Building permits
    - City development maps
    - Tax assessment records
    - City directory listings
    - Grant deeds
- **Waste haulers** should be identified for a site (based on company records, interviews, etc.) and may provide hazardous waste manifests (which may also be retrieved from state regulatory agencies, such as the Office of Hazardous Waste).
- **Useful historical information** may also come from the Department of Transportation and Department of Public Works.
- **County court records** may provide useful information if previous lawsuits exist for a certain site/company, including potentially useful testimonies and exhibits. Also, any nuisance/pollution complaint should be recorded.

- **County's recorder office, city directories, yellow pages** may provide information (e.g., chain of title) that helps identify past occupants and locations.
- **Public utilities** may provide documents related to the site, if applicable.
- **Public libraries, national archives, and agencies** may provide fire insurance maps; national archives may be used for operations during the times of world wars, including military-related industry records. In addition, industry trade literature, business magazines, newspapers, or Chamber of Commerce literature may provide accurate historical information.
- **Insurance agencies** may provide information on site features and operations.
- **Interviews with present and past site operators, managers, and workers** could provide accurate information on operations, materials and wastes, disposal practices, as well as any incident that was not otherwise documented (spills, leaks, overflows, etc.).
- **Secretary of State filings as well as the Security and Exchange Commission** may be used for company succession research, which may help reveal liability and various potentially responsible parties (PRPs) that operated at a site.

Hints for Successful Use of Historical Document Review to Solve Forensic Puzzles

- **Never assume some documents are not useful.** Check all documents briefly to screen for key issues. It is better to briefly go through all documents rather than spend more time for a selected few (without looking at everything).
- **Expect the unexpected.** While one may look for key issues, one should always keep an open mind for unexpected clues. Some clues may not be predicted, but an experienced forensic scientist will figure out and identify issues when keeping an open mind.
- **Look for details.** It is in the details that the forensic solving power resides. Never underestimate the details. A forensic case may start and be based on that small, apparently insignificant, detail.
- **Understand the "big picture."** Read, read, and read. Before forming an opinion, assimilate comprehensive information on the case.
- **Interpret the relevant details within the big picture**. This is always true, no matter how big or small the case is.

3.2 Photographic Review

This section focuses on the use of photographic information in forensic investigations. While any photographs may be useful in forensic investigations, aerial photographs are mostly used, and these are discussed here.

Review of photographs associated with a site complements the historical document review and should ideally include all the available photos taken over the years for the site and surrounding areas. The aerial and other photographic documentation may reveal the location of environmentally relevant features (e.g., location and size of chemical and waste storage areas, operation areas, site buildings), the surrounding land use and topography, as well as potentially problematic areas (e.g., stained or unusual-looking areas, ponds, landfills). In addition, since photos are usually available at different points in time, any recorded or unrecorded changes could be deduced related to site features and operations. Moreover, in rare cases, an accidental leak or spill may be captured in photographic documents providing strong forensic evidence.

Photographic review may include photogrammetry as well as photo interpretation. Definitions and distinctions are provided in the following material.

Photogrammetry is defined as "the art, science and technology of obtaining reliable information about physical objects and the environment, through processes of recording, measuring, and interpreting imagery and digital representations of energy patterns derived from non-contact sensor systems" (Colwell, 1997). Photogrammetric data were traditionally produced from aerial photographs using very precise photo measurement devices called analytical stereoplotters. Photogrammetric devices, typically calibrated to the micrometer level, enable the scientist to create complex mathematical models that correct for known distortions in the photographs. From these three-dimensional photo models, highly accurate measurements and positional data can be derived for mapping and analytical purposes (Brilis et al., 2000).

Photogrammetry is distinct and should not be confused with photo interpretation. While the first refers to the measurement of objects, the second aims to identify objects or contaminant-relevant features.

An excellent review of the use of aerial photography to solve environmental forensic disputes was provided by Ebert (2007). The method was largely used and developed for military, biological, and archeological purposes. In fact, some of the first and still-useful publications on principles of photo interpretation were written by archeologists (Crawford, 1923, 1924).

Aerial photographs are pictures taken from the air (e.g., from aircraft, balloons, etc.). Worldwide, hundreds of millions of aerial photographs exist that were taken over more than a century. These pictures document the natural environment and human interactions and changes of that environment. In general, any site operating since the 1900s may be recorded in this huge international archive of pictures. In the United States, systematic coverage of the country has occurred since the 1930s;[1] thus, it is expected that aerial pictures of any site after 1930 exist. Apart from the historical international archived pictures, site-specific photographs may be available within site files (e.g., company records) or could be produced by former site workers and operators.

The acquisition and review of historical aerial photographs and any available pictures of the site and vicinity should accompany the historical document review, representing one of the first steps in environmental forensic investigation. While a forensic scientist should review the photographs and be accustomed to using the information for forensic purposes, the help from a photogrammetrist may be useful in some cases. Photogrammetrists are scientists specializing in using and interpreting information from aerial photographs and other imaged data (e.g., remote sensing). It is ultimately up to the scientist to evaluate each case on a specific basis and decide when additional outside help from a photogrammetrist is needed. In many cases, the key relies in acquiring as many photographs as possible and carefully reviewing the information while interpreting it within the site-specific context established based on a thorough document review.

3.2.1 Criteria for Selecting and Reviewing Aerial Photos

While any photo of a site may have some forensic relevance and should not be discarded, when time and budget limit the acquisition of aerial photos, several criteria may be used to guide the acquisition of the most suitable photos. Thus, when acquiring aerial photographs, the forensic scientist should consider the following main criteria for selection of adequate photographs:

1. **Photographic scale** is a function of the distance from the photographed object and camera focal length (Scale = Focal length/Flight height). Usual scales of pictures from before 1980 are 1:24,000 or 1:34,000 (1 corresponds to a 6-inch lens). For 1:24,000 scale, an inch on the photo is equivalent to 2,000 feet on the ground. At such scale, a 50-gallon drum measures only about a thousandth of an inch in diameter. In forensic investigations, obviously, the picture with the largest scale reveals the more detailed information related to the site itself and should be obtained (1:5,000 or larger if possible). However, useful information may be deduced also from smaller scales, such as the surrounding areas/sites. In most cases, obtaining two scales (one showing the site as detailed as possible and one showing the immediate site vicinity) may be good enough for the purpose of forensic investigations. Note that the site position may not always be in the center of the photo.
2. **Photo format** refers to the following:
    a. **Type of medium:** The photo medium may be one of the following main types: paper print, film positive, film negative, or

   digital data. Generally, the digital format, which is increasingly available, may be suitable for most forensic purposes, allowing the best quality for magnified photos (see also further discussion in this section) as well as being amenable for use in GIS (Geographic Information System) format.
   b. **Size of the finished product:** Concerning the photo size, some common sizes for paper prints are 9 by 9, 4.5 by 4.5, and 9 by 18 inches. In general, the biggest available size is the best for forensic investigations.
3. **Film format:** Format includes the following main categories:
   a. **Black and white (B&W):** These are also known as panchromatic photos and is the most common type of historical photos.
   b. **Color (natural color):** These photos are less common but provide the best forensic evidence.
   c. **Color infrared (CIR)** photos have been available only since the 1960s and are best suited to differentiating vegetated and nonvegetated areas.

In addition, the forensic scientist should be aware of and check the following associated useful information:

- **Film annotations** (demonstrative examples were provided by Grip et al., 2000), such as the following:
  - photo date
  - aircraft altitude (usually reported in feet)
  - focal length
  - provider name
  - photo center geographic coordinates in degree:minute:second latitude/longitude
  - flight information
- **Photo angle:** Most aerial pictures are taken at an angle and should not be seen as maps (at a 90° angle); this is why it is important to consider how the object of interest (e.g., a site building or another feature) may be distorted due to the photo angle. These distortions may be removed by a photogrammetric process.
- **Photo magnification:** Since most aerial photographs are unavailable in scales larger than 1:5,000, magnification of the image is usually needed. When photo magnification is needed, digitizing an aerial photo is better than enlarging the photo on the same film transparency (Grip et al., 2000).

3.2.2 What to Look For

For the forensic investigation, there are no unusable photos, just as there is no useless information. Thus, it is recommended to gather any available photo and look for the same type of general information as recommended in the previous section on historical document review. Of particular interest when reviewing aerial and any other photos is to look for the following:

- **Site features and any changes of the features in time.** Things of particular relevance include chemical and waste storage areas, manufacturing areas, chemical transfer areas, ASTs, drum storage, railroad tracks and cars, laboratory areas, testing areas, warehouses, construction work, and any changes in building appearance.
- **Site operations** may be deduced from reviewing site features mentioned as well as from any other particular observation (e.g., a leaking drum, a person cleaning or transferring chemicals, other human activities of environmental impact that may be visible in some pictures).
- **Surrounding sites** and any changes in their features with time.
- **Land use in surrounding areas** and any changes.
- **Discolorations and unusual colors** as well as any staining or dark patterning in a picture—on the ground or features at the site or surrounding areas.
- **Changes in colors** that may be attributable to certain changes in products of operations.
- **Integrity of asphalt/cement surfaces.**
- **Ponds or patches of accumulating liquid** at the site and surrounding areas.
- **Drains, ditches, channels.**
- **Abandoned features.**
- **Stressed vegetation,** which may be a sign of acute contamination events.

3.2.3 Where to Look

To search for aerial photographs, the study area should be defined in terms of latitude and longitude for the four corners of a rectangle surrounding the area of interest.

Once the study location is defined, available aerial photos may be searched at local (e.g., state agencies, town and county offices) or federal (e.g., federal agencies) levels, with many photos currently available online at governmental agency sites. It is recommended to start with a broader search of the database of the various federal agencies listed in this section and then go to local agencies if still needed. In many cases, the aerial photographs needed may be found at one of the listed federal agencies.

Recommended **sources of historical aerial photos and maps** generally applicable to most U.S. locations include the following:

- **U.S. Geological Survey (USGS):**
  - Web address for searches: http://eros.usgs.gov/.
  - Photo and maps coverage:
    - Photographs in all types of media (print, negative, positive, digital) and formats (B&W, color, CIR) are available for a time period covering the 1940s to the present.
    - Historical maps since 1884 are available (see http://docs.unh.edu/nhtopos/nhtopos.htm).
  - Other information: At the EROS Data Center, near Sioux Falls, South Dakota, the USGS maintains the National Land Remote Sensing Data Archive, including, in addition to 49 million satellite images, some 8 million aerial photographs of the United States.
- **National Archives and Records Administration:**
  - Web address for searches: http://www.archives.gov/index.html.
  - Photo and maps coverage:
    - Photographs are available only in print media and B&W format for a time period covering the 1930s to the 1960s.
    - Historical maps since 1774 are available.
  - Other information: This agency holds over 9 million aerial photos and more than 2 million maps.
- **Library of Congress:**
  - Web address for searches: http://www.loc.gov/index.html.
    - The card catalog is also found online at http://catalog.loc.gov/.
  - Photo and maps coverage:
    - Photographs in print and digital media and all formats (B&W, color, CIR) are available for a time period covering the 1900s to the present.
    - Historical maps since the 1500s are available.
  - Other information:
    - This is the best place to obtain some of the oldest and rarest historical information.

    - The Library of Congress has a rich collection of older photos (1900–1940s); it also has the largest cartographic collection in the world, including more than 4.5 million maps; a useful publication to become familiar with the available resources can be accessed at http://www.loc.gov/rr/geogmap/guide/.

- **U.S. Department of Agriculture (USDA):**
  - Web address for searches: http://www.apfo.usda.gov/.
  - Photo and maps coverage:
    - Photographs in print, negative, and positive media and B&W and CIR formats are available for a time period covering the 1940s to the present.
    - Historical maps since the 1900s are available.
  - Other information: The USDA stores all its aerial photography in the Aerial Photography Field Office (APFO) in Salt Lake City, Utah.
- **National Oceanic and Atmospheric Administration (NOOA),** National Ocean Service:
  - Web address for searches: http://oceanservice.noaa.gov/.
  - Photo and maps coverage:
    - Photographs in print, negative, and positive media and in all formats (B&W, color, and CIR) are available for a time period covering the 1940s to the present.
    - Historical maps since the 1700s are available.
  - Other information: This agency has conducted aerial surveys of the U.S. coastline and airports and holds approximately 500,000 photographic negatives indexed and archived.

Some pictures from the sources listed may be obtained for free on the Internet, providing all the needed information for forensic evaluation. For high-resolution prints of certain characteristics, requests may be made on the Internet or via e-mail, phone, fax, or in person. It is recommended to check using the web addresses provided and find out details on how to order needed aerial photos from each of the listed agencies.

When time for conducting historical aerial photo research is limited, specialized companies may be used for this purpose. Examples of specialized companies (within the United States) that provide high-resolution photography on request include

- **GeoSearch** (http://www.geo-search.net/site/html/)
- **Environmental Data Resources** (http://www.edrnet.com/)

3.2.4 Application Examples

In forensic investigations, photographic review provides additional historical information that may complement or confirm information from the historical file review. In addition, the use of photographic evidence is compelling in litigated cases and should be used in trial exhibits to provide a straightforward and easy-to-understand way of conveying information to judges and juries.

In specific cases, photographic review could provide additional extremely relevant information that can be used to age-date released contaminants, as well as to calculate waste volumes in landfills and changes over time. Examples include the following:

1. **Age-dating of contaminants at a wood treatment plant.** Ebert (2007) (see also http://www.ebert.com) described a case study in which contaminants to a drainage ditch were age-dated based on photographic evidence. This was possible using historical aerial photos of the plant taken at distinct times (1959 and 1965). The key was the observation that untreated woodpiles are lightly colored (almost white), while the treated wood is dark. Thus, by checking the color patterns in the aerial pictures versus distance to the drainage ditch, it was easy and straightforward to see that only in the 1959 picture no treated wood was near the drainage ditch, while in the 1965 picture treated wood appeared next to the ditch, indicating that the release of chemicals to the ditch must have started after 1959 and before 1965. The transport mechanism was leaching with rainwater (plentiful in the southeastern area of the United States where the site was located).
2. **Identification of product transfer and spillage at a U.S. circuit board fabrication plant** (Ebert, 2007). A close-up of a circuit board fabrication area was used to show a hydrant and a hose used to wash out drums and carboys; the effluent could be seen running and emptying into a drain. In addition, a dark stain was visible and interpreted as resulting from product transfer spillage due to its proximity to an open storage area (of chemicals in containers) and a drain. This evidence was confirmed when associated with other lines of evidence, such as former employees' testimonies.
3. **Calculation of landfill volumes over time and allocation between responsible parties.** Grip et al. (2000) described the use of stereoscopic aerial photographs to calculate landfill thickness over time (1948–1971 timeframe) using a terrain model based on a triangulated irregular network. The forensic relevance consisted of establishing the waste volume changes over time periods associated with distinct responsible parties that sent waste to the landfill. Such calculations may further be used to allocate among contributing parties.

Hints for Better Understanding and Interpreting Aerial Photographs

- **Always interpret aerial and other photographs within the site context** considering site operations and features from other lines of evidence.
- **Consider the photographic scale,** which is a function of the distance from the photographed object and of camera focal length (Scale = Focal length/Flight height). Usual scales of pictures from before 1980 are 1:24,000 or 1:34,000 (1 corresponds to a 6-inch lens). At such a scale, a 50-gallon drum measures only about a thousandth of an inch in diameter.
- **Consider the topography of depicted terrain** (flat or with hills), which will influence the relative size of a feature.
- **Consider the heights of various objects** (depicted in a photo), which affect how they are represented in a photo; this is usually referred to as radial displacement. Unless an object is in the exact center of a photo, the object may appear to lean outward to a degree that increases with height.
- **Consider the shadows in a picture,** which may interfere with photo interpretation.
- **Keep in mind that not all dark staining or pooling is indicative of chemical spills**. Many times, it is simply the accumulated water that may appear dark in a picture. However, even then, accumulated water may have an impact on fate and transport of spilled chemicals and may still have environmental relevance.
- **Consider the dynamic changes between various shots in time** and always keep in mind that it is the consistency and correlation with other lines of evidence that enable and validate photo interpretations.
- **Stereoscopic viewing should be considered and helps in aerial photo interpretation.** This refers to the availability of adjacent photos (stereo pairs) that are viewed with a stereoscope to provide a three-dimensional view of the ground and various features. Stereoscopes are of various sophistications and range in price from $20 to tens of thousands of dollars. A recommended type for forensic investigations is the mirror stereoscope, which can be fitted in a parallel tracking mount (Ebert, 2007).
- **Consider photo resolution and photographic media,** which may affect interpretation; thus, one needs to know what to require when gathering photos. There is some debate in this respect, with some photogrammetrists recommending obtaining positive film transparencies as basic data for interpretation, while others recommend obtaining the paper print. However, the resolution

and contrast performance of duplicating films may vary widely, which could affect the interpretation when paper prints are used.

- **A good forensic option is the use of enlargements made from original film negatives** (Ebert, 2007). Enlargements may be produced digitally with a high-resolution scanner. When a pair of such photos is available (from the same area, in distinct frames), the use of a stereoscope is also recommended.
- **Digital image processing should be done with care and objectivity,** avoiding intentional alterations of the photos. Double-checking of the digital image with the original photo enlargement and using a stereoscope (if possible) are recommended.
- The ultimate environmental forensic goal, similar to archeological research, is to **deduce and explain things that can never be seen in a picture.** That is, in our case, to elucidate the systemic effects of ongoing human behavior on the environment using scattered information of various instants in time from the reviewed photos.

3.3 Market Forensics

The emergence of contaminants with uncontrolled-release mechanisms such as those from consumer products, along with the increasing availability of sales and other relevant product information data, created the need and the opportunity for the development of a new forensic technique referred to as market forensics. This technique relies on the use of product formulation and market sales data to estimate the anthropogenic contributions of targeted contaminants (from consumer products) and their environmental load to investigated wastewater treatment facilities (DeLeo et al., 2011).

Market forensics can be applied to evaluate anthropogenic contributions of basically any ingredient from consumer products that meets the following conditions:

- May create contamination issues when released in the environment.
- Has alternative natural sources and/or anthropogenic sources other than consumer products.

3.3.1 Application Example

Market forensics was successfully used to evaluate human contribution of detergent (fatty) alcohols[2] in the environment at a Virginia community

(Luray), resulting in the identification of anthropogenic contributions of these chemicals and estimation of their total daily loads[3] (DeLeo et al., 2011). The relative potential alcohol loadings from consumer products obtained through market forensics data (over a 24-week period) were confirmed by the chemical analysis of the investigated wastewater treatment plant influent, validating the method (Mudge, 2010).

3.3.2. Main Steps

Market forensics consists of the following **main steps**:

1. **Identification of the major consumer products categories** that contain the targeted contaminant (ingredient). This may be done using published human health risk assessments of targeted ingredients, as well as advice from industry experts from consumer product manufacturers. In the application example mentioned, DeLeo et al. (2011) identified six categories of products containing alcohol-based ingredients: laundry detergent, liquid fabric softener, dish detergent, soap, shampoo, and deodorant. More than 1,000 individual branded products were identified in the six mentioned product categories.
2. **Acquisition of market sales data for the identified products** representative for the study location; various information resources may be used. In the application discussed, DeLeo et al. (2011) used the Symphony IRI Group (2011) publication, including data from major grocery store chains (note that data from Wal-Mart are not available in the IRI database).
3. **Estimation of the load of the targeted contaminant** in the influent for selected wastewater treatment plants within the sales region. The following steps may be followed:
    a. Representative consumer products should be acquired (from the identified categories) and may be chemically analyzed for the targeted ingredient presence and concentration.
    b. A daily per capita use rate of selected consumer products should be developed; existing surveys may be used as sources of information. Based on that and the chemical analysis for each representative consumer product's targeted ingredient, a daily per capita use of the targeted ingredient may be deduced.
    c. The obtained daily per capita use of the targeted ingredient may be applied (multiplied) to the number of residents served by the investigated wastewater treatment plant, resulting in

a daily influent load of the targeted ingredient, as well as the chemical profile of targeted ingredient in wastewater influent (e.g., the proportion of individual chemicals within the ingredient chemical type, such as proportion of individual fatty alcohols representative of fatty alcohol daily influent load from identified consumer products in a certain area).

3.3.3 Advantages and Limitations

While the increasing availability of information on product sales and composition makes marketing forensics a cost-effective and appealing alternative to classic analysis-based techniques (e.g., field campaigns), a series of limitations exists, such as related to data availability and inherent variability. In addition, the accuracy and precision of the method has not been systematically tested; both over- and underestimation of data are possible. In this context, market forensics is quite useful not as stand-alone evidence but rather as an additional line of evidence with data being carefully interpreted within each site's specific context and envisioned limitations.

Market forensics is ready to be used to complement results from other forensic methods and add an additional validation level and increased defensibility to forensics conclusions.

Hints for Using Market Forensics

- **For defensible arguments, it is recommended that market forensics results be backed up by testing data.** If testing data are not achievable, market forensics data may provide a possible scenario that should be interpreted within a site-specific context.
- **Alternative anthropogenic sources for targeted contaminant (ingredient) other than consumer products should be considered,** and if such sources are likely, data from a market forensics approach would not identify anthropogenic versus natural inputs. Depending on the issue at hand, data may still be useful to identify certain anthropogenic sources and contributions.
- **Check all sources of consumer product sales data** before deciding which to use.
- **Check the time dependency (variability) of data and possible seasonal patterns**, making sure you use the most representative timeframes for the issue at hand. When in doubt, use data over the longest available timeframe.

Notes

1. The oldest aerial photo in existence today was taken from a hot air balloon and shows some areas of Boston in 1860. However, no systematic coverage by aerial photography exists until the mid-1930s.
2. Note that alcohols not only are present in consumer products but also occur naturally in the environment.
3. Note that natural and anthropogenic contributions may also be distinguished by isotopic testing, which is generally less practical and more expensive than a market forensics approach.

4

Fingerprinting Techniques Targeting the Contaminants and/or Associated Compounds

4.1 Chemical Fingerprinting Techniques

Chemical fingerprinting is a generic term referring to a multitude of techniques that investigates the chemical patterns of contaminants and associated chemicals in the environment to identify the source or age of releases and apportion contributions. Chemical patterns comprise both the type and the concentration of the contaminants in the studied environment.

4.1.1 Comprehensive Chemical Fingerprinting[1]

4.1.1.1 Method Principle and Steps

The method principle consists of analyzing the type and chemical concentration of individual contaminants in the study environment (soil, sediment, water, dust, or air, as well as biota or living organisms) and comparing the results with the type and concentration of contaminants linked to various sources or alterations expected based on age of releases. Either *a priori* knowledge of potential source composition or comparison source samples (representative for original sources) is needed to interpret results and identify sources.

This method is especially useful for pollutants composed of a complex mixture of individual compounds, such as crude oil and various petroleum distillate products, PAHs (polycyclic aromatic hydrocarbons), PCBs (polychlorinated biphenyls), furans, and dioxins. For these complex mixtures of individual compounds, standard environmental testing, aiming for risk assessment and site remediation, usually only investigates a very small fraction of individual compounds (i.e., only those known to pose risks). However, analytical methods exist to characterize a much larger number of individual compounds, such as in the case of crude oil and petroleum distillates (hundreds of hydrocarbons may be identified and quantified) or PCBs (various congeners could be individually reported and quantified).

The chemical fingerprinting method may also be applied for

- Compounds with degradation intermediates (e.g., chlorinated hydrocarbons).
- "Contaminant cocktails" specific to certain sources, such as
  - waste streams;
  - spent mix solvents;
  - certain application formulations (e.g., certain commercial formulations).

When applying chemical fingerprinting, the following **general steps** may be followed:

1. **Evaluation of site conditions and nature of contaminants.** This is a necessary step before starting any testing program and should be done during the document review phase of the project. Based on the information obtained, a relevant forensic sampling and analysis plan can be proposed. This may also help decide which classes of compounds may be present at a site apart from the contaminant of concern (COC). Please keep in mind that any contaminant may have relevance in the forensic evaluation. Basically, this step will establish the location of representative samples from the contaminant plume and location of suspected sources, as well as which contaminants to test for (any contaminant suspected to be present regardless of the environmental risks they may pose). This step may also reveal important information on suspected source characteristics (e.g., which potential other chemicals or additives were present there and could have been released along with the COCs).
2. **Identification of appropriate analysis techniques.** Once the nature of contaminants and the location of their potential sources are established, available analytical techniques should be checked. Usually, analytical techniques with the lowest detection limits should be preferred. The forensic scientist should understand the limitations associated with various available techniques as well as potential interferences. In addition, if the chemical data obtained are to be compared with historically reported data, analytical techniques consistent with those previously used should be preferred. If such analytical techniques do not offer the best forensic resolution, the sample may be analyzed using multiple techniques. Consistency and high resolution should be targeted.
3. **Chemical analysis of environmental samples.** Forensically representative environmental samples should be obtained and analyzed for the presence and concentrations of contaminants according to the previous steps. The results are expressed in chemical concentration units (e.g., micrograms per kilogram for solids, micrograms per liter for liquids, or milligrams per cubic meter for air samples[2]).

4. **Chemical analysis of suspected source samples.** It is recommended that suspected sources are identified and sampled. If material from suspected sources is not available for sampling, then it is indicated to collect environmental samples as close as possible to the suspected sources (soil data may still retain a representative source signature and are to be preferred to groundwater data). While source or close-to-source sampling is useful, it is not always necessary. If historical monitoring or documented source composition information exists, one can use such information to compare with the chemical fingerprint from the study environment. The existence of such information should be revealed in the first stage of historical document review (see Section 3.1), which is why it is so important to conduct a thorough historical document review at the beginning of any forensic investigation.
5. **Data analysis and interpretation.** This step may comprise the use of various display techniques (e.g., histograms, double-ratio plots, star diagrams), diagnostic ratios, as well as multivariate statistics (e.g., Chemometrics may be used to interpret results—chemometrics is a discipline concerned with the application of statistical and mathematical methods to chemistry; see a review by Brown et al., 1996). Regardless of the data analysis technique used, reliable interpretations need to be rooted in a deep understanding of site-specific conditions and contaminant fate and transport. For example, knowing that MTBE (methyl tertiary-butyl ether) travels faster than BTEX (benzene, toluene, ethylbenzene, and xylenes) when gasoline is released to groundwater may help interpret the presence of MTBE behind the BTEX plume as more likely from a distinct release (potential distinct source or distinct release time). Similar interpretation may be provided when 1,4-dioxane is found behind a chlorinated solvent plume front. To gain a profound understanding of contaminant fate and transport, the knowledge of both contaminant physical-chemical properties and the geology/hydrogeology of the released environment (for terrestrial releases) should be gained. In addition, site conditions should be well understood (e.g., conductive to biological or abiotic degradation, volatilization, solubilization/water washing), and their variations in time should be figured out (based on available data and trends). For example, if a release happened below a building that was at some point demolished, the plume conditions below that building would be expected to change from anaerobic or less aerobic to more aerobic. This should be taken into account when reconstructing contaminant plume evolution in time to track it to sources. Obviously, environmental modeling of plume behavior should record such information and any other changes expected to influence subsurface conditions.

6. **Data mapping** is a facultative step used to help with interpretation and overall evaluation as well as communicating the results. It is recommended to create two- and three-dimensional (2D and 3D, respectively) maps with multiple data layers for various periods of interest.

4.1.1.2 Analytical Techniques

Today, there is an abundance of analytical instruments and methods that can be used for chemical fingerprinting, including both fixed and mobile equipment. Of all these, probably gas chromatography (GC) is the most commonly used method to fingerprint organic volatile and semivolatile compounds. Other analytical techniques are commonly used for analysis of organic contaminants as well as inorganic contaminants, including spectrometric, gravimetric, colorimetric, and electrophoresis-based methods, as well as laser ablation microanalysis.

This section briefly overviews some of the common analytical techniques from the user perspective. It is not within the aim of this book to provide a comprehensive review of analytical techniques or methodological details. The reader is provided specific references for more detailed information.

Basically, any compound that volatilizes without decomposing may be measured using GC methods. The identification of individual compounds in mixtures is readily accomplished when GC is coupled with mass spectrometry (MS), usually referred to as GC/MS. In addition, 2D GC (GC X GC) using two chromatographic columns is capable of separating an order of magnitude more compounds from a complex mixture such as crude oil and petroleum products. A comprehensive review of the current state of the art in GC has been published (Dorman et al., 2010), including modern techniques such as GC X GC and portable and microfabricated GC technology. High-performance liquid chromatography (HPLC) may also be used in some cases (e.g., determination of pesticide residue in fruit-based soft drink as reported by Garcia-Reyes et al., 2008).

Apart from chromatographic techniques, other analytical techniques for chemical fingerprinting include

- Petroleum products and crude oil screening methods that complement each other such as (Fernandez-Lima et al., 2009) the following:
  - Ion mobility/mass spectrometry (IM/MS) provides unique petroleum fingerprints for fast identification of signature conformational/compositional patterns and usually is used to identify the most abundant heteroatom classes by size/shape speciation;
  - Fourier transform ion cyclotron resonance (FTICR) MS provides comprehensive heteroatom class distributions (for petroleum products). It is used to resolve and identify all elemental compositions by chemical speciation.

- Methods used for metal or other inorganic contaminants analysis:
    - Inductively coupled plasma mass spectrometry (ICP-MS) is used for analysis of ultratrace amounts of metal contaminants (see additional information in a comprehensive review by Beauchemin, 2006).
    - Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is used for lead (Pb) and other metal analysis.
    - Laser ablation microanalysis generally is used in conjunction with ICP-MS or ICP-AES to detect trace amounts of metals (e.g., Pb) (Ghazi, 2007).
    - Atomic absorption spectroscopy (AAS) is used to analyze perchlorate as well as metals in solution.
    - Raman spectroscopy is used for perchlorate analysis.
- Methods used for analysis of radioactive elements:
    - Gamma-ray spectrometry is used for radioactive elements (e.g., ^{137}Cs, ^{210}Pb).
    - Thermal ionization mass spectrometry (TIMS) may also be used for radioactive elements.
- Other methods with potential forensic applicability include the following:
    - Fourier transform infrared (FTIR) spectrometry is used for very complex mixtures (see a comprehensive review by Nyquist et al., 1990).
    - Molecular fluorescence, phosphorescence, and chemiluminescence spectrometry are highly sensitive techniques that may be used in field monitoring (see more details on these methods in the work of Lowry et al., 2008).
    - Electrospray ionization mass spectrometry (ESI MS) (Eide and Zahlsen, 2005) may be used for perchlorate and biological macromolecules and may be coupled with chromatography.
    - Tandem MS/MS is used for dioxin measurement.
    - Gravimetric techniques such as those for perchlorate may also be used.
    - Colorimetric techniques may also be of relevance for some applications.
    - Electrophoresis-based techniques are also available.

Recent advances in chemical analytical instrumentation include miniature and mobile powerful measuring devices, such as the following:

- Miniature mass spectrometer: Examples of its use include detection of explosives (such as TNT, Tetryl, or HMX) directly from surfaces (Sanders et al., 2010) and environmental monitoring, including determination of toxic compounds in air using a selective solid sorbent and toxic gases (with detection limits ranging from 800 ppt to 3 ppm) (Ouyang et al., 2009).

- Portable Raman spectrometer (RS): Described by Carron and Cox (2010) as the method with powerful "fingerprinting" ability in the "unknown."
- The X-ray portable fluorometer is a powerful semiquantitative instrument that can be used to screen surfaces for hot spots of metals (e.g., in order to select sampling location). This type of device is typically used as the first step in a forensic investigation involving metal contamination in soil.

Recommended comprehensive reviews related to chemical fingerprinting method applications were provided by Douglas et al. (2007) and Wang et al. (2005).

4.1.1.3 Main Influencing Factors/Limitations

Basically, anything that influences the fate and transport of contaminants may influence the original chemical fingerprint and should be evaluated when chemical fingerprinting is used. The main limiting factors of chemical fingerprinting include the following:

1. **Weathering/age of the release/distance from the source.** Once contaminants are released in the environment, they start to alter. This alteration or change in original chemical composition (fingerprint or pattern of individual composing contaminants) increases with time since the release occurred and distance from the release point. Given enough time or distance, the alteration can result in indiscernible or irrelevant fingerprints. The various processes altering released contaminants are collectively referred to as *weathering*, which usually is comprised of the following main environmental transformations/alterations:
    - **Biodegradation** is the degradation or biochemical transformation of released contaminants mediated by environmental microorganisms (which usually feed on contaminants and act as catalysts to speed the rate of various transformation processes). Biodegradation is typically the main weathering factor along with evaporation (for volatile compounds) that account for most environmental alterations of released contaminants. While biodegradation "cures" the environment, it also alters the forensic evidence and could seriously affect the original chemical fingerprint until rendering it invalid. While there are no clear rules, chemical fingerprinting is mostly applicable to fresh or little-weathered releases. This limitation may be addressed using only those individual compounds that are more resistant to biodegradation to

build the chemical fingerprint. In addition, the availability of historical monitoring data could overcome this limitation, providing historical monitoring is available. It should be pointed out here that while biodegradation and other weathering processes represent a limitation for source identification, they may prove useful to age-dating investigations (e.g., relative age assignments).

- **Chemical degradation** is a less-prevalent process compared to biodegradation, but it could become an important mechanism for some particular contaminants (e.g., 1,1,1-TCA). Unlike biodegradation, the speed of chemical degradation can more easily be predicted and thus could be used to age-date a release, but only when it is prevalent over biodegradation and other processes (e.g., in the case of 1,1,1-TCA). Chemical degradation, similar to biodegradation, results in altering the original chemical fingerprint. Thus, it is recommended that compounds resistant to chemical degradation be selectively used to generate fingerprints.
- **Evaporation** is the transition into the gaseous phase, usually from the liquid phase of contaminants that are referred to as volatile or semivolatile. This is a more common process for organic contaminants, but some inorganic contaminants, such as metals, may be volatile themselves (e.g., Hg) or could be transformed into volatile compounds (such as arsine or various methylated forms of metals). The end result of evaporation is similar to that of bio- or chemical degradation in the fact that it may substantially alter the original chemical fingerprints remaining in soil or water. This limitation may be addressed by selected use of less-volatile compounds in building representative chemical fingerprints.
- **Water washing** refers to the dissolution of released contamination when in contact with water (e.g., precipitation, groundwater, or surface water) and possible precipitation from water under certain conditions (transitioning from liquid/dissolved into a solid phase). Water washing will also alter the original chemical fingerprints, potentially rendering them unrecognizable. Again, this limitation may be addressed by selected use of less-soluble compounds in chemical fingerprints.
- **Dilution, diffusion, and dispersion** are the main physical processes of contaminant transport in groundwater and the subsurface in general, resulting in altering the original chemical composition of a release away from the source. The further away from the source a study area is, the higher the occurrence of this type of alteration is. Thus, a reduction in contaminant concentration away from a source may not necessarily indicate the occurrence of degradation processes and could be simply due to these physical processes. While these processes will not directly alter the chemical

fingerprint (individual contaminant patterns), transformation processes (e.g., biodegradation) may be enhanced due to resulting lower concentrations of contaminants. Therefore, dilution, dispersion, and diffusion create favorable conditions for chemical alteration processes to occur, ultimately resulting in the change of original fingerprints. In addition, lower contaminant concentrations could make chemical analysis (detection) more difficult.

- **Adsorption/desorption** consist of binding of released contaminants to porous media (e.g., soil, clay, silt, sand) or any other adsorptive materials. This may selectively slow the transport through soil or with groundwater for those compounds that have higher affinity to bind to soil, therefore resulting in alteration of the original chemical fingerprint. These processes are strongly influenced by the total organic carbon (TOC) content of soils. Understanding soil composition along with physical-chemical properties of contaminants will help select the best individual contaminants to be used in chemical fingerprints (of mixtures).

The weathering effect may be overcome by considering the proportions or ratios of contaminants with similar fate and transport rather than their absolute value and by using the fingerprints of only those compounds resistant to weathering (e.g., biomarkers in case of oil spills). As mentioned, it is recommended to select for fingerprinting purposes those contaminants with similar properties and fate and transport (within a complex contaminant mixture such as crude oil, petroleum products, PCBs, and other contaminants; also see discussion of method principle).

2. **The release environment/changing conditions** influence the weathering patterns and should always be considered in forensic evaluations. For example, in the case of oil spills, there is a big difference between a spill released in an aquatic environment (e.g., ocean or river), which is very conductive to weathering processes, versus a spill released at the subsurface, below the groundwater table, where conditions are generally less favorable for weathering processes. In the first case, a representative spill sample should be collected as soon as possible following the spill (within a few days in general), while in the latter case, a sample representative for the original chemical fingerprint may still be collected years after the release occurred. Information on the released environment is usually gathered through geological surveys, boring logs, general environmental monitoring, and the like. The information gathered usually reflects recent conditions, which may or may not be representative for historical conditions; any potential changes in time should be carefully evaluated through historical document and aerial photo review. Construction work may influence the subsurface conditions, as well

as previous releases, landscaping, and so on. A good understanding of site conditions and potential changes over time is crucial for accurate interpretation of chemical fingerprinting data.

3. **Co-contaminants** (presence of other contaminants in the environment) could influence the fate and transport of released contamination. For example, the presence of LNAPL (light nonaqueous phase liquid) free product in the subsurface could increase the ability to retain or adsorb released organic contaminants and thus would substantially delay vertical migration of the contaminants through soil. Also, the co-presence of LNAPL and DNAPL (dense nonaqueous phase liquid) would influence the fate and transport of DNAPL compounds, retarding their vertical migration through soil since DNAPL contaminants will tend to partition into the LNAPL phase. In addition, in the presence of LNAPL, degradation of DNAPL compounds such as chlorinated solvents will likely be enhanced. Therefore, it is essential to understand which other contaminants are present along with or in the vicinity of studied contamination, regardless of the environmental risk they may pose.
4. **Multiple releases**, especially involving the same type of contaminants or mixtures released at distinct times in a certain area, will render any comprehensive chemical fingerprinting attempt invalid. Such cases may be common at sites with a long history of storing/using the same type of contaminants, such as petroleum storage facilities, refineries, gas stations, bulk chemical storage facilities, dry cleaners, industrial sites, and the like. There is, however, one exception when chemical fingerprinting may work at sites with multiple releases, namely, when it can be proven that older releases have been completely degraded, and thus what we see in the fingerprint is the result of a most recent release.
5. **Physical presence of contaminants at the time of sampling.** It should be obvious that something needs to be physically present in order to be fingerprinted. Although it seems logical that the presence of contamination is the triggering factor for the forensic investigation, in some cases the legal action (litigation) may be brought up after a site has been cleaned, aiming to recover the remedial costs. In such a situation, the forensic investigation may not allow the use of any testing requiring the presence of the contaminants themselves (e.g., physical type of evidence). There is no overcoming this limitation when using chemical fingerprinting or other methods described in this chapter. Yet, other forensic methods may be used even in the absence of released contamination (e.g., tree-ring fingerprinting, DNA fingerprinting).

The main influencing factors previously mentioned should always be considered when interpreting chemical fingerprinting data. This is why thorough document and aerial photo reviews, along with basic testing to figure out environmental conditions in the release area, as well as potential changes during the years (since the release is suspected), are essential for interpreting chemical fingerprints.

4.1.1.4 Applications

Chemical fingerprinting is probably the most commonly used environmental forensics method (apart from historical document review). This is because of the generally wide availability and cost affordability of chemical analysis. In some cases, monitoring data (chemical analysis) may be sufficient to obtain defensible fingerprints. By definition, chemical fingerprinting may only be applied when a mixture of contaminants (individual constituents) was released and is present in the environment. At first glance, this technique may not work for a single-contaminant release. However, there are exceptions. The following explains both the "classic" and the "emerging" applications of (comprehensive) chemical fingerprinting to forensically investigate contaminants released in both mixtures and individually. Examples of specific fingerprinting techniques are also included.

4.1.1.4.1 Classic Applications for Contaminants Released as Mixtures

As discussed, comprehensive chemical fingerprinting is a powerful forensic technique for contaminants released in mixtures. In theory, the higher the number of individual components of a mixture, the higher the forensic power of chemical fingerprinting will be since more complex patterns may be obtained and compared. In addition, the potential for obtaining original unique signature patterns is higher. In fact, any contaminants released in mixtures (e.g., raw materials, waste, or runoff) that may be characteristic of sources could be successfully chemically fingerprinted.

Typical examples of "ideal" candidates for chemical fingerprinting along with some representative fingerprinting techniques are presented in this section for oil spills, PCBs, dioxins, and furans.

4.1.1.4.1.1 Chemical Fingerprinting of Oil Spills Crude oil and various petroleum distillates (e.g., gasoline, jet fuel, kerosene, mineral spirit, Stoddard solvent, fuel oil, diesel number 2, diesel number 4, Bunker oil, hydraulic oil, motor oil, lubricating oil) are mixtures of thousands of individual components, mainly hydrocarbons and heterocyclic compounds.

Chemical Composition of Crude Oils: Basis for Source Differentiation
Crude oils are complex mixtures of individual compounds, including thousands of hydrocarbons and nonhydrocarbons. Ranging from small, volatile to very large, nonvolatile compounds, crude oil components are classified into saturates, aromatics, resins, and asphaltenes (SARA). Typical classes of compounds associated with each of these main classifications are as follows:

- **Saturates**, or saturated compounds, include hydrocarbons that only contain single (sigma) covalent bonds, including
  - **Alkanes,** composed of:
    - **n-Alkanes** (n-paraffins), which are normal or straight-chain alkanes; n-alkanes with a high number of carbons (e.g., over the range nC18–nC40) are usually referred to as waxes;
    - **Iso-alkanes** (iso-paraffins), which consist of branched alkanes (e.g., isoprene);
    - **Biomarkers,** such as isoprenoids (branched alkanes derived from living organisms that have a repeating isoprene unit).
  - **Cycloalkanes** (naphthenes), including compounds such as:
    - **Nonalkylated cyclic alkanes** (e.g., cyclohexane).
    - **Alkylated cyclic alkanes.** For example, n-Alkylcyclohexanes (cyclohexanes with a single alkyl side chain of varying carbon numbers from C1 to around C25) represent a class of cyclic alkanes of forensic utility due to their broad boiling ranges and greater resistance to biodegradation compared to n-alkanes (Stout and Wang, 2008); their distribution pattern is distinct in different oils.
    - **Biomarkers** (e.g., sesquiterpanes, diamondoids, tricyclic diterpanes, tricyclic triterpanes, steranes [tetracyclic triterpanes], hopanes, and other pentacyclic triterpanes), which are complex molecules derived from living organisms (including multiple cycles and alkyl groups bound to the cycles).
- **Aromatics,** or aromatic compounds, include chemicals with one or more aromatic rings. An aromatic ring is composed of six carbon atoms and contains three delocalized double bonds. Aromatics include the following:
  - **Monoaromatics** (one aromatic ring) such as:
    - BTEX and other alkylated benzenes (e.g., trimethylbenzenes).
    - Biomarkers, which are complex molecules derived from living organisms such as monoaromatic steranes.
  - **Polyaromatics** (two or more fused aromatic rings) or **PAHs,** which in crude oils mostly consist of two-, three-, and four-ring PAHs, including:
    - **Parent or nonalkylated PAHs** (C0-PAH) (e.g., all 16 priority pollutant PAHs indicated by the Environmental Protection Agency [EPA]).
    - **Alkylated PAHs** with one through five carbon alkyl groups attached to the aromatic rings; classes of C1- through C5-alkylated PAHs are referred to as homologue series

    (e.g., C2-naphthalenes) and include all constitutional isomers with a certain number of carbon atoms in various arrangements bound to the aromatic rings.
  - **Biomarkers**, complex molecules derived from living organisms such as **triaromatic steranes**.
  - Some **polyaromatic heterocyclics,** such as aromatics that include sulfur in the ring structure (e.g., benzothiophenes, dibenzothiophenes typically analyzed and reported along with PAHs).
- **Resins**, which include mostly **polar compounds** containing, apart from carbon and hydrogen, oxygen, nitrogen, sulfur, or metals. Examples of compounds in this class are phenols, acids, alcohols, pyrols, and mercaptans.
- **Asphaltenes** include very large compounds, sometimes containing oxygen, nitrogen, metals, or sulfur. These compounds are not dissolved in petroleum but dispersed as colloids. Very little is known about the molecular configuration of asphaltenes (Wang et al., 2006a).
- **Porphyrins**, which are complex derivatives of porphine (degradation product of chlorophyll) consisting of four pyrrole units joined by linkages between component pyrrole nuclei. Most of the porphyrin material in crude oils is chelated with metals (e.g., V, Ni). These compounds constitute a unique class of biomarker compounds.

Details related to chemical structure, nomenclature, and properties of crude oil compounds were provided by Wang et al. (2006a). In addition, a comprehensive review of crude oil chemistry and various individual compounds identified in crude oils was published by Fingas (2012).

Of highest forensic relevance are compounds resistant to weathering and characteristic for sources, including the following:

- **Polyaromatic hydrocarbons (PAHs)** are mixtures of various individual hydrocarbons (hundreds of PAHs have been identified) with two or more fused benzoic or aromatic rings. Such compounds may be mainly of petrogenic (derived from petroleum products) or pyrogenic (derived from incomplete combustion processes) origin. Natural (biogenic) PAHs also exist (usually from diagenesis, biosynthesis, and fossil fuels). A recommended review of PAHs and their forensic use was provided by Boehm (2006).
- **Biomarkers** are derived from living organisms (polymerization of isoprene units); they have a variety of chemical structures belonging to various classes of crude oil chemicals, as listed previously. Excellent reviews of biomarker chemistry and use in fingerprinting was provided by Wang et al. (2006a,b).

Fingerprinting of Crude Oil Spills and Petroleum Distillates

The proportion between various individual components and classes of compounds in crude oils varies based on the geological formation from the area of oil origin as well as a series of environmental factors. Thus, determination of chemical composition of spilled oil provides useful information for source identification. This is also known as chemical fingerprinting of the oil. The wealth and variety of individual oil compounds make chemical fingerprinting not only challenging but also efficient in identifying sources.

Comprehensive chemical fingerprinting of crude oil and petroleum distillates involves the identification of individual oil compounds. While any oil compounds may be used in fingerprinting, some are more useful for source identification than others and are therefore more targeted in fingerprinting studies. This is the case for several classes of compounds that are present in all crude oils and are stable in the environment, such as biomarkers (e.g., isoprenoids, diamondoids, tricyclic terpanes, steranes, hopanes) and PAHs. Other oil compounds may also be useful in evaluating the degree of weathering of spilled oil and identifying the presence of biogenic material that adds similar individual hydrocarbon compounds to some from the crude oil.

Fingerprinting of an oil spill is generally done using the following main techniques:

- Review of chromatograms
- Review of histograms
- Use of diagnostic ratios, which may be typically analyzed further through
  - Double-ratio plots
  - Multivariate statistics
- Biomarker regression technique
- Multivariate statistics using individual compound concentrations

This section briefly overviews these main crude oil[3] and petroleum distillate chemical fingerprinting techniques, emphasizing fingerprinting ratios of forensic relevance for source identification or weathering evaluation along with age-dating of a spill. The selected information is based on many publications as well as on the author's experience. Application examples are provided briefly in the next section; this section focuses on listing forensically relevant ratios, explains the principles behind their use, and provides selected references from literature in support of the ratios presented. It is highly recommended to go over the listed references when using any of the ratios in order to become familiar with their use and limitations. A few case studies illustrating the use of some of these ratios and techniques in oil fingerprinting are presented in Section III of this book.

Review of Chromatograms

Chromatograms are graphical representations of the signal (response) from the testing equipment (chromatographer) in time as a result of sample composition. Basically, many peaks of different sizes (e.g., heights and areas) may appear over time. Note that the time is represented on the *x* axis, while the intensity of instrument response (in millivolts, mV) reflected in the peaks is included on the *y* axis. For crude oil and petroleum products, each peak represents an individual compound (usually a hydrocarbon), while the intensity (e.g., height or area of a peak) is correlated to the abundance of that individual compound in the mixture (oil).

Representative examples of chromatograms for crude oil and some common petroleum distillates are provided in Figures 4.1–4.4. Some of the displayed chromatograms have the individual peaks identified by the laboratory, which is useful when interpreting chromatographic data. When this information is not provided by laboratories, one can ask for it or use the exact retention times (which should be reported for each identified/quantified compound) to identify which individual compound is associated with each observed chromatographic peak.

Note that, typically, the compounds with lower molecular mass (fewer carbon atoms in case of hydrocarbons) appear (elute) faster so are toward the left of chromatograms. From left to right, the mass and structural complexity of individual compounds generally increases along with their resistance to biodegradation and other weathering processes. Therefore, weathered oils would be depleted in the peaks toward the left of the chromatogram, and if weathering is advanced, most or all individual peaks may be depleted (no longer noticeable), while the so-called unidentified complex mixture (UCM) becomes prevalent. The UCM is typically comprised of high molecular weight compounds that cannot be chromatographically separated (resolved) and thus identified through individual peaks. The UCM typically looks like a hump. The bigger the hump, the higher the UCM and thus the more degraded the oil (the UCM increases in proportion due to the increased prevalence in the oil mixture of the complex oil compounds contributing to the UCM versus the simpler compounds contributing to individual peaks, which are degraded faster).

Those interested may refer to case studies in Section III for some examples of weathered oils with associated UCMs. Note also that the slight UCM noticed for the unweathered crude oil presented as an example in Figure 4.1 does not suggest weathering happened since many fresh crude oils may display some UCM due to the presence of a large number of unresolved individual compounds in crude oils. The fact that the oil from the Figure 4.1 example is not degraded (weathered) is also suggested by the prevalence of peaks toward the left of the chromatogram.

Evaluation of GC/FID (flame ionization detection) and GC/MS chromatograms (resulting from analysis by GC with FID or an MS detector) is the first forensic step when conducting a fingerprinting study. The information

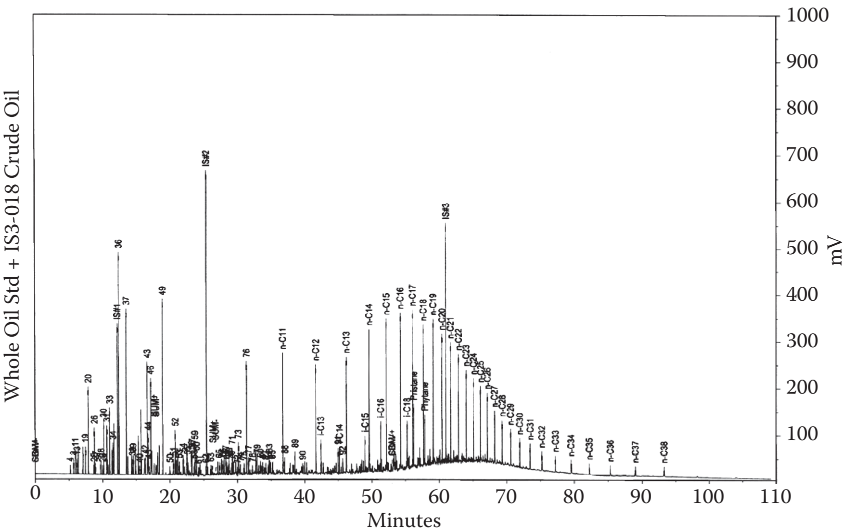

FIGURE 4.1
Example of a crude oil chromatogram. Notice that many individual peaks are identified as n-alkanes, from crude oil ranging from n-C11 to n-C38 in this case; these peaks are characteristics for total ion chromatogram (TIC), when no specific groups of hydrocarbons are targeted for detailed analysis. The n-alkanes are predominant in unweathered crude oils such as the one from this example. (Analysis performed by Zymax Forensics.)

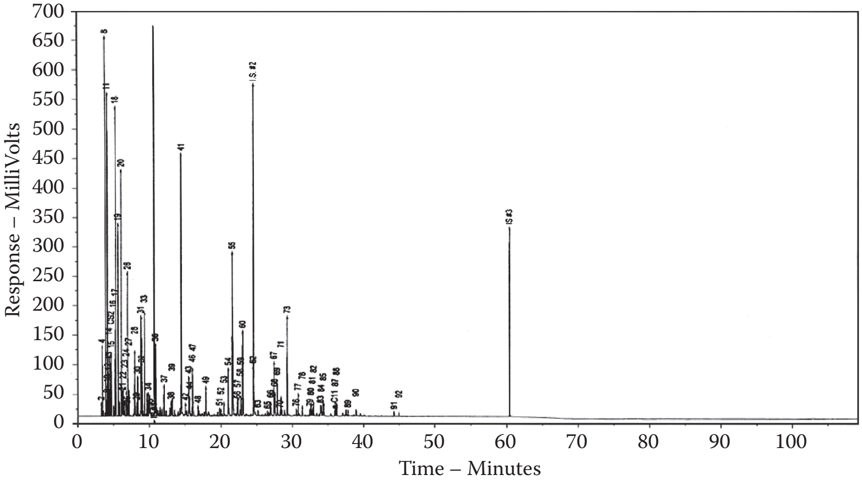

FIGURE 4.2
Example of a gasoline chromatogram. This is a fresh gasoline, as noticed by the prevalence of peaks toward the left; notice that all peaks appear in the left side of the chromatogram since the gasoline carbon range is low until about n-C12. (Analysis performed by Zymax Forensics.)

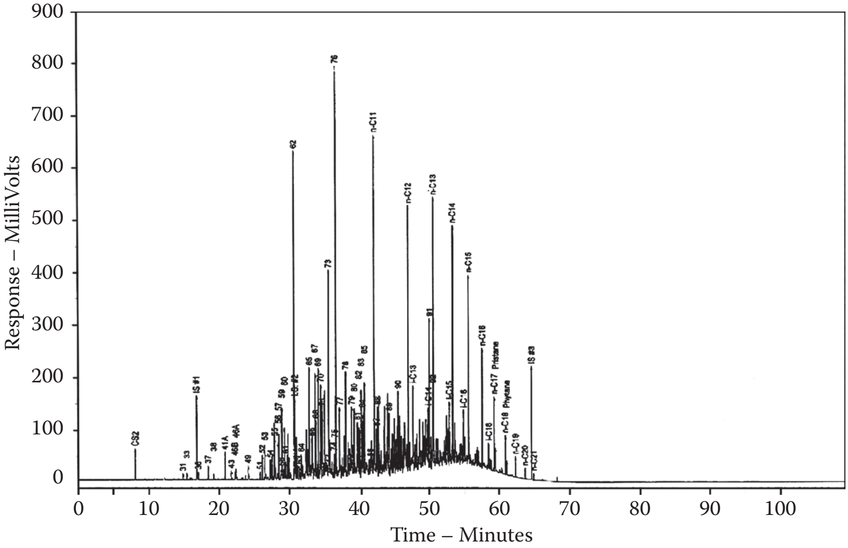

FIGURE 4.3
Example of a Jet-A chromatogram (Jet-A is still considered a light distillate [as gasoline]). Notice the expansion of carbon range toward n-C19 as well as the appearance of a slight UCM and shifting of peaks more toward the right. (Analysis performed by Zymax Forensics.)

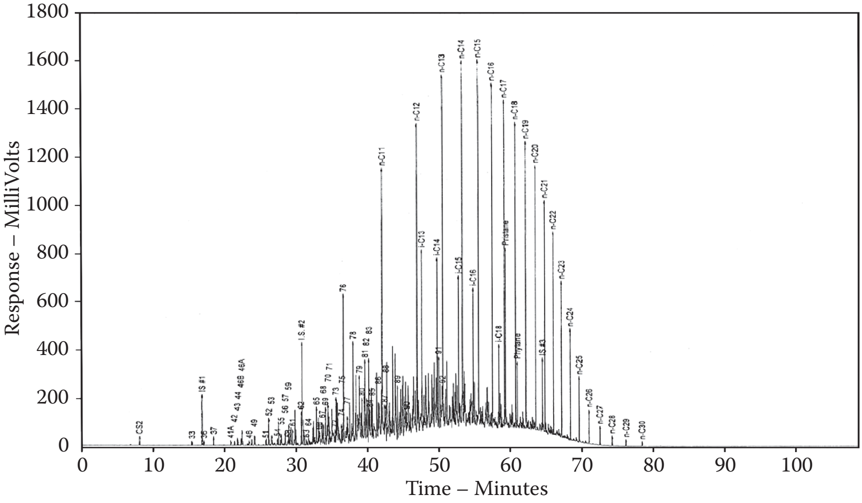

FIGURE 4.4
Example of a diesel fuel chromatogram. Diesel number 2 is representative for middle distillates; notice the expansion of carbon range toward n-C26–n-C27 as well as the presence of a UCM and shifting of peaks farther toward the right; this is a fresh product, as are those from previous examples. (Analysis performed by Zymax Forensics.)

presented in GC/FID chromatograms provides overall data on the presence/absence of oil, the carbon range, the distribution of n-alkanes and isoprenoids, as well as the shape and size of the UCM. The information from the GC/MS chromatogram usually provides detailed fingerprints of certain groups of studied hydrocarbons (e.g., hopanes, steranes, PAHs).

Chromatograms provide useful information for visual sample matching or evaluation of sample weathering degree. Based on the GC/FID result, a semiquantitative evaluation may be performed by estimating various individual hydrocarbon proportions according to corresponding peak height or area. When the GC/FID is operated under optimal peak resolution conditions, the method also may be used for quantitative measurements.

For crude oils and petroleum products, chromatograms may be quite specific, allowing differentiation of oils of distinct origin. In some cases, this specificity may also be reflected by distinct chromatographic patterns for various weathering stages of spilled oil. In addition, it is generally easy to differentiate what type of product versus crude oil is present in a sample (see examples from Figures 4.1–4.4).

Note that biodegradation and other weathering processes decrease lower n-alkane peaks first (toward the left of the chromatogram) and increase the UCM. At advance biodegradation stages, no n-alkane peaks may be visible, and a high UCM is usually observed. Typically, the presence of a UCM is linked to biodegradation processes.

Review of Histograms

Histograms are bar diagrams, each bar representing an individual compound, while the bar's height equals the contaminant concentration. Evaluation of saturated hydrocarbons (SHCs) and PAHs is usually done using both chromatograms and histograms.

SHC histograms for crude oils typically include C9–C40 n-alkanes and isoprenoids. A tiered review approach is recommended:

- Tier 1 evaluation investigates the general SHC sources; in this case, SHC profiles help:
    - Establish the presence and prevalence of biogenic materials, based on the typical prevalence of odd over even hydrocarbons in the C21–C35 range.
    - Evaluate the presence of petrogenic material through the identification of isoprenoid hydrocarbons usually associated with petrogenic sources.
- Tier 2 evaluation focuses on specific sources to be investigated; in this case, SHC profiles may help evaluate oil weathering and specific sources. For this tier, specific fingerprints of potential/candidate sources are needed for comparison.

A similar tiered approach also may be indicated when evaluating PAHs histograms:

- Tier 1 classification establishes the general source types (e.g., petrogenic, biogenic, pyrogenic) and is based on the following principles (Douglas et al., 2007; Boehm, 2006):
    - *Petroleum PAHs* (originating from crude oil and distillate products) have low parent PAH abundance relative to the alkylated PAH homologues. For example, using a naphthalene homologue series, the following proportions are associated with petroleum sources: C0–N < C1–N < C2–N > C3–N > C4–N.
    - *Pyrogenic PAHs* (originating from partial combustion or pyrolysis of organic matter) exhibit specific distributions with the prevalence of parent PAH relative to the alkylated homologues. For example, using naphthalenes, the following proportions are associated with pyrogenic sources: C0–N > C1–N > C2–N > C3–N > C4–N. Also, pyrogenic PAHs are usually more enriched in heavier PAHs (e.g., four to six rings), but lighter PAHs may also be associated with some pyrogenic sources.
    - *Biogenic PAHs* are revealed by the presence of perylene or retene formed through oxidation of sediments containing decaying organic debris. Note that some crude oils may also contain some perylene.
- Tier 2 classification establishes individual sources. For example, if petrogenic/oil spills are triggering the investigation, tier 2 evaluation looks at the petrogenic signature of the sample (if any is present) to compare the PAH profiles of each sample with the suspected source signature (i.e., histogram pattern). Statistical analysis also may be used, helping to confirm the presence/absence of the suspected source signature.

Diagnostic Ratios

Table 4.1 lists selected source diagnostic ratios. In principle, a ratio is relevant for source identification when the following conditions are met:

- The individual compounds used in the ratio are resistant to weathering.
- The individual compounds used in the ratio have similar composition and thus similar physical-chemical properties.
- The individual compounds used in the ratio can be reported quantitatively at low detection limits.

TABLE 4.1

Source Diagnostic Ratios for Crude Oils

Diagnostic Ratio	Chemical Class	Selected References
Pristane/phytane	SHCs (isoprenoids)	Wang et al., 2006b; Stout et al., 2001; Hansen et al., 2007; Peters et al., 2005; Stout and Wang, 2008
n-C17/pristane	SHCs (n-alkanes/isoprenoids)	
n-C18/phytane	SHCs (n-alkanes/isoprenoids)	
n-C18/pristane	SHCs (n-alkanes/isoprenoids)	
Norpristane/pristane	SHCs (isoprenoids)	Stout et al., 2001
n-C18/n-C30	SHCs (n-alkanes)	Stout et al., 2001
CPI (carbon preference index) = [(C25 + C27 + C29 + C31 + C33)/(C26 + C28 + C30 + C32 + C34) + (C25 + C27 + C29 + C31 + C33)/(C24 + C26 + C28 + C30 + C32)]/2	SHCs (n-alkanes)	Stout and Wang, 2008
D2/P2 (C2-dibenzothiophenes/C2-phenanthrenes) D3/P3 (C3-dibenzothiophenes/C3-phenanthrenes) D1/P1 (C1-dibenzothiophenes/C1-phenanthrenes)	PAH homologue series (including some polyaromatic heterocyclics): alkyl dibenzothiophenes and alkyl phenanthrenes	Stout et al., 2001; Boehm, 2006; Hansen et al., 2007; Peters et al., 2005; Wang and Stout, 2007; Hegazi and Andersson, 2007
C1-C/C3-C (C1-chrysenes/C3-chrysenes) C4-N/C2-F (C4-naphthalenes/C2-fluorenes) C3-DBT/C3C (C3-dibenzothiophene/C3-chrysene)	PAH homologue series (including some polyaromatic heterocyclics): alkyl PAHs	Peters et al., 2005
R/C4-P (retene/C4-phenanthrenes) BaF/4-MPy (benzo(a)fluorene/4-methylpyrene) 2-MPy/4-MPy (2-methylpyrene/4-methylpyrene) 1-MPy/4-MPy (1-methylpyrene/4-methylpyrene)	PAHs: alkyl phenanthrenes, alkyl pyrenes, benzo(a)fluorene and retene	Hansen et al., 2007
4,5-Dimethylphenanthrene/∑methylphenanthrenes	PAHs: alkyl phenanthrenes	Boehm, 2006
Methylphenanthrene indices: MPI 1 = 1.5(2MP + 3MP)/(P + 1MP + 9MP) MP1 2 = 3(2MP)/(P + 1MP + 9MP) MPR = 2MP/1MP	PAHs: alkyl phenanthrenes (various methyl phenanthrenes or MPs)	Stout et al., 2001; Hansen et al., 2007

continued

TABLE 4.1 (continued)
Source Diagnostic Ratios for Crude Oils

Diagnostic Ratio	Chemical Class	Selected References
Methyl-dibenzothiophene index: MDR = 4MDBT/1MDBT	PAHs/polyaromatic heterocyclics: alkyl dibenzothiophenes (DBT)	Stout et al., 2001; Hansen et al., 2007; Stout and Wang, 2008
(Benzo[b]fluoranthene + benzo[k]fluoranthene)/chrysene Perylene/chrysene Indeno[1,2,3-cd] pyrene/benzo[g,h,i]perylene Benzo(b)fluorene/benzo[a]pyrene Benzo[b]fluoranthene/benzo[a]pyrene Benz[a}anthracene/chrysene Benzo[e]pyrene/benzo[a]pyrene Benzo[b]fluoranthene/benzo[j,k]fluoranthene Benzo[b]fluoranthene/benzo{a}anthracene Benzo[b]fluoranthene/benzo[k]fluoranthene	Heavy (high molecular weight) PAHs (HPAHs) (nonalkylated)	Douglas et al., 2007; Boehm, 2006
(C23 + C24)/(C28 + C29) tricyclics (C28 + C29) tricyclics/hopane	Biomarkers: tricyclic terpanes and hopane	Stout et al., 2001
C23/C24 tricyclic terpane	Biomarkers: tricyclic terpanes	Peters et al., 2005; Wang et al., 1998, 2006b; Stout and Wang, 2008
C21/C23 tricyclic terpane	Biomarkers: tricyclic terpanes	Wang et al., 2006b; Stout and Wang, 2008
C26/C25 tricyclic terpane C28/C29 tricyclic terpane	Biomarkers: tricyclic terpanes	USGS, 2012
C23 tricyclic terpane/hopane C24 tricyclic terpane/hopane C28 tricyclic terpane/hopane C29 tricyclic terpane/hopane (C28 + C29) tricyclic terpanes/hopane Tricyclic terpanes (C19–C26)/hopane	Biomarkers: tricyclic terpanes and hopanes	Wang et al., 1998, 2006b; Stout and Wang, 2008; Hansen et al., 2007
Pentacyclic triterpane indices: Ts/hopane (18α(H),21β(H)-22,29,30-trisnorhopane) Moretane/hopane C29 αβ-25-norhopane/hopane C29 αβ-30-norhopane/hopane Oleanane/hopane Gammacerane/hopane Σ (C31–C35 homohopanes)/hopane C28 bisnorhopane/hopane	Biomarkers: hopanes and other pentacyclic triterpanes	Stout et al., 2001; Wang et al., 2006b; Stout and Wang, 2008; USGS, 2012; Hansen et al., 2007

TABLE 4.1 (continued)

Source Diagnostic Ratios for Crude Oils

Diagnostic Ratio	Chemical Class	Selected References
C31 homohopane (22S)/hopane C35 pentakishomohopane (22S)/C34 tetrakishomohopane (22S)	Biomarkers: hopanes	USGS, 2012
Tm/Ts (17α(H),21β(H)-22,29,30-trisnorhopane/18α(H),21β(H)-22,29,30-trisnorhopane) C32(*S*)/C32(*R*) (bishomohopane stereoisomers) C33(*S*)/C33(*R*) trishomohopane stereoisomers) C31(*S*)/C31(*R*) (homohopane stereoisomers)	Biomarkers: hopanes	Wang et al., 1998, 2006b; USGS, 2012
C29 αββ(*R* + *S*)/total C29 steranes C27 αββ/∑C27–C29 αββ steranes C28 αββ/∑C27–C29 αββ steranes C29 αββ/∑C27–C29 αββ steranes	Biomarkers: steranes	Stout et al., 2001; Wang et al., 2006b; Hansen et al., 2007
Sterane C27 ααα/hopane	Biomarkers: steranes and hopane	USGS, 2012
C29 ααα (20S)/C29 ααα (20R) steranes C29 αββ (20S + 20R)/C29 ααα (20S + 20R) steranes	Biomarkers: steranes	Hansen et al., 2007
C27 αββ/C29 αββ steranes C28 αββ/C29 αββ steranes	Biomarkers: steranes	Wang et al., 1998, 2006b
C27 βα diasterane (20S)/C27 βα diasterane (20S)	Biomarkers: diasteranes	Stout and Wang, 2008
C20 TA/C20 TA + C21 TA C27 TA (20R)/C28 TA (20R) C26 TA (20R)/C28 TA (20R) C28 TA(20R)/C28 TA(20S) C26 TA (20S)/[C26 TA (20S) + C28 TA (20S)] C28 TA (20S)/[C26 TA (20S) + C28 TA (20S)]	Biomarkers: triaromatic steranes (TAs)	Wang et al., 2006b; Hansen et al., 2007

Note: The ratios from Table 4.1 may also be used for source fingerprinting of petroleum distillates as long as the individual compounds from ratios are present in those distillates.

While various classes of compounds may be used for source identification, most of the diagnostic compounds belong to the cyclic biomarkers (e.g., hopanes and steranes) and PAH classes as shown in Table 4.1. This is to be expected since these compounds are highly resistant to weathering, and analytical methodologies sensitive to low amounts of contamination are commonly available.

Of note is the use of longer-chain n-alkanes in source fingerprinting, especially in identification of contributions from biogenic material. Specifically, n-alkanes in the range of n-C23 through n-C35 may be used to evaluate interference from natural organic matter (NOM; e.g., plant debris), which may change the spilled oil fingerprint especially in sediments. This is based on the fact that NOM contains a clear prevalence of odd-number n-alkanes versus even-number ones—characteristics for epicuticular leaf waxes. The degree of odd-numbered n-alkane enrichment may be quantitatively evaluated through the carbon preference index (CPI).

Table 4.2 lists selected weathering ratios. In principle, a ratio is relevant for evaluating the degree of weathering and the age of a spill when the following conditions are met:

- The individual compounds used in the ratio have quite distinct weathering resistance (e.g., one compound is much more affected by a certain type of weathering than another one); compounds more sensitive to a certain type of weathering (e.g., evaporation, biodegradation, water washing) are preferred to evaluate particular types of weathering processes and their prevalence in studied environment.
- The weathering pattern for the selected compounds (used in ratios) is well established within the study environment.
- The individual compounds used in the ratio can be reported quantitatively at low amounts.

A brief discussion of bio- and photodegradation and their effect on oil spills is presented next, focusing on susceptibilities of various diagnostic classes and compounds. This discussion should be useful for the use of various ratios presented in Table 4.2 in age-dating and forensic evaluations of oil spills. In addition, it is highly recommended that the selected references are consulted before any of the ratios are used.

Biodegradation and Photodegradation Susceptibilities of Various Oil Compounds

Biodegradation and photodegradation are the only weathering processes that destroy oil components, breaking them into smaller particles (simpler chemicals) and ultimately completely transforming them into basic innocuous molecules such as water and carbon dioxide.

Biodegradation has been shown to have the potential to affect and destroy all the petroleum compounds. Given enough time, even the most resistant oil compounds (such as biomarkers) may be biodegraded. In the marine environment, biodegradation may start immediately after an oil spill affecting various oil compound classes simultaneously but at different rates. The following biodegradation susceptibility order generally applies for the main oil hydrocarbon classes (Prince and Walters, 2007; Stout et al., 2002):

n-Alkanes > Monoaromatics > Iso-alkanes > Acyclic isoprenoids > Alkylated benzenes and PAHs > Steranes > Hopanes > Diasteranes > Nonhopanoid triterpanes > Aromatic steroids > Porphyrins

TABLE 4.2

Weathering Ratios for Crude Oils

Ratio	Compound Class	Application/ Weathering Evaluation	References
n-Pentane/n-heptane 2-Methylpentane/2-methylheptane	SHCs (n-alkanes and isoalkanes)	Evaporation	Kaplan et al., 1997
Benzene/cyclohexane, toluene/methylcyclohexane monoaromatics/total paraffins	Monoaromatics/ SHCs (cycloalkanes, alkanes)	Water washing	Kaplan et al., 1997
Perylene/benzo(a)pyrene naphthobenzothiophenes/chrysene C2-Naphthobenzothiophenes/ benzo[a]pyrene C3-Naphthobenzothiophenes/ benzo[a]pyrene Naphthobenzothiophenes/benzo[a] pyrene C2-Naphthobenzothiophenes/ C2-chrysenes	PAHs (including nonalkyl PAHs and alkyl PAHs—homologue series and some polyaromatic heterocycles)	Evaporation (changes due to evaporation were reported as being higher than those due to aerobic biodegradation)	Douglas et al., 2007
C3-Dibenzothiophene/C3-chrysene C2-DBT/C3-DBT (C2-Dibenzothiophenes/ C3-Dibenzothiophenes) C2-P/C3-P (C2-Phenanthrenes/ C3-Phenanthrenes) C2-N/C1-P (C2-Napthalenes/ C1-Phenanthrenes) Aromatics/sulfur aromatics	PAHs (alkyl PAHs—homologue series) and polyaromatic heterocycles	Differentiation of weathered oil	Boehm, 2006; Hansen et al., 2007; Peters et al., 2005; Hegazi and Andersson, 2007
C0-Naphthalenes/C2-naphthalenes C3-Naphthalenes/C3-phenanthrenes C2-Benzothiophenes/ C3-naphthalenes	PAHs (alkyl PAHs and polyaromatic heterocycles)	Degree of weathering (evaporation)	Kaplan et al., 1997
C27 αββ sterane/C29 αββ sterane C28 αββ sterane/C29 αββ sterane C27 αββ sterane/(C27 αββ sterane + C28 αββ sterane + C29 αββ sterane)	Biomarkers (steranes)	Differentiation of weathered oil	Wang et al., 2006b
C0-Chrysene/total chrysenes C1-Chrysenes/total chrysenes C2-Chrysenes/total chrysenes C3-Chrysenes/total chrysenes C4-Chrysenes/total chrysenes	PAHs (parent and alkyl PAHs)	Biodegradation and photodegradation	Stout et al., 2001; Garrett et al., 1998
C3-Phenanthrenes/C3-chrysenes	PAHs (alkyl PAHs)	Biodegradation	Garrett et al., 1998

continued

TABLE 4.2 (continued)

Weathering Ratios for Crude Oils

Ratio	Compound Class	Application/ Weathering Evaluation	References
Sterane C27 αα (*S*)/sterane C27 αα (*R*) Sterane C29 αα (*S*)/sterane C29 αα (*R*) Sterane C28 αα (*S*)/sterane C28 αα (*R*) Diasterane 27(*S*)/diasterane 27 (*R*)	Biomarkers (steranes and diasteranes)	Biodegradation	Wang et al., 2006b; Prince and Walters, 2007; Stout et al., 2001
C27, C28, and C29 ααα/αββ sterane epimers (*m*/*z* 217)	Biomarkers (steranes)	Biodegradation	Wang et al., 2006b
C27 diasterane (*S* + *R*)/C27 sterane (*S* + *R*)	Biomarkers (steranes and diasteranes)	Biodegradation	Wang et al., 2006b
Methyldibenzothiophenes ratio: 4-MDBT:2-/3-MDBT:1-MDBT 4-MDBT/1-MDBT 2-MDBT/4-MDBT	PAHs (polyaromatic heterocycles)	Biodegradation	Wang et al., 1998; Stout and Wang, 2008; Hansen et al., 2007
Methylphenanthrenes ratio: (3+2-Methylphenanthrenes)/(4-/9-+1-methylphenanthrenes) 2-Methylphenanthrene/1-methylphenanthrene MPI 1 = 1.5(2MP + 3MP)/(P + 1MP + 9MP) MPI 2 = 3(2MP)/(P + 1MP + 9MP)	PAHs (alkyl PAHs)	Biodegradation	Wang et al., 1998; Stout and Wang, 2008; Hansen et al., 2007
Methylnaphthalenes (MPs) ratio: (1,3+1,6-Dimethylnaphthalenes)/Total C2-naphthalenes 2-Methylnaphthalenes/1-methylnaphthalenes (2,6-Dimethylnaphthalenes + 2.7-Dimethyl-naphthalenes)/1,5-dimethylnaphthalenes	PAHs (alkyl PAHs)	Biodegradation	Wang et al., 1998; Stout and Wang, 2008
Methylfluorenes ratio: Methylfluorene/C1-fluorenes	PAHs (alkyl PAHs)	Biodegradation	Wang et al., 1998
Acenaphthene/fluorene Dibenzofuran/fluorene	PAHs	Biodegradation	Douglas et al., 2007

Note: The ratios from Table 4.2 may also be used for weathering evaluation of petroleum distillates as long as the individual compounds from ratios are present in those distillates.

For PAHs, the following susceptibilities to biodegradation are generally reported:

- Between PAH homologue series, the biodegradation order is (Wang et al., 1998):

  Alkyl naphthalenes > Alkyl dibenzothiophenes > Alkyl fluorenes > Alkyl phenanthrenes > Alkyl chrysenes

- Within each homologue series, the following biodegradation susceptibility generally applies (Prince and Walters, 2007; Stout et al., 2002; Wang et al., 1998):

  Parent PAH > C1-alkyl PAH > C2-alkylPAH > C3-alkyl PAH > C4-alkyl PAH

- In relation to SHCs, the following biodegradation susceptibility order was proposed (Dutta and Harayama, 2000):

  n-Alkanes > Naphthalenes > Iso-alkanes > Fluorenes > Phenanthrenes > Dibenzothiophenes

In what concerns individual PAH isomers (within homologue groups), no general rule exists related to biodegradation susceptibility. However, biodegradation patterns have been established in some cases. For example,

- 2-/3-Methyldibenziothiophene (MDBT) biodegraded at the fastest rate between the methyldibenzothiophenes isomeric series, while 1-methyldibenzothiophene was slightly more resistant to biodegradation than 4-methyldibenzothiophene (Wang et al., 1998).
- A significant change in the relative distribution of alkylated naphthalenes and methylfluorenes denoted the following biodegradation susceptibility:
  - (3+2-Methylphenanthrenes) > (4-/9-+1-methylphenanthrenes) (Wang et al., 1998); other authors reported a consistent biodegradation susceptibility (Stout and Wang, 2008): 3-methylphenanthrene > 2-methylphenanthrene > 1-methylphenanthrene > 9-methylphenanthrene;
  - (1,3+1,6-Dimethylnaphthalenes) > other C2-naphthalenes (Wang et al., 1998);
  - Methylfluorene > other C1-fluorenes (Wang et al., 1998).

In what concerns biomarkers, although known for their great resistance to weathering, biomarkers are eventually also biodegraded. Similar to PAHs, biomarker biodegradation has been proven to be isomer specific (Wang et al., 1998). However, a longer time is needed for biomarker biodegradation than for PAHs, and some short-term laboratory studies did not result in observable biomarker depletion (Wang et al., 1998). Of the selected biomarker ratios given in Table 4.2, many are isomer ratios, which are usually specific indicators for biodegradation occurrence; they may also be used as source indicators (unless advanced weathering and biodegradation are suspected to have occurred).

When the only discriminatory traits expected for oils of similar composition (e.g., from the same rock formation, such as spilled extracted oil versus natural seeps from the same geological formation) are biodegradation stages, isomer ratios may provide high diagnostic tools. This was proven useful by the U.S. Geological Survey (USGS, 2012) looking to differentiate between platform oils and natural seeps as potential sources of tarballs washing out on California beaches.

The following biodegradation susceptibility was observed for biomarkers (Wang et al., 2001):

- For steranes: C27 > C28 > C29 with 20R ααα > 20(R + S)αββ > 20S ααα.
- For hopanes: C35 > C34 > C33 > C32 > C31 with 22R > 22S; also hopane > C31 (22S) and C32 (22S).
- The most biodegradation resistant hopanes and steranes were C29–18 α(H), 21 β(H)-30-norneohopane, and C29-αββ 20R and 20S stigmasteranes.

It has to be noted that some variations in the biodegradation order (susceptibility) may appear in various environments based on the composition of microbial communities. At the same time, interfering factors may influence the biodegradation ratios (e.g., interference from biogenic material in sediments).

As a general rule for all oil compounds and classes, exceptions to the established biodegradation orders presented in this section may appear in various environments, potentially affecting the individual biodegradation susceptibilities. While the biodegradation susceptibilities generally established may work in many environments, each case should be considered with an open mind and potential exceptions to the rule also considered. It is the role of the forensic scientist to decide when an apparent contradictory weathering pattern is an exception to the rule or may be due to analytical errors or other factors. It is recommended to check the literature for reported exceptions that may match the case at hand and could increase the confidence in considering exceptions.

Photodegradation is potentially a significant process in the degradation of crude oils spilled in marine environments (Garrett et al., 1998). In contrast with biodegradation, photodegradation seems to particularly affect some specific classes of oil compounds. While the saturated compounds (SHCs) are resistant to photodegradation, aromatic compounds were shown to be affected by photooxidation with the production of polar compounds (Garrett et al., 1998). For SHCs, an exception was observed only for aliphatic sulfur compounds (Garrett et al., 1998), but this class represents only a tiny fraction of SHCs. Of note is that the photodegradation changes in aromatic compounds (e.g., PAHs) are distinct and opposite to the changes due to biodegradation and other weathering processes (e.g., evaporation). For example, in the case of PAHs, the rate of photooxidation often increases with increasing alkylation (Stout and Wang, 2007). Basically, a greater size and increasing alkyl substitution increase the sensitivity of aromatic compounds to photodegradation (Garrett et al., 1998).

For some PAH homologue series (e.g., alkylated phenanthrenes and dibenzothiophenes), similar rates have been reported for both biodegradation and photodegradation (Garrett et al., 1998). For these compounds, their distribution/proportion may remain constant when affected by both of these processes equally. For other more biodegradation-resistant PAH homologue series, such as alkylated chrysenes, the effect of photodegradation may be easily distinguishable from their distribution patterns.

Considering susceptibility to both bio- and photodegradation, along with the fact that biodegradation occurs at significantly lower rates, the chrysene homologue series could be used to point out the occurrence of photodegradation. This could establish the fate and transport of PAHs accumulated in sediments (e.g., if they were initially exposed to the sun coming from a surface spill or if they have never been exposed to the sun, such as coming from a deep-water spill or a seep).

Petrogenic versus Pyrogenic Sources of PAHs

Table 4.3 presents selected diagnostic ratios commonly used for differentiating between petrogenic versus pyrogenic sources of PAHs (which are usually the main PAH sources in sediments and soils). Additional useful information is provided in the histogram review section.

Note that a third general source for PAHs is the diagenetic process in sediments, which results in PAHs such as perylene and retene formed through oxidation of sediments containing decaying organic debris.

Biomarker Regression

Biomarker regression (sometimes referred to as R^2 evaluation) consists of comparison of biomarker composition (usually hopanes and steranes) of a sample versus a control oil or candidate source oil. The comparison is made by plotting the biomarker concentration data of an individual sample versus the biomarker concentration data of the source candidate sample. This technique may be used with biomarker diagnostic ratios instead of individual compound concentrations also.

TABLE 4.3

Fast Guide to Diagnostic Ratios Used to Differentiate between Petrogenic versus Pyrogenic Sources of PAHs

Ratio	Fingerprinting Prinicples	References
Phenanthrene/anthracene (P/A)	P/A > 10 for petrogenic sources P/A < 10 for pyrogenic sources	Boehm, 2006
Fluoranthene/pyrene (Fl/Py)	Fl/Py > 1 → pyrolitic origin Fl/Py < 1 → petrogenic origin	Boehm, 2006; Douglas et al., 2007; Meniconi and Gabardo, 2002
Benzo[a]anthracene/chrysene (BaA/C)	BaA/C > 0.9 → pyrolitic origin BaA/C < 0.4 (or equal) → petrogenic origin	Douglas et al., 2007; Boehm, 2006; Meniconi and Gabardo, 2002
ΣMethylphenanthrenes/phenanthrene (ΣMP/P) 4,5-Dimethylphenanthrene/Σmethylphenanthrene	ΣMP/P < 2 → pyrolitic origin ΣMP/P > 2 → petrogenic origin Also for source differentiation for fossil fuel (e.g., oil vs. coal)	Boehm, 2006; Meniconi and Gabardo, 2002
MP/P (methylphenanthrenes/phenanthrene ratio): (3-MP + 2-MP + 9-MP + 1-MP)/P	MP/P < 0.5 → exclusive pyrogenic MP/P > 3.5 → exclusive petrogenic	Saha et al., 2012
MPy/Py (Methylpyrenes + Methylfluoranthenes)/(Pyrene + Fluoranthene)	MPy/Py < 0.15 → exclusive pyrogenic MPy/Py > 1.5 → exclusive petrogenic	Saha et al., 2012
MC/C (Methylchrysenes + Methylbenz[a]anthracenes)/(Chrysene + Benz[a]anthracene)	MC/C < 0.2 → exclusive pyrogenic MC/C > 2.0 → exclusive petrogenic	Saha et al., 2012
MPAHs/PAHs ΣMethyl PAHs/(Phenanthrene + Fluoranthene + Pyrene + Chrysene + Benz[a]anthracene)	MPAHs/PAHs < 0.3 → exclusive pyrogenic MPAHs/PAHs > 2.2 → exclusive petrogenic	Saha et al., 2012
Pyrogenic index (PI): Σ(3- to 6-ring EPA PAHs)/Σ(5 alkylated PAHs)	Petrogenic vs. pyrogenic	Stout and Wang, 2008

TABLE 4.3 (continued)

Fast Guide to Diagnostic Ratios Used to Differentiate between Petrogenic versus Pyrogenic Sources of PAHs

Ratio	Fingerprinting Principles	References
Pyrogenic index: (Acenaphthylene + Acenaphthene + Anthracene + Fluoranthene + Pyrene + Benz[a]anthracene + Benzofluoranthenes + Benzopyrenes + Perylene + Indeno[1,2,3-cd]pyrene+dibenz[a,h] anthracene + Benzo[g,h,i]perylene)/[(C0 to C4 naphthalenes) + (C0 to C4 phenanthrenes) + (C0 to C3 dibenzothiophenes) + (C0 to C3 fluorenes) + (C0 to C3 chrysenes)]	Pyrogenic vs. petrogenic PAHs	Peters et al., 2005
(Anthracene + Fluoranthene + Benz[a]anthracene + Benzofluoranthenes + Benzopyrenes)/[(C1 + C2 phenanthrenes) + (C1 + C2 dibenzothiophenes)]	Pyrogenic vs. petrogenic PAHs	Peters et al., 2005

A coefficient of determination, referred to as R^2 (square R), is calculated based on the correlation analysis mentioned previously. Values of R^2 that are closer to 1 denote a match with the plotted suspected source (candidate source oil).

While biomarker regression is a powerful technique, information from R^2 evaluation should be compared with information from other lines of evidence (e.g., GC/FID, n-alkanes, isoprenoid and PAH histograms, diagnostic ratios) before a final forensic conclusion is reached. In addition, if advanced oil weathering is expected, the biomarker regression may not work, and low R^2 may not necessarily indicate non-matches.

Multivariate Statistics: Chemometric Evaluations

Statistical classification is one of the ultimate forensic tools to assess relationships between samples and identify sources and contributions when abundant data exist. Exploratory data analysis through multivariate statistics is used in fingerprinting studies to identify similarities between samples and candidate sources (through clustering of samples with similar characteristics) and to evaluate the compositional characteristics affecting the result the most (i.e., characteristics that are mostly responsible for resulting sample classification or clustering). In addition, some techniques may identify the number of end members in a mixture and their composition and contribution to the mixture (e.g., polytopic vector analysis [PVA], cluster analysis).

Multivariate statistical analyses such as principal component analysis (PCA) and hierarchical cluster analysis (HCA) have been employed to analyze chemical data for pattern recognition. These statistical techniques, along with PVA, may be particularly useful for evaluating a large number of samples based on a large number of parameters/diagnostic characteristics.

The following steps should be considered for the employment of multivariate statistical analysis (PVA is used here for exemplification):

1. Autoscale of the chemical data
2. Testing of the distributions for normality
3. Detection and elimination of outliers in the dataset
4. Use of the gap statistic test to determine the number of clusters
5. Use of the silhouette statistic also to determine the number of clusters
6. Running of the *k*-means algorithm to partition and classify the samples into *k* clusters
7. Use of PCA scores and loading plots as a means to visualize the results of the cluster analysis
8. Generation of histograms of the clusters to visualize the resulting hydrocarbon compositions (corresponding to each cluster) and assigning general and specific sources

A brief description of multivariate statistic techniques is provided in the section dedicated to statistical techniques in Chapter 5.

Other Techniques

Other (less-common) diagnostic techniques applicable to crude oil fingerprinting include the evaluation of the following classes of oil compounds:

- *n-Alkylcyclohexanes (CHs)* are cyclohexanes with a single alkyl side chain of varying carbon numbers; these compounds can be detected by GC/MS in SIM (selective ion monitoring) mode at an *m*/*z* value of 83. They have a broad boiling range (side chain in the range C1–C15) and higher resistance to biodegradation than n-alkanes. They may reveal the boiling range of a sample (even when differences are subtle) and thus establishing the product(s) present the sample (Stout and Wang, 2008). Their distribution patterns could be compared between samples and have source discriminatory power.
- *Diamondoids* are SHCs with three or more fused cyclohexane rings, resulting in a diamond-like structure. They are present in crude oils and distillate products (where they are in higher abundance due to concentration during oil distillation). Their distribution may be linked to specific sources, and numerous diagnostic ratios have been developed using diamondoids, as well as several diagnostic ratios (Stout and Wang, 2008).
- *Sesquiterpanes* are lighter biomarkers. Useful diagnostic sesquiterpanes are bicycloalkanes that occur in crude oils and contain approximately 15 carbons. Their chemical structure includes either a drimane or a eudesmane skeleton. The drimane-based

TABLE 4.4

Main Petroleum Distillates

Refined Product/Petroleum Distillate	Boiling Range (°F)
Gasoline	80–437
Naphtha	85–450
Mineral spirits	210–400
Stoddard solvent	260–550
Military aviation fuel (JP-4, JP-5, JP-8)	150–570
Kerosene	300–572
Diesel number 1	320–540
Diesel number 2	320–750
Diesel number 4	500–1,000
Heating oil number 6 or Bunker C oil	650–1,150
Lubricating oil	350–1,100
Hydraulic oils	520–1,100
Tars or asphalts	520 to > 1,200

sesquiterpanes are of more use in oil fingerprinting since they were proven ubiquitous in crude oils. These biomarkers are of high value for lighter oil distillate products. A useful overview of sesquiterpanes use as petroleum diagnostic compounds is provided by Stout and Wang (2008).

Selected Fingerprinting Techniques for Petroleum Distillates

Table 4.4 presents the main petroleum distillates based on their approximate boiling ranges.

Since many practical cases involve gasoline and diesel number 2/fuel oil releases, selected fingerprinting techniques are provided for these petroleum distillates in Table 4.5. Fingerprinting of high boiling hydrocarbons was described by Kaplan (2001).

Laboratory Tests for Oil Fingerprinting Investigations

The forensic scientist should have a well-established fingerprinting strategy, which is the basis for appropriate laboratory testing selection in consultation with the analytical laboratory. Table 4.6 includes examples of common fingerprinting testing for oil and oil products that can be requested from specialized laboratories. There are many other testing types that may be done (based on GC/MS in SIM mode) to target specific classes of compounds with relevance in fingerprinting (e.g., sesquiterpanes, diamondoids).

4.1.1.4.1.2 Chemical Fingerprinting of PCBs and Dioxins/Furans **Polychlorinated biphenyls** are mixtures of more than 200 individual compounds called *congeners* (biphenyls with various combinations of one to ten chlorine atoms bound to the phenyl groups). The following facts about

TABLE 4.5

Fast Guide to Specific Fingerprinting Techniques for Light and Middle Petroleum Distillates

Technique Name and Reference	Technique Principle	Application
Toluene/n-C8 ratio for gasoline in soil (Schmidt et al., 2002)	Toluene/n-C8 ratio in gasolines changed over the years—observation that is based on a large number of analyzed samples: • Ratio < 5 → sample fits into the 1973–1983 group • Ratio: 5–10 → sample fits into 1984–1993 group • Ratio > 10 → sample fits into 1994–2001 group • Ratio < 3 → possibly manufactured before 1973 Most probable year of release may be deduced using log transformed data.	Gasoline products in soil (regular or midgrade product) that are • Less than 50% evaporated and little affected by other types of weathering • Not mixed with other hydrocarbons or with a different gasoline spill
Butane ratio: n-C4/(n-C4 + i-C4) (Beall et al., 2002)	The difference in butane ratios (n-C4 refers to normal butane, while i-C4 refers to isobutane) may be used to distinguish automotive gasolines from one another when evaporation is not an important factor. Evaporation should be considered since n-butane has less volatility compared to isobutane.	Gasoline products: • Fresh gasoline or • Lightly weathered gasoline (little to no evaporation)
Pentane ratio: i-C5/(i-C5 + *n*-C5) (Beall et al., 2002)	This ratio (n-C5 refers to normal pentane, while i-C5 refers to iso-pentane) can be used to forensically delineate gasoline releases. However, as in the case of the butane ratio, evaporation should be considered as it may change the original ratio.	Gasoline products: • Fresh gasoline or • Lightly weathered gasoline (little to no evaporation)
Iso-octane ratio: 2,2,4-TMP/(2,2,4-TMP + 2,2,3-TMP + 2,3,4-TMP + 2,3,3-TMP) (Beall et al., 2002)	Since the various iso-octane or trimethylpentane (TMP) isomers have a similar fate and transport, the iso-octane percentages could be useful to forensically differentiate gasolines. Gasolines may have different TMP ratios/proportions based on the acid-catalyzed processes used to produce TMP isomers.	Gasoline products (fresh or lightly weathered products are preferred)
Rb ratio = benzene + toluene)/(ethylbenzene + xylenes) (Kaplan, 2003)	The Rb ratio was empirically shown to decrease in time after a gasoline release to groundwater (due to fate and transport and weathering processes): • Rb < 5 → near the source and immediately after a spill; Rb between 1.5 and 6 may be indicative of NAPL. • Rb between 0.8 and 1.1 → original gasoline. • Rb < 0.5 → gasoline residence time greater than 10 years. If monitoring data are available for 10 or more years, it is recommended to plot Rb vs. time.	Gasoline dissolved groundwater plumes: method was empirically proven helpful for dating dissolved gasoline plumes

TABLE 4.5 (continued)

Fast Guide to Specific Fingerprinting Techniques for Light and Middle Petroleum Distillates

Technique Name and Reference	Technique Principle	Application
Ratios of selected compounds over total resolved hydrocarbons (TRHs) (M. Wade, personal communication, 2010)	The use of TRHs makes the proposed ratios that follow comprehensive and having a high diagnostic power: • [Benzene + Toluene]/TRH • [Ethylbenzene + Xylenes]/TRH • C3-alkylbenzenes/TRH • C4- and C5-alkylbenzenes/TRH	Gasoline products
	Oxygenates are organic oxygenated compounds that have been added to gasoline over the years. The detection of the following main oxygenate compounds in a sample may help establish the source and age of the released gasoline: • *MTBE (methyl tertiary butyl ether):* Introduced in gasoline in 1979; its proportion increased from approximately 7 vol% to 11 vol% by 1981 and to 15 vol% by 1988. By 1990, MTBE was added to winter gasoline in about 15 vol%. Up to 17 vol% MTBE was added to gasoline by 1992 as a response to the Clean Air Act; by 1995, MTBE added to gasoline dropped to 11 vol% in reformulated gasoline; in 1999, MTBE was the most widely used oxygenate in the United States; after 2000, MTBE started being banned in different states. • *TBA (tertiary butyl alcohol):* Introduced in gasoline at 7 vol%; by 1981, added TBA increased to 10 vol%, and it was blended with methanol. • *TAME (tertiary amyl methyl ether):* First manufactured in 1987 and introduced into gasoline in different combinations with MTBE in the early 1990s; its first appearance in California was recorded in winter 1993; by 1996, TAME reached maximum usage. • *ETBE (ethyl tert-butyl ether):* Its use in gasoline was recorded in four locations in 1995 (with a maximum in Louisville, KY); in 1996, minor use was recorded in Baltimore, MD.	Gasoline products

continued

TABLE 4.5 (continued)

Fast Guide to Specific Fingerprinting Techniques for Light and Middle Petroleum Distillates

Technique Name and Reference	Technique Principle	Application
Oxygenate use (Petrisor, 2006b)	• *Ethanol:* Used as a gasoline additive for a long time (starting in the 1930s and 1940s) and recently has been increasingly used as a replacement for MTBE. However, ethanol is likely not going to be detected unless the gasoline product is fresh since it is rapidly biodegraded in the environment.	
Christensen–Larsen technique (Christensen and Larsen, 1993)	This method is based on the observed decrease of n-C17/pristane ratio in diesel number 2 products released to soil. Based on observations at several sites in Denmark (by Christensen and Larsen) with known recorded releases of diesel number 2, the following age-dating is proposed: • n-C17/pristane > 1.5 → less than 5 years • n-C17/pristane = 1 → 10 years • n-C17/pristane > 1 → 5–10 years • n-C17/pristane = 0.4 → 15 years • n-C17/pristane = 0 → 18 years or more Note that while this may be a convenient age-dating technique in some particular situations, this method has many limitations to its applicability, with some main ones indicated in the next column. However, as with any fingerprinting technique, it is necessary to carefully read the original reference and any other literature references to understand its use and limitations.	Diesel number 2 fuel in soil (minimum 100 mg/kg of TPH present in soil) when a series of conditions are met: • Similar climatic conditions to those from Denmark • Implies knowledge of initial ratio which should be consistent to the range published by Christensen and Larsen (1993) (possible to obtain also from literature) • One sudden release (no subsequent releases) • Recommended more than one sampling event in time • Recommended for sites with minimum infiltration • Check site conditions (oxygen, nutrients, oil) to avoid sites with excessive or little degradation • Original diesel product (unspilled) has an n-C17/pristane ratio of 2–3 (similar to the products from the Christensen and Larsen study)

TABLE 4.5 (continued)

Fast Guide to Specific Fingerprinting Techniques for Light and Middle Petroleum Distillates

Technique Name and Reference	Technique Principle	Application
Ratios of classes of compounds and total resolved compounds (TRCs) (M. Wade, personal communication, 2010)	The use of classes of compounds and total resolved compounds makes the proposed ratios that follow comprehensive and having a high diagnostic power: • n-Alkanes (n-C9 to n-C24 range)/TRC • Isoprenoids/TRC • n-Alkanes/isoprenoids The n-alkanes within the middle distillate range are mostly between n-C9 and n-C24. Isoprenoids present in middle distillates are in the range of 13 to 20 carbon atoms: IP13 to IP20.	Middle distillate products
Alkylated PAH ratios (Stout et al., 2002)	PAHs are present in middle distillates. As discussed for crude oils, PAHs are typically used in fingerprinting studies because of their higher resistance to weathering. Some of the high diagnostic PAH ratios include the following: • D2/P2 (C2-dibenzothiophene/C2-phenanthrene) • D3/P3 (C3-dibenzothiophene/C3-phenanthrene) Typically, a double-ratio plot of D3/P3 vs. D2/P2 helps visualize differences and cluster samples based on sources (see example in the cited reference by Stout et al., 2002).	Middle distillate products
Diamondoids diagnostic ratios (Stout and Wang, 2008)	Diamondoids are saturated hydrocarbons that have three or more fused cyclohexane rings, resulting in a "diamond-like" structure. A series of ratios that include selected diamondoid compounds has been proposed for source identification of middle distillates: • MAI = 1-Methyladamantane/(1-Methyladamantane + 2-Methyladamantane) • EAI = 2-Ethyladamantane/(1-Ethyladamantane + 2-Ethyladamantane) • MDI = 4-Methyldiamantane/(1- + 3- + 4-Methyldiamantane)	Middle distillate products

continued

TABLE 4.5 (continued)

Fast Guide to Specific Fingerprinting Techniques for Light and Middle Petroleum Distillates

Note: The use of any of the techniques briefly described in Table 4.5 requires the careful reading of the original reference provided under the "Technique Name and Reference" column for each method. This table serves as a guide to indicate some common fingerprinting techniques, their principles, and where to gather more information for their use. Please keep in mind that any case is distinct, and that it is the role and judgment of the forensic scientist to decide when and how to apply a forensic technique to a particular case. It is possible that even if all the conditions are met for application of a certain technique, the technique may still not work. This is why confirmation of results through multiple independent lines of evidence is recommended.

TABLE 4.6

Examples of Common Laboratory Testing for Fingerprinting Oil and Oil Products

Analysis	Application	Forensic Relevance
C3–C10 (PIANO gasoline-range distribution) by high-resolution GC/FID	Gasoline fingerprinting	• Identifies over 90 compounds • Compares compositional similarities between samples (relative percentage) • Degradation ratios provide information on age of product
Oxygenated blending agents MTBE, DIPE (diisopropyl ether), ETBE, TAME, TBA, ethanol by EPA 1625 modified	Gasoline fingerprinting	• Quantifies oxygenated additives in gasoline • Provides information on age of unleaded gasoline
EDB, MMT (methylcyclopentadienyl manganese tricarbonyl), and organic lead concentrations by GC/ECD	Gasoline fingerprinting	• Quantifies alkyl lead compounds and lead scavenger EDB, as well as the octane booster MMT • Provides information on age of leaded gasoline
C3–C44 (whole oil) by high-resolution GC/FID	Crude oil fingerprinting	• Identifies up to 149 compounds • Includes gasoline-range PIANO analysis • Assists in identification of types of free product or crude oils • Degree of degradation provides information on product age
Full-scan GC/MS	Crude oil fingerprinting	• Provides alkanes, alkylbenzenes, PAHs, and polycyclic biomarkers (e.g., hopanes, steranes), which may be used to reveal complex oil fingerprints • Degree of degradation provides information on the age of a product

PCBs would help in understanding the fate and transport and better interpretation of the forensic fingerprints:

- PCBs are manufactured chemicals (produced between the beginning of the 1930s until the 1970s, with production ceasing in 1977 in the U.S.).
- Natural formation was not reported.
- Broad industrial use of PCBs was recorded in transformers/electrical equipment and capacitors; PCBs were also used in carbonless copy paper, printing inks, hydraulic fluids. although PCBs have been banned since 1977, they are still present in equipment.
- PCBs may be considered global contaminants—they are ubiquitous (present in all media).
- PCBs are DNAPLs with almost no water solubility; they tend to accumulate in topsoils.
- PCBs are semivolatile and have been proven to be transported by air over long distances.
- PCBs are strongly bound to soil (lipophilic). They tend to accumulate in the adipose tissue (fat) of animals and humans.
- Persistence in the environment is due to the general good resistance of PCBs to weathering; this trait makes PCB fingerprinting possible, even for old releases. However, in time, some degradation occurs for PCBs released in the environment, and this should always be considered when interpreting fingerprinting results.

The following terms are useful when discussing PCBs:

- **Congener** = An individual compound (with 1 to 10 Cl atoms).
- **Homologues** = All individual compounds with the same number of Cl atoms (but bound to the aromatic ring in various positions), yielding 10 homologue classes.
- **Aroclors** = Commercial formulations (mixtures of various congeners in various proportions)—for PCBs manufactured by Monsanto—predominant in the United States.
- **Askarel** = Chlorobenzene/PCB mixtures used as dielectric fluids.
- **Clophen, Phenoclor, Pyralene, Kanechlor, Fenoclor** = Commercial formulations (from other manufacturers than Monsanto).

Dioxins and furans: *Dioxins* refer to chlorinated dibenzo-p-dioxins (CDDs); *furans* refer to chlorinated dibenzofurans (CDFs). These are mixtures of many individual compounds (containing various numbers of Cl atoms that can attach to the benzoic rings, which is any combination of one to eight attached Cl atoms). They have triple-ring structure consisting in two benzene rings connected by one (for CDFs) or two (for CDDs) oxygens. These compounds are not manufactured but may be produced inadvertently during chemical manufacturing of other compounds or during incomplete combustion (including from backyard burning). The following facts about dioxins/furans would help in understanding the fate and transport and better interpretation of forensic fingerprints:

- Dioxins/furans are inadvertently produced by anthropogenic activities (e.g., incomplete combustion and chemical manufacturing). They are typically present as complex mixtures.
- Natural formation occurs by forest fires and volcanoes.
- Widespread occurrence of dioxins/furans was reported in all media, meat, milk, fish, and human body, indicating that background levels should be considered in forensic investigations.
- Dioxins/furans are DNAPLs with very low water solubility.
- Dioxins/furans have little volatility.
- Dioxins/furans are usually strongly bound to soil (lipophilic).
- Persistence in the environment is well recognized for dioxins/furans. However, they may be subjected to atmospheric photooxidation and photolysis of nonsorbed species in gaseous phase or at water– or soil–air interface.

The following terms are useful when discussing dioxin/furans:

- **Congener** = An individual compound (with one to eight Cl atoms).
- **Homologues** = All individual compounds with the same number of Cl atoms (but bound to the aromatic ring in various positions), yielding eight homologue classes.
- **2,3,7,8-Substituted CDD/CDF** = All individual congeners with Cl atoms in positions 2, 3, 7, and 8 (and other—one or more—Cl atoms in other positions).
- **2,3,7,8 TCDD TEQ** = Concentration of each 2,3,7,8-substituted CDD/CDF × Toxicity equivalent factor.

Fingerprinting Principles: Since PCBs and dioxins/furans have much in common, their chemical fingerprinting is based on similar principles as discussed next:

- Dioxins/furans and PCBs may be chemically fingerprinted based on
  - Congener profiles (see example in Johnson et al., 2006);
  - Homologue profiles (see examples in Johnson et al., 2006, and Shields et al., 2006);
  - Commercial formulation (e.g., Aroclors) profiles;

TABLE 4.7

Recorded Uses of Aroclors

	Dielectric Fluids		Hydraulic/Lubricants/ Heat Transfer Fluids				Plasticizers			Miscellaneous Industrial			
Aroclor	**Capacitor**	**Transformer**	**Heat Transfer**	**Hydraulic Fluid**	**Vacuum Pumps**	**Gas Transmission Turbines**	**Rubber**	**Synthetic Resin**	**Carbonless Copy Paper**	**Adhesive**	**Wax Extender**	**Dedusting Agents**	**Ink; Cutting Oil; Pesticide Extender**
1221	X					X	X			X			
1232				X			X			X			
1016	X*												
1242	X*	X	X	X		X	X*		X*	X*	X*		
1248				X	X		X	X		X			
1254	X	X*		X	X		X	X		X	X	X	X
1260		X		X	X			X				X	
1262								X					
1268								X			X		

Source: Based on Johnson, G.W., Quensen, J.F., III, Chiarenzelli, J.R., and Hamilton, M.C. 2006. Polychlorinated Biphenyls. In: *Environmental Forensics: Contaminant Specific Guide*, edited by R.D. Morrison and B.L. Murphy, Elsevier Academic Press, Burlington, MA, 187–225.

Note: X = recorded specific use; X* = recorded principal use.

  - Commercial formulation usage and profile (for PCBs) (see Table 4.7);
  - Concentration trends (lateral and vertical) away from suspected source(s).
- Data may be analyzed using the following:
  - Profile evaluation (comparison of concentration patterns of individual congeners, homologues, or commercial formulations, similar to histogram evaluation for oil products) (see examples)
  - Spatial concentration distribution patterns, including two-dimensional (2D) and three-dimensional (3D) GIS (geographic information system) representations
  - Standardization methods are generally used for dioxins/furans
  - Multivariate statistics techniques are usually employed to discern patterns/sample grouping and apportion contributions; note that samples need to be comparable
- Background values should be considered in forensic evaluations, especially since both PCBs and dioxins/furans are ubiquitous in environment.

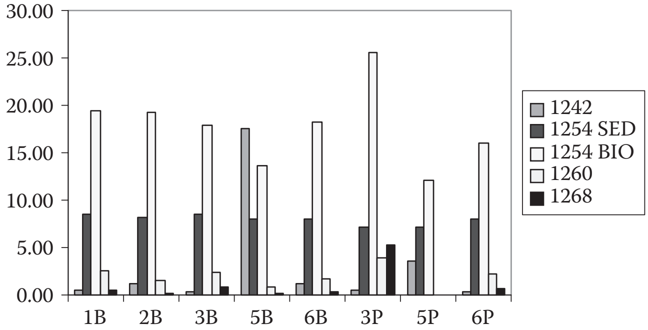

FIGURE 4.5
Aroclor profiles in building samples. Aroclor concentrations are in micrograms per kilogram on the *y* axis, and samples are listed on the *x* axis. For each sample, the first white block (toward the left) represents concentrations for Aroclor 1254; the second white block (toward the right) represents concentrations of Aroclor 1260.

Figure 4.5 illustrates the use of Aroclor profiles in a forensic investigation related to the presence of PCBs in a commercial building. Eight samples were taken from the building, including concrete walls and floors, inside piping, and the suspected source (a compressor, oil sitting on compressor footing). The samples were analyzed for Aroclor composition.

The results displayed in this figure denote the consistency between samples and with the suspected source. Some simple statistics were applied to these results, such as comparing the average, maximum, and minimum concentrations of each Aroclor in samples with the value in the suspected source. Such comparison confirmed the similarity of Aroclor profiles in samples with those in the suspected source. The findings were also confirmed by the historical file review. In this particular example, Aroclor profiles provided relevant fingerprints used to solve the forensic puzzle. However, many PCB investigations are much more complex, requiring the use of homologue or congener profiles along with multivariate statistics.

Table 4.7 provides recorded specific uses of various Aroclors adapted after Johnson et al. (2006). The original referenced material is information from Monsanto Industrial Chemical Company as reported by Durfee et al. (1976).

Limitations and Recommendations: The following limitations may apply to both PCB and dioxins/furan fingerprinting:

- Potential Aroclor misidentification.
- Congener versus Aroclor data: usually, congener data are recommended for forensic investigations. The following should be considered:
  - Total PCB concentration based on Aroclor data may underestimate the real concentrations;
  - Congener reconstructed after Aroclor data may not correspond to reality for weathered samples.

- Homologue patterns cannot be used for forensic evaluations of altered samples; for example, as shown by Johnson et al. (2006), the altered profile of Aroclor 1254 is much more similar to the profile of unaltered Aroclor 1242. Thus, using homologue profiles for weathered samples may be misleading in a forensic investigation.
- Weathering: Higher chlorinated mixtures (e.g., Aroclors) may look like lower chlorinated mixtures due to weathering, given enough time since the release occurred; thus, the information from historical file review should always be consulted/considered before interpreting chemical fingerprints.
- Coelution may happen, especially for tissue matrices samples.
- The lower the detected concentration is, the higher the uncertainty will be.

Useful reference material for more details related to chemical fingerprinting of these contaminants are recommended:

- For PCBs, the article by Johnson et al. (2006)
- For dioxins/furans, the article by Shields et al. (2006)

4.1.1.4.1.3 "Classic" Application Examples Specific application examples for the "classic" use of comprehensive chemical fingerprinting are as follows:

- Age-dating of petroleum products using specific "diagnostic" ratios (Christensen and Larsen, 1993; Wade, 2001; Schmidt et al., 2002; Murphy, 2007).
- Source identification of petroleum products using ratios of compounds that do not change easily and have similar fate and transport or are somehow related (Yang et al., 1995; Kaplan, 2003; Beall et al., 2002; Zemo, 2009).
- Source identification using diagnostic ratios. Usenko et al. (2010) described the use of PAH ratios from snow, lichens, and sediments to identify a local aluminum smelter as a major source.
- Source identification using correlation plots (Lesage and Lapcevic, 1990). The shape of such plots could also help identify sources and contributions, as well as any "outliers" (samples highly distinct from the others).

4.1.1.4.2 "Emerging" Applications for Individual Contaminants

4.1.1.4.2.1 Chemical Fingerprinting of Chlorinated Solvents Comprehensive chemical fingerprinting may also be applied for single chemicals when degradation products are formed in the release environment. Typical examples are provided by the common chlorinated solvents, including PCE (perchloroethylene), TCE (trichloroethylene), and 1,1,1-TCA (1,1,1-trichloroethylene). In this case, degradation ratios could be used to evaluate the source contributions and timing of the release (for well-established conditions), as illustrated next.

Understanding Chlorinated Solvents

Before interpreting or even planning to obtain fingerprinting data, one should understand the general properties and subsequent implications of a targeted contaminant or group of contaminants. Of particular importance is to establish if natural sources exist for targeted compounds. If they do, background values should be evaluated (this is generally not an issue with chlorinated solvents). The following is relevant information related to chlorinated solvents:

- Chlorinated solvents are manufactured chemicals, including PCE, TCE, 1,1,1-TCA, MC (methyl chloride), CT (carbon tetrachloride), 1,2-DCA (1,2-dichloroethane). (CT was the first manufactured chlorinated solvent, introduced in the 1900s with major uses as a cleaner and raw material in the manufacture of chlorofluorocarbons (CFCs). Its use as dry cleaner was surpassed by PCE by the late 1940s. The production of commercial scale TCE started in the United States in 1921 with the main uses in vapor degreasing and dry cleaning (with 92% used in vapor degreasing by 1952). 1,1,1-TCA was first produced in the United States in the mid 1930s with significant use recorded since the mid-1950s. With a lower boiling point than PCE and TCE, 1,1,1-TCA had special use in cleaning applications of computer boards and electric components.).
- They have broad industrial use in degreasing, dry cleaning, equipment cleaning, and manufacturing, leading to myriad anthropogenic sources.
- Natural formation is not expected and was only shown for a few chlorinated solvents; therefore, natural sources are insignificant.
- Chlorinated solvents are DNAPL volatile compounds with some water solubility.
- They do not stick to soil.
- They are persistent in the environment (degrade/transform over a very long time).
- Chlorinated solvents may be degraded over time (especially under reducing conditions) with well-defined degradation pathways and products. Although for a long time, only reductive biodegradation was accepted as a potential degradation pathway, recently more and more evidence exists for other possible degradation pathways, including under aerobic conditions (usually being much slower

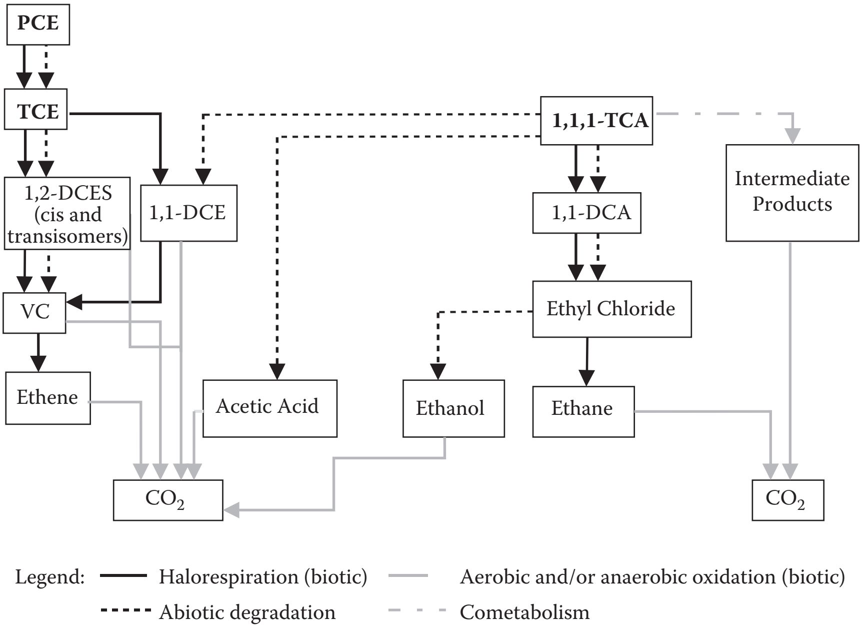

FIGURE 4.6
Degradation pathways for main chlorinated solvents (marked in bold). (Adapted from HydroGeoChem, Inc., AZ.)

pathways) as well as abiotic degradation. The main degradation pathways of chlorinated solvents are shown in Figure 4.6. They involve both biotic and abiotic degradation.

The biotic pathways involve:

- Anaerobic reductive dechlorination, also known as halorespiration (replacing halogens with hydrogen atoms)
- Aerobic oxidation, in which the chlorinated compound/solvent acts as an electron donor and source of organic carbon for microorganisms, while oxygen acts as electron acceptor
- Anaerobic oxidation, by which the chlorinated compound/solvent acts as an electron donor and source of organic carbon, while nitrates, ferric iron, sulfates, and other compounds act as electron acceptors (for oxygen -depleted zones)

The abiotic pathways involve reactions without microbial facilitation/involvement. For potential abiotic reactions, the following are possible:

- Substitution of OH radicals for Cl (hydrolysis)
- Substitution of HS (from sulfides) for Cl

- Reductive dechlorination (in the presence of ferrous iron)
- Elimination of HCl to form a double bond (also known as dehydrohalogenation)

The cometabolic pathways involve partial degradation of chlorinated compounds/solvents by enzymes from microorganisms growing on different substrates. These pathways are usually limited under natural conditions.

Method Principle and Steps

- Chlorinated solvents may be chemically fingerprinted based on their degradation products.
- Data may be analyzed using
    - concentration ratios (see example in Figure 4.7);
    - spatial concentration distribution patterns (horizontal and vertical), 2D and 3D GIS representations.
- The ratio of chlorinated hydrocarbons/degradation products may be used to
    - evaluate multiple sources (contributions) to a plume.
    - for 1,1,1-TCA, age-dating the release to groundwater is possible also (when TCE/PCE were not coreleased with 1,1,1-TCA).
- Degradation pathways should be evaluated along a contaminated plume (sample locations) before interpreting results.

Examples and Limitations

The principle for using comprehensive chemical fingerprinting in chlorinated solvent forensic investigations is described for a few distinct application examples:

1. **The use of degradation ratios plots to identify sources.** A typical example consists of source investigation of chlorinated solvents by analyzing parent versus degradation products at various distances downgradient from a main identified source. The method consists of measuring the groundwater molar concentration ratio [DCE]/([TCE] + [PCE]) at various distances from the main suspected source. Plotting this ratio against distance will help evaluate if there are other contributing comingling sources. Thus (as seen in the hypothetical situation depicted in Figure 4.7), any sudden decrease of the measured ratio recorded downgradient could signal fresh solvent additions that could only be from separate plumes/sources. In this hypothetical case, two potential source additions to the main PCE/TCE plume are suspected downgradient from the main source.

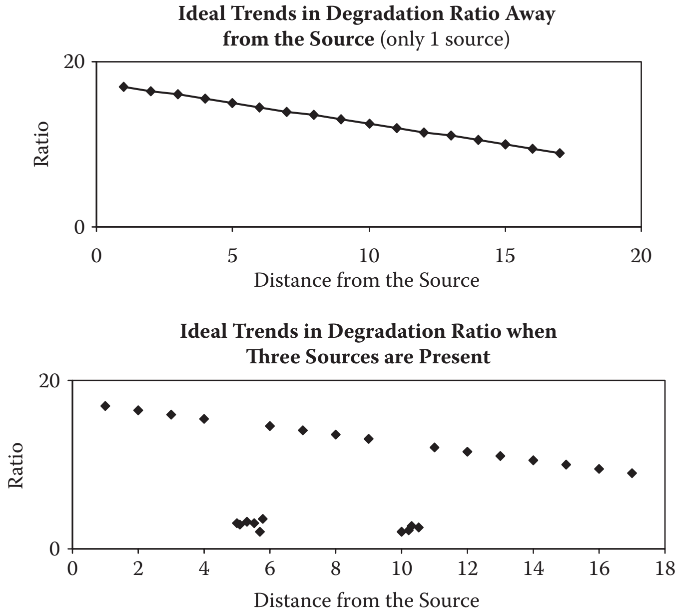

FIGURE 4.7
[DCE]/([TCE] + [PCE]) degradation (molar) ratio plots for source identification (of TCE and PCE), ideal trends (source distance is in feet × 100).

A practical application was described by Morrison et al. (2006). The advantage of the method resides in its simplicity and usually its cost benefit since it can take advantage of years of monitoring data available at many sites.

2. **Age-dating of 1,1,1-TCA releases** is another example of a chemical fingerprinting application in chlorinated solvent forensic investigations. In the case of 1,1,1-TCA, age-dating may be done because chemical hydrolysis was proven as the main degradation pathway. The method is applicable to groundwater plume dating. Obviously, if the source of 1,1,1-TCA is at the surface or at some distance above the groundwater, the age-dating should be refined by an estimate of the time needed for the release to vertically percolate the soil/porous media until reaching groundwater. Many laboratory experiments have established the rate of this transformation, which mainly depends on the ambient temperature (of groundwater) and thus could be quite accurately approximated in the studied environment. The reactions of 1,1,1-TCA degradation comprise the following steps:

$CH_3CCl_3 \rightarrow CH_3C^+Cl_2 + Cl^-$ Rate-limiting step

$CH_3C^+Cl_2 + Cl^- + 2H_2O \rightarrow CH_3COOH + 3\ HCl$ Rate constant = Ks

$CH_3C^+Cl_2 + Cl^- \rightarrow CH_2\ CCl_2 + HCl$ Rate constant = Ke

Basically, all that one needs to know is the amount of both 1,1,1-TCA and its main degradation product 1,1-DCE (in groundwater). Once these are known, either a graphical representation or the following equation may be used to calculate the estimated release time of 1,1,1-TCA (Gauthier and Murphy, 2003):

$$t = 3.63 \times 10^{-22} \exp[54.065/(1 + 3.66 \times 10^{-3}T)] \ln[1 + 4.76(\text{conc. DCE}/\text{conc. TCA})],$$

where T = temperature (F); conc. = concentration (mg/L); t = time since the 1,1,1-TCA entered the groundwater (years).

This age-dating method may be improved if data for 1,1,1-TCA and 1,1-DCE concentrations are available for several sampling events (at various times) (the more events, the better). In such a situation, one can plot $\ln(1 + k[\text{DCE}]/ke[\text{TCA}])$ as a function of time, resulting in a line that intersects the x axis (time axis) at the time of the release. Note that K is the total abiotic rate constant being calculated as sum of Ks and Ke. While this method provides estimates for the age of 1,1,1-TCA, the results should not be considered more than an estimate and only when other lines of evidence do not contradict this estimate. This is because many interfering factors may render such age-dating less accurate, including the following limiting factors (Petrisor and Wells, 2008a):

- Any processes that may transform or produce more 1,1-DCE than what is derived solely from 1,1,1-TCA. Thus, the presence of other chlorinated solvents may interfere with age-dating results and should be evaluated in each case.
- Other degradation pathways for 1,1,1-TCA. For example, reducing concentration due to biotransformation under anaerobic or aerobic conditions may change the representative concentration of this solvent used to calculate the age. Even though biodegradation does not seem to be a major degradation mechanism for 1,1,1-TCA, it may happen in certain environments more than in others, and it should be carefully evaluated (e.g., DNA testing may help confirm the potential for biodegradation of certain more conductive environments).
- Groundwater conditions and sorption to soil and sediments may also interfere with age-dating accuracy since they may lower the actual concentrations measured in groundwater.

- Location of samples may interfere with the accuracy of age-dating. Thus, samples should be collected from the closest area to the plume front with the highest contaminant concentrations.
- Temperature of groundwater is a critical factor, and any variation should be closely monitored. Alternatively, one may estimate groundwater temperature based on the mean annual air temperatures with a correction factor of 1°C increase for every 40 m of depth (due to Earth's geothermal gradient).
- As with any chemical fingerprinting technique, multiple releases of the same chemical (in this case, 1,1,1-TCA) over time may render the method unusable. The method can be applied only when one main release happened at a site.

4.1.1.4.2.2 Chemical Fingerprinting of Metals Similar to chlorinated solvents, metals do not occur as mixtures but rather as individual contaminants. This is why, at first glance, it may seem that comprehensive chemical fingerprinting may not be applicable to metals. This may seem especially the case since, in contrast to chlorinated solvents, metals do not degrade. However, the fact that the extraction and use of metals generally involve more than one metal opens the gate to chemical fingerprinting. In the case of metals, association/correlation of various metals in a sample may indicate the source type and help solve the forensic puzzle. The method principle and some application examples are provided to illustrate this emerging use of the chemical fingerprinting technique. First, some main facts related to metals in the environment are reviewed that will enable better interpretation of chemical fingerprinting results.

Understanding Metals

Relevant information related to metals includes the following:

- Metals are naturally present in all media; therefore, background values should be considered in forensic and other investigations.
- Many anthropogenic sources also exist, including: mining, foundries, industry, agriculture, vehicle emissions, older paints, and lumber/treated wood.
- Metals do not degrade, just change phase/chemical associations; therefore, they may become more or less mobile in the environment.
- Metals are usually tightly bound to topsoil (with some exceptions, such as arsenic [As]).
- Metals may be transported over long distances in air (bound to PM (particulate matter) or as gases in the case of Hg, for example).
- Metals are persistent in the environment, probably more than any synthesis or xenobiotic compounds since they ultimately never degrade.

Method Principle and Examples

- Metals may be chemically fingerprinted based on the following:
  - Associations with other metals: in-depth knowledge of metal applications or suspected sources is needed
  - Chemical speciation testing
  - Concentration trends (lateral and vertical at different depths) away from suspected sources
- Data may be analyzed in various ways, including:
  - Concentration ratios
  - Correlation plots (2D, 3D) (see examples in Figure 4.8)
  - Spatial concentration distribution patterns (see Figure 4.9)
- **Multivariate analysis** may be used to discern patterns/sample grouping when a large amount of data is available; the results may be used to apportion contributions.

One type of comprehensive chemical fingerprinting application to metal forensic investigations is illustrated in Figure 4.8. This figure provides examples of metal correlation plots using data from urban soils. In this example, while there is correlation between Pb and Zn, there is basically no correlation between Pb and Cr. Therefore, if the forensic investigation targets the source

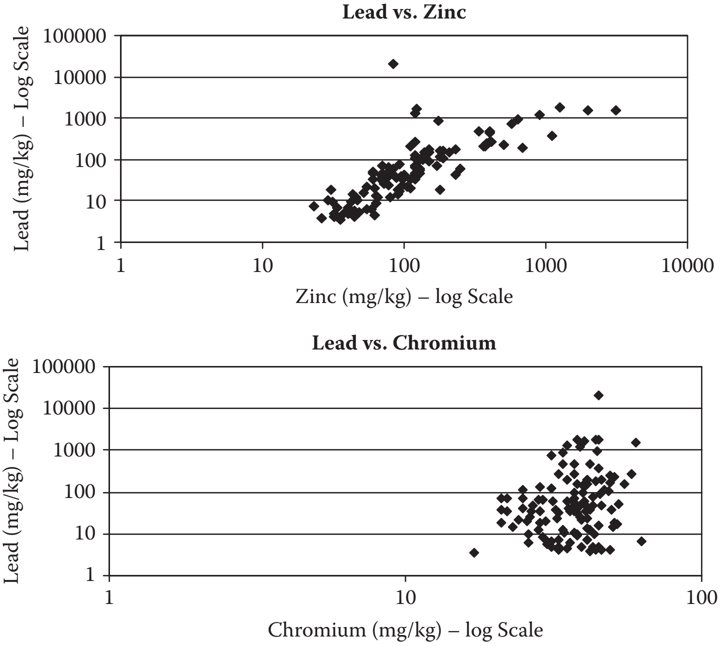

FIGURE 4.8
Examples of metal correlation plots.

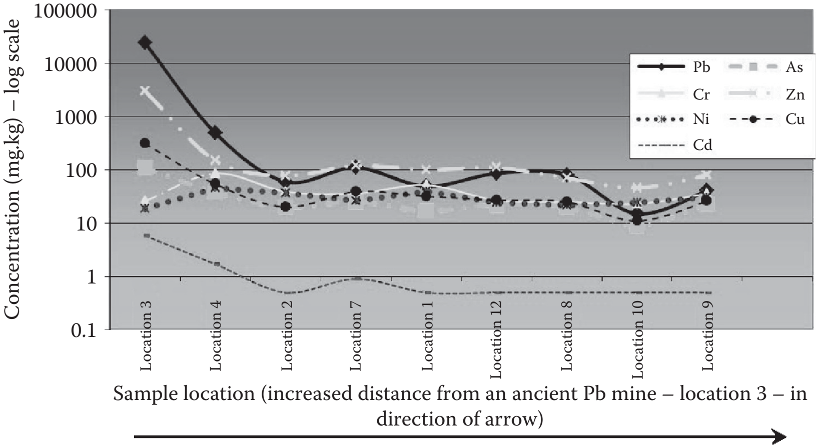

FIGURE 4.9
Example of metal spatial distribution patterns.

of Pb in these soils, a common source for Pb and Zn (but not for Cr) may be suspected. Such a source may be Pb paint (from old buildings) as Pb paint is known also to contain Zn. In addition, paint may be a source of soil contamination in urban areas, especially if a point source is not present in the study area. Other potential Pb sources should be evaluated before a final conclusion is made, and other metal correlation plots should also be evaluated to see if Pb correlates with other metals apart from Zn. Note that while such correlations between metals are more qualitative evaluations and only indirectly may suggest or eliminate sources, the data may provide valid forensic evidence if confirmed by other independent lines of evidence, such as document review or mineralogical fingerprinting, which is discussed in Chapter 5.

Another type of application of comprehensive chemical fingerprinting to metal forensic investigations is illustrated in Figure 4.9, consisting of plotting the recorded chemical concentrations of various metals in a medium (i.e., soil) versus distance from the main suspected source. If that is the only source of metals, a general decreasing trend for all metals away from the suspected source is to be expected (until reaching background values). That trend would be more or less similar with what is depicted in Figure 4.9, which used data away from ancient mine operations (in this example). If such decreasing trend is not evident or if sudden increases of metals occur downgradient to the main suspected source, it is deduced that the main suspected source may not be a source or that multiple sources of metals exist in the study area, respectively.

Another example of the use of metal correlation plots to evaluate metal sources was provided by Hall and Tinklenberg (2003), who used 3D plots to distinguish between paint manufacturers based on the concentration of three metals: Pb, Zn, and Ti (all known to be part of paint pigments).

Hints for Successful Forensic Use of (Comprehensive) Chemical Fingerprinting

- **More is better.** One should require analysis of more individual compounds (as feasible). In a forensic investigation of complex contaminant mixtures (such as crude oil and distillates, PCBs, dioxins, furans, PAHs), it is recommended to ask the laboratory to perform detailed analysis for as many as possible individual components from the targeted pollutant mixtures. For example, a chromatographic scan and analysis for a full hydrocarbon range (C3–C44) should be performed for a suspected crude oil or petroleum release (in soil or water), while a "forensic TO15 method" or a forensic analysis method for VOCs (volatile organic compounds) in air should be required for forensic investigations of vapor intrusion (VI) issues.
- **More detailed analysis with a higher sensitivity** (analysis in SIM mode) should follow after a general initial contaminant characterization.
- **Always check with the laboratory and ask to use the most sensitive methods** (with the lowest detection limits for targeted contaminants) to make sure forensically significant values will be captured. Even when a contaminant does not pose a health risk, it could be forensically significant.
- **Check the reported data versus the original lab sheets and instrument data.**
- **The exact lab methods used for various sample batches should be reviewed.** Any potential influence on results may affect comparability and should be considered.
- **Consider potential false-positive and false-negative results,** especially for outliers or when data are close to the detection limit.
- **Understand laboratory flags for data.** Some unquantifiable data (e.g., with a J flag) may not be used in mathematical calculations and models, but simply the fact that a certain compound was found may be forensically relevant regardless of exact quantification.
- **Laboratory reports should be checked for QA/QC (quality assurance/quality control)** data (which should be acceptable) before using the data for forensic interpretations. Fewer but high-quality data are more desirable than an abundance of low-quality data.
- When building chemical databases for a site, **always double-check for errors.** A single error may not matter for site remediation but could make a forensic "difference."
- **Consider effects of cocontamination** and how various compounds may interact with each other. For example, the copresence

of petroleum products along with PCBs or chlorinated solvents may delay the vertical migration of PCBs/chlorinated solvents because they would tend to be associated (partition into) with petroleum compounds, as both are organic chemicals. This is emphasized when free-phase petroleum products exist in the subsurface.

- **Always distinguish between free phase** (also referred to as free product) **and dissolved contamination.** This usually influences the sampling methods, the analytical laboratory methods for chemical identification and fingerprinting, as well as data interpretation and modeling. For example, benzene may be present in groundwater as both dissolved and a component of a free product floating on top of the water. In such a case, the copresence of free product affects the fate and transport of the dissolved phase, and both free product and water samples from below the free product would be taken and separately analyzed. The same is true for the presence of free product in soil; in this case, instead of the dissolved phase of benzene, one should check the amounts of benzene potentially adsorbed to soil versus what is still a component of entrapped free product.
- **Interpret data within the geological/lithological context and site history.**

4.1.2 Signature Chemicals

The signature chemical technique is another method based on chemical analysis (which may be classified under the chemical fingerprinting category of techniques) and is largely applicable to many sites and contaminants. *Signature* chemicals are chemicals (compounds) found at contaminated sites along with COCs and are associated with just a particular potential source and not with others or absent from a particular suspected source. Thus, their presence at contaminated sites along with COCs provides direct "physical" evidence that a particular suspected source contributed to the studied contamination (COCs) or that a particular suspected source may be eliminated. Usually, signature chemicals are present in small (insignificant) amounts that do not pose health or other risks and are hardly even noticed or mentioned in environmental reports. However, from a forensics point of view, signature chemicals are quite representative for that "detail" that can provide clues like those in classic detective stories.

This technique is based on chemical analysis and monitoring, but it is distinct from comprehensive chemical fingerprinting (discussed in the previous section) in that it uses a detailed rather than a comprehensive approach. While a compelling chemical fingerprint comprises many individual profiles (compound concentrations), the signature chemical evidence may be based solely on one identified signature compound, as long as its presence is proved at a site along with the COCs and its link to a particular suspected source (of the COCs) may be defensibly demonstrated. In addition, a plausible mechanism for the release of the signature chemical along with the COCs should be identified, increasing the defensibility of signature chemical evidence. Note that both signature chemicals and comprehensive chemical fingerprinting methods may take advantage of existing monitoring data at many sites and thus are cost efficient.

4.1.2.1 Understanding Signature Chemicals

Although not regularly mentioned in environmental reports, signature chemicals may be easily identified in many cases as they are usually reported as detected (among other analyzed chemicals) in original laboratory reports, which are generally attached to the main environmental report or should be available on request. Thus, a forensic investigator should look exactly for such "hidden" details apart from the typical reported environmental data focusing on COCs. As detailed in the next section, the forensic investigator should first identify potential signature chemicals at a site based on historical file review and an understanding of what makes a chemical a potential signature chemical (see further discussion in this section). Once one or more potential signature chemicals are identified, the site monitoring data should be consulted, going back to original lab reports to check if any of the identified potential signature chemicals was ever reported as detected (regardless of the amount). Then, a spatial representation of the detections over time and space may help consolidate the argument and use the signature chemical as evidence for contributions of a certain suspected source.

Note that the identification of signature chemicals requires a thorough review of site history and operations to establish if any of the detected chemicals may serve as a signature for any of the suspected sources.

Signature chemicals can be identified based on the following characteristics:

- They are linked to a specific suspected source or lacking from a specific source.
- They are usually not COCs.
- Subsequently, they are usually not risk drivers and may not be discussed at all in environmental reports.

The traits of ideal signature chemicals are as follows:

- Association with COCs through detection in the same samples, areas, or contaminated plume and through evidence of being handled and potentially released along with COCs
- Persistence in the environment
- Presence at detectable levels

- Ease of detection
- Source specificity (linked only to or absent from a suspected source in the study area)
- Ideally not common environmental contaminants
- Similar fate and transport with the COC
- Ability to concentrate in the COC waste (e.g., higher boiling point, low vapor pressure)
- Sufficiently mobile to be present in commingled groundwater plumes

Usually, signature chemicals are established during the historical file review based on either:

- **General information** (e.g., a well-known application that uses a certain compound that is not used by other sources/applications in the area) or
- **Specific information** (e.g., in the case of two storage facilities that used a series of chemicals, some of which may only be associated with one source).

Examples of signature chemicals are provided in the section on applications and limitations that follows the next section on method principle and steps.

4.1.2.2 Method Principle and Steps

The signature chemicals technique is based on the presence/absence of certain chemicals other than the COCs that are linked to or absent from certain suspected sources. The method provides direct evidence related to the contributions or absence of contributions from a particular suspected source to a plume.

The following are the main practical method steps:

1. **Identification of potential signature chemicals** through
   - historical document review (general and/or site-specific information) or
   - data evaluation.
2. **Validation of identified signature chemicals** relative to fate and transport as compared to the COCs (see more information on the next page).
3. **Additional data acquisition as needed.** Testing (for chemical concentration of identified and validated signature chemicals) may be performed to confirm the presence or absence of signature chemicals from the studied environment unless relevant data

already exist (within site-monitoring data); the data are reported in chemical concentration units (e.g., μg/kg for solids or μg/L for liquid samples).

4. **Reporting/data analysis:**
    - Concentration plots (signature chemical vs. COC) may provide additional validation when correlation is observed between the signature chemical and the COC;
    - Spatial concentration distribution pattern (horizontal and vertical) 2D and 3D GIS representations of signature chemical and COC (see example in Chapter 5). The spatial representation helps interpret the data and provides powerful exhibits.

Note that validation of signature chemicals is an important step in applying this method and includes a side-by-side comparison of chemical and physical properties of the signature chemical and the COC. To be a valid signature chemical, generally similar fate and transport with the COC are a must. In addition, if the identified signature chemical is suspected to have been present in low original amounts, its potential to concentrate in the environment compared to the COC is a plus. Examples are some chlorinated solvent impurities that start in tiny amounts (in original solvent) but concentrate in the waste solvent.

Impurities of chlorinated solvents that will be enriched after a vapor degreasing cycle in the solvent waste include the following:

- For 1,1,1-TCA waste:
    - CCl4
    - 1,2-dichloroethane (1,2-DCA)
    - TCE
    - 1,1,2-TCA (1,1,2-trichloroethane)
    - PCE
- For TCE waste:
    - PCE
    - Bromodichloromethane
    - 1,1,2-TCA
- For PCE waste:
    - PCA (tetrachloroethane)
    - Pentachloroethane
    - Hexachloroethane

Considering the potential concentration of some solvent impurities in waste solvent (see the previous discussion), this may help evaluate sources of an individual solvent when only a release of another solvent is recorded (e.g., PCE may be released as an impurity in waste TCE even if it was never used at a site). Moreover, the potential exists for the combined presence of listed impurities (verified with an MSDS [Material Data Safety Sheet] or other specific applicable sources) to help distinguish between manufactured versus environmentally formed (through biodegradation) solvent (e.g., in case of TCE).

When proportions of use in mixtures (including COCs) are known, specific calculations may be performed to evaluate the concentration of signature chemical/additive at the point of release. The higher the concentration is, the higher the chance to detect and use the signature chemical data within the forensic evaluation. Examples are provided in Table 4.8.

Table 4.8 provides examples of analyses that may be performed during the validation step. For each main chlorinated solvent and associated stabilizers, some relevant characteristics (such as effective solubility) are calculated (based on mole fraction and aqueous solubility) that make it possible to estimate potential concentrations expected at the point of release. Obviously, the higher the concentration of a stabilizer is at the point of release, the higher the potential of using it in forensic investigations will be.

As can be seen from these examples, the proportion of any given additive in the solvent mixture is relevant and helps better predict the environmental fate and transport and its validity as a signature chemical. To evaluate such a proportion, one needs to know the mass fraction of a component in the still bottom (after the use of the solvent) (see examples in Section 4.1.2.4.1).

TABLE 4.8

Evaluation of the Ability of Stabilizers to Concentrate in 1,1,1-TCA and TCE Waste

Evaluated Compound	Mass Fraction in Still Bottoms (wt%)	Mole Fraction	Aqueous Solubility (mg/L)	Effective Solubility (mg/L)	Stabilizer Expected Concentration (μg/L)
Stabilizers of 1,1,1-TCA:					
1,4-Dioxane	16.6%	0.2	10,000,000	2,045,261	>100,000
Nitromethane	2.7%	0.048	11,100	530	>10,000
2-Methyl-3-butyn-2-ol	15.3%	0.2	10,000,000	1,963,840	>100,000
Nitroethane	3.3%	0.047	45,000	2,127	>10,000
Stabilizers of TCE:					
Pyridine	0.94%	0.015	10,000,000	154,850	>100,000
Epichlorohydrin	0.30%	0.0043	65,900	281	>1,000
p-t-Amyl phenol	0.026%	0.00022	168	0.037	<1

Source: Based on Mohr, T.K.G. 2011. Forensic Applications for 1,4-Dioxane and Solvent Stabilizers. Presented at GRA Forensics Conference, Irvine, CA, April.

4.1.2.3 Examples of Potential Signature Chemicals

Table 4.9 provides examples of contaminant classes that can be "ideally" tracked with this method.

Representative examples of gasoline and chlorinated solvent additives are provided in Tables 4.10 and 4.11, respectively. Some of the additives shown may be used as signature chemicals on a site-specific basis. Their use in a particular case may be verified by checking various documents, including the following:

- Site/company records
- MSDSs/Chemical Safety Data Sheets
- Trade literature/patents

TABLE 4.9

General Examples of Potential Signature Chemicals

Contaminant	**Potential Signature Chemical**
Manufactured chemicals (e.g., chlorinated solvents)	Additives/stabilizers, impurities
Refined petroleum products (e.g., gasoline)	Additives (e.g., oxygenates, alkyl Pb compounds, proprietary additives)
Waste streams	Component(s) uniquely associated with the waste
Co-stored/co-released chemicals (e.g., from a chemical storage facility or manufacturing site)	Any co-stored contaminants not used at other potential sources in the study area
Landfill leachate	Any leached contaminant absent from other sources in the study area

TABLE 4.10

Examples of Gasoline Additives

Additive Type	**Examples**
Antiknock compounds	Alkyl lead compounds Organomanganese compounds
Antioxidants/stabilizers	p-Phenylenediamine Alkyl-substituted phenols
Corrosion inhibitors	Carboxylic acids Diimides
Dyes	Azo-benzene-azo-naphthols Phenyl-azo-naphthols (red, orange, bronze) Alkylamino-anthraquinones (blue)
Detergents	Amines Amine carboxylates
Anti-icers	n-Alcohols (short chains) Amines and ethoxylated alcohols with long hydrocarbon chains

Source: Based on Morrison, R. 1999. *Environmental Forensics Principles and Applications*. CRC Press, Boca Raton, FL.

TABLE 4.11

Examples of Chlorinated Solvent Additives

Solvent	Additive Type	Examples
TCE	Antioxidants	Amines (0.001–0.01%) Epichlorohydrin and esters (0.2–2%)
PCE	Stabilizers	Amines Epichlorohydrin and esters
1,1,1-TCA	Stabilizers	1,4-Dioxane (0–4% by weight) Nitromethane, n-methylpyrrole Butylene oxide 1,3-Dioxolane, secondary butyl alcohols
1,2-DCA (produced in Japan)		Polychlorinated ethanes
Chloroform	Stabilizers	Bromochloromethane, CCl4, dibromochloromethane, 1,1-DCA; 1,2-DCA; *cis*-1,2-DCE; *trans*-1,2-DCE; dichloromethane; diethyl carbonate; ethylbenzene; 2-methoxyethanol; nitromethane; pyridine; 1,1,2,2-TCA, TCE; xylenes
Dichloromethane (MC)	Stabilizers	Phenol, hydroquinone, para-cresol, resorcinol, thymol, 1-naphthol, amines

Source: Based on Morrison, R. 1999. *Environmental Forensics Principles and Applications*. CRC Press, Boca Raton, FL.

Table 4.12 provides examples of chlorinated solvent stabilizers with verified use. Some of these may be used as potential signature chemicals at solvent sites. Their usefulness and validity should be evaluated on a case-specific basis by checking various documents, including the following:

- Site/company records
- MSDSs (note that MSDSs may not always reveal all additives, especially those that are proprietary formulations, in amounts less than 1%, or considered nontoxic or nonvolatile)
- Product fact sheets and consumer guidance from major solvent producers
- Marketing literature by the major solvent producers
- Trade literature
- Patents
- Toxicological literature in which scientists analyzed the exact composition of technical-grade solvents for a comprehensive determination of all toxic agents

TABLE 4.12

Examples of Verified Chlorinated Solvent Stabilizers

1,1,1-TCA	TCE	PCE	MC
1,4-Dioxane	1,2-Butylene oxide	4-Methylmorpholine	1,4-Dioxane
1,3-Dioxolane	Diisobutylene	2,6-Di-tert-butyl-p-cresol (Ionol)	1,3-Dioxolane
Toluene	Epichlorohydrin	Diallylamine	Nitromethane
Tert-Butyl alcohol	Triethylamine	2-Isopropyl-5-methyl-phenol (thymol)	Methanol
Methyl ethyl ketone	bis(2-Propyl)amine	Tripropylene	Ethanol
2-Methyl-3-butyn-2-ol	2-Isopropyl-5-methyl-phenol	Cyclohexene oxide	Amylene
Nitromethane	Pentanol-2-triethanolamine	Benzotriazole	Cyclohexane
Nitroethane	Isobutyl alcohol	β-Ethoxyproprionitrile	Tertiary butylamine
Acetonitrile	Ethyl acetate	4-Methoxyphenol	1,2-Butylene oxide
Methyl butynol	N-Methylpyrrole	n-Butyl glycidyl ether (butoxymethyl oxirane)	Phenol
Isopropyl nitrate	P-t-Amyl phenol	Epichlorohydrin	Thymol
1,2-Butylene oxide			Propylene oxide
Isobutyl alcohol			Cyclohexane
1,3,5-Trioxane			
tert-Amyl alcohol			
n-Methylpyrrole			
Dimethoxymethane			

Source: Based on Mohr, T.K.G. 2011. Forensic Applications for 1,4-Dioxane and Solvent Stabilizers. Presented at GRA Forensics Conference, Irvine, CA, April 2011.

4.1.2.4 Applications, Limitations, and Recommendations

Several practical applications of the signature chemical technique are possible, including the following:

- **Source identification.** A real case along with various potential applications related to the use of signature chemicals for source identification is discussed further in this section; the following main types of source investigations may be successfully tackled using signature chemicals:
    - **Commingled groundwater plumes:** The signature chemicals provide physical evidence related to the presence or lack of contributions from suspected sources.
    - **Vapor intrusion contributions** from various sources to indoor air if signature chemicals are identified in indoor air while being specifically linked to certain suspected sources (e.g., groundwater, soil gas, and in home device background).
    - **Alternative application of the method:** It should be noted that even when a chemical cannot be conclusively identified with a certain source, it may still be used as a signature chemical as long as it definitely cannot be linked to other sources, such as on-site sources at a contaminated site. In this situation, the presence of the signature chemical at a site denotes probable contributions from off-site locations (yet to be identified).

- **Age-dating** is another application of the signature chemical technique that is discussed further (with some examples) in this section; age-dating involves the estimate of release time based on
  - Signature chemical breakdown and/or
  - Commercial availability of the signature chemical.
- **Differentiate between manufactured versus environmentally formed compound** (e.g., for chlorinated solvents). The potential for this application exists, but practical applications could not yet be tracked. The following is the principle behind this potential application: the presence of specific stabilizers and impurities along with the main chlorinated solvent (COC) may indicate the presence of a manufactured product instead of one resulting from degradation of another chlorinated compound in the environment. Such information may ultimately help identify suspected sources if they handled manufactured chlorinated solvents.
- **Estimate release contributions in commingled plumes.** In some specific conditions (i.e., sites with only a single release), this particular application could help establish the amount of a certain released compound (i.e., chlorinated solvent) in a commingled plume. For example, if a 1,1,1-TCA commingled plume exists in groundwater and one suspected contributing source can be linked to a certain signature chemical (e.g., a stabilizer linked to a certain application), then the concentration of the signature chemical may be used to evaluate contributions from that particular source to the groundwater plume—providing also that the exact original formulation of 1,1,1-TCA and the signature chemical concentration of the spilled product are known or could be defensibly deduced.

4.1.2.4.1 Source Identification Applications

4.1.2.4.1.1 Case Study Example: Two Chemical Bulk Storage and Packaging Facilities in California A real case study in which I successfully applied this technique to identify sources/contributions is illustrated in Chapter 9 (Case Study 9.1). It involved the use of Freon 113 as a signature chemical to establish contributions from one site to shallow groundwater and vadose zone contamination of a neighboring site. The challenging aspect of this case was the fact that both sites had been involved in the same business of bulk storage and repackaging of chemicals, and both sites had recorded historical releases. In addition, most of the handled and released chemicals were similar between the two sites. Freon 113 was an exception as it was not used by one site (except just one drum of product containing Freon 113 was recorded during the years in question), while it was massively used by the other site. To make the case even more challenging, Freon 113 was not monitored in groundwater or soil at the site that did not use it since it was not considered to be a problem. By chance, however, Freon 113 was detected in several soil gas surveys conducted in the vadose zone of that site. When detections were shown on a map, their pattern clearly indicated the other neighboring site as the likely source since the detections were toward the other site, particularly toward the Freon 113 historical handling area on that site. More information and some illustrations are provided in Chapter 9, which presents this particular case study, with signature chemicals being one of the independent lines of evidence used in this case.

One more thing worth pointing out here is that this case illustrates how a common environmental contaminant such as Freon 113 may become, in specific conditions, a valuable signature chemical. Thus, although a large part of this section is dedicated to discussing unusual and less-common environmental contaminants, such as various additives or stabilizers in petroleum or chlorinated products, signature chemicals may also be provided by environmental contaminants commonly reported at many sites but that happen not to have been used/released at particular sources from the case at hand.

The advantage of using these common contaminants as signature chemicals is that often chemical data exist in monitoring reports, and additional testing may not be required. Of course, as in any forensic investigations, the forensic scientist should carefully consider and eliminate any other potential source for such chemicals (except the particular suspected source for which the chemical is considered to be a signature).

4.1.2.4.1.2 Other Potential Applications A series of other potential applications of signature chemicals for source identification is discussed next. They relate to the use of specific site operation knowledge to identify potential signature chemicals (single compounds or mixtures), typically less-usual compounds (not common contaminants). Once identified, chemical analyses may be specifically requested in representative environmental samples. Usually, an analytical method exists for these less-common compounds (see examples in the tables that follow). However, it is the responsibility of the forensic investigator to find adequate labs that provide the lowest detection limits.

PCE Source Identification based on PCE Usage. Table 4.13 provides examples of additives reported to be associated with certain applications of PCE. Such information may help distinguish the source (usage) of PCE between potential candidates that have used PCE for distinct applications.

Based on chemical properties, the two stabilizers marked in bold in Table 4.13 may be used as signature chemicals to differentiate between dry cleaner and dielectric fluid uses of PCE. Thus, if only one of them is detected in the investigated groundwater plume, the

TABLE 4.13

Additives Reported Associated with Certain Applications/Manufacturers of PCE

Application	Additive/Stabilizer
PCE as a dielectric fluid	**n-Methyl-pyrrole**
	Penthaphen
PCE used in dry cleaning (DowPer from Dow Chemical)	4-Methyl morpholine
PCE used in dry cleaning (PerSec from Vulcan)	Diallylamine
	Tripropylene
PCE used in dry cleaning (from PPG)	Cyclohexene oxide
	β-Ethoxyproprionitrile
	n-Methyl morpholine
	4-Methoxyphenol
PCE used in dry cleaning	**n-Butyl glycidyl ether (n-BGE)**

Source: Based on Mohr, T.K.G. 2010. *Environmental Investigation and Remediation: 1,4-Dioxane and Other Solvent Stabilizers*. CRC Press, Boca Raton, FL.

Note: **Bold** = stabilizers that may used as signature chemicals to differentiate between dry cleaner and dielectric fluid uses of PCE.

source associated with that particular PCE application (that used that specific chemical) may be identified as the likely source of PCE.

Please note that identifying manufacturers may also seem possible based on specific stabilizer packages/data; however, such application should be regarded with much caution. Due to potential variability in manufacturing processes, it is hard to use the association by itself to identify the manufacturer. Site-specific data (especially historical), however, may increase the chances of successfully applying such a technique, which should be evaluated on a site-specific basis.

1,4-Dioxane Source Identification Based on Specific Uses. Table 4.14 provides examples of specific mixtures of compounds reported as associated with 1,4-dioxane in certain applications of this chemical. Again, such information may help in forensic investigations. However, every site should be evaluated on a site-specific basis before deciding if this type of information may be relevant to select and use the signature chemical technique.

1,1,1-TCA Source Identification Based on Historical Formulations of Commercialized Product. Another example of potential forensic application of the signature chemical technique for source identification is based on the historical formulations of 1,1,1-TCA, including some specific recorded stabilizers and impurities. An example provided in Mohr's book (2010) lists the stabilizers and impurities of 1,1,1-TCA recorded for some manufacturers in 1965. These data are provided in Table 4.15.

TABLE 4.14

Examples of Specific Mixtures Reported as Associated with Certain Applications

Application	Specific Mixture or Associated Chemicals
1,4-Dioxane in aircraft deicing fluids	Ethylene glycol or propylene glycol Surfactants pH buffer Dyes 1,4-Dioxane
1,4-Dioxane in liquid scintillation cocktails	1,4-Dioxane (80%) Naphthalene Methanol Ethylene glycol Diphenyloxazole 1,4-bis-(5-Phenyloxazolyl)benzene
1,4-Dioxane as ether supplement **in fuels**	1,4-Dioxane Benzene, toluene Glycols
1,4-Dioxane in printing inks	1,4-Dioxane Propylene glycol (up to 20%)

Source: Based on Mohr, T.K.G. 2010. *Environmental Investigation and Remediation: 1,4-Dioxane and Other Solvent Stabilizers*. CRC Press, Boca Raton, FL.

4.1.2.4.2 Age-Dating Applications

Stabilizers and impurities associated with solvent production feedstock documented during certain periods of time may be used to age-date the solvent release. For example, in the case of PCE, alkylamines and hydrocarbons were added to early formulations, while later stabilizers included morpholine derivatives (Gerhartz, 1986).

A representative example was provided by Morrison and Hone (2010) related to age-dating PCE or TCE releases based on the following manufacturing details:

- Prior to 1950, TCE was almost exclusively produced from acetylene.
- Between 1950 and 1978, the dominant TCE production feedstock shifted from acetylene to ethylene:
    - Between 1963 and 1967, about 85% of the TCE produced in the United States is estimated to have been manufactured using acetylene as a starting material.
    - In 1968 and 1969, about 65% and 55%, respectively, of the manufactured TCE were using acetylene as starting material, while in 1971 the value decreased to about 51%.
    - By 1973–1974, only about 8% of manufactured TCE was using an acetylene process

TABLE 4.15

1,1,1-TCA Formulations from Four Suppliers Recorded in 1965 (Data in vol%)

Ingredients	**Octagon Process Company**	**Fisher Chemical Company**	**Phillips–Jacobs Chemical Company**	**Eastman Kodak Company**
1,1,1-TCA	65	94	95.5	95
Stabilizers:				
1,4-Dioxane	—	3.6	3.4	4.5
1,2-Dimethoxymethane	0.24	—	—	—
tert-Butyl alcohol	3.64	—	—	—
Nitromethane	1.3	—	—	—
Diethylether	Trace	—	—	—
sec-Butyl alcohol	—	0.2	0.2	0.3
Impurities:				
TCE	7.6	—	—	—
1,2-DCA	22	2.1	0.8	—
1,1-DCE	0.06	Trace	Trace	Trace
1,1,2-TCA	Trace	—	—	—
1,2-DCE	Trace	—	Trace	Trace
2-Chlorobutane	—	Trace	—	—

Source: Based on Mohr, T.K.G. 2010. *Environmental Investigation and Remediation: 1,4-Dioxane and Other Solvent Stabilizers*. CRC Press, Boca Raton, FL, citing Saunders, 1965.

- After 1978, acetylene was no longer used as feedstock for TCE commercial production.

The age-dating technique is based on recorded distinct formulations of TCE and PCE based on the feedstock material used in the manufacturing process, namely (Morrison and Hone, 2010): TCE produced using acetylene as feedstock material (in the mid-1960s) was reported to contain substantial amounts of 1,1,2,2-TeCA (1,1,2,2-tetrachloroethane); therefore, the presence of 1,1,2,2-TeCA and possibly its degradation products 1,1,2-TCA and 1,2-DCA[4] along with a TCE or PCE release may be used to age-date the TCE/PCE release as prior to 1978. However, such age-dating should be done with caution and only when several conditions are met, including

- No other reasonable sources of 1,1,2,2-TeCA and 1,1,2-TCA exist;
- No other sources of 1,2-DCA exist, such as leaded gasoline (1,2-DCA is a known lead scavenger) or any other non-PCE/-TCE sources.

Similar to the previous example, information may be related to specific chlorinated solvent formulations linked to certain time periods and manufacturers. Such information becomes extremely valuable to forensic investigators as it may be used to age-date releases otherwise impossible to age-date.

Another example provided by Morrison and Hone (2010) relates to the use of amines such as trimethylamine as acid acceptors in TCE formulations until 1954, while in the mid-1950s amines started being replaced by non-alkaline formulations such as those based on a pyrrole-based six- to seven-component mixture developed by DuPont.

Table 4.16 provides another example of chlorinated solvent formulations during certain timeframes. The information is based on data presented in the textbook by Mohr (2010) as reported in toxicological literature. Specifically, the exact composition of pre-1986 technical-grade 1,1,1-TCA was measured and reported. This information, by itself, is not sufficient to defensibly demonstrate a pre-1986 release timeframe unless additional information becomes available denoting a distinct 1,1,1-TCA formulation post-1986. Site-specific data may also be used in this respect. Obviously, the exact composition of spilled product will be altered after the environmental release; however, the knowledge of fate and transport of individual compounds versus 1,1,1-TCA may help establish expected groundwater general profiles at the time of sampling.

While the use of stabilizers and other additives for age-dating and source identification is tempting, it should always be employed with caution and

TABLE 4.16

Composition of Technical-Grade 1,1,1-TCA Recorded Pre-1986

Composing Chemical	Concentration
Stabilizers:	
1,4-Dioxane	3.8 wt%
1,2-Epoxybutane	0.47 wt%
Nitromethane	0.27 wt%
n-Methyl pyrrole	<0.0001 wt%
Impurities:	
Chloroform	100 ppm
Carbon tetrachloride	250 ppm
TCE	200 ppm
1,2-DCA	2,300 ppm
1,1-DCE	398 ppm
1,2,3-TCA	41.8 ppm
trans-1,2-DCE	50 ppm
PCE	475 ppm

Source: Based on Mohr, T.K.G. 2010. *Environmental Investigation and Remediation: 1,4-Dioxane and Other Solvent Stabilizers*. CRC Press, Boca Raton, FL.

preferably backed up by another independent line of evidence. Moreover, a series of conditions should be met to apply this age-dating technique, including the following:

- A thorough historical file review should be performed to establish certain stabilizers/additives as potential signature chemicals.
- Once this is accomplished, adequate analytical techniques should be available to test for the identified compound (which generally is not a common contaminant targeted by routine analytical methods).
- A plausible release mechanism should be evaluated and the selected signature chemical should have similar fate and transport with the COC.

4.1.2.4.3 Limitations and Recommendations

A series of limitations may apply to this method. Table 4.17 provides some examples and ways to mitigate listed limitations.

Hints for Successful Forensic Use of Signature Chemicals

- **The "signature chemical" is that "unfitting detail" that remains unobserved** until a "Hercule Poirot" becomes involved. The forensic investigator is after all an "environmental detective" who should check and observe various details. When something does not fit, it should not be dismissed as unimportant but rather further investigated.
- **Always ask to check all existing monitoring data reported by the lab.** The nondetects may also be forensically significant. For example, if an identified signature chemical was analyzed for but has never been detected at a site, the particular source linked to the signature chemical should be excluded (unless there are reasonable explanations accounting for the complete destruction of the signature chemical).
- **Comprehensive monitoring data may help identify signature chemicals.** Look usually for those chemicals that are present in low enough amounts to not pose a risk or are environmentally friendly but are present selectively in some areas only. This can help backtrack to the potential source (from the area with detections). A historical investigation may be initiated at that point to further define and confirm the potential signature chemical identified while reviewing the extensive monitoring data.

TABLE 4.17

Limitations and Recommendations for Signature Chemicals

Influencing Factors/Limitations	Recommendations
The signature chemical has distinct fate and transport compared to COCs.	Perform validation (before testing).
The signature chemical is in tiny amounts and thus may escape detection.	Make sure the laboratory is using SIM analysis targeting the lowest detection limits that can be achieved.
There may be multiple potential sources for the signature chemical in the study area.	Evaluate on a case-specific basis and also include background evaluations.
The site was mitigated; thus, testing for any identified signature chemical is useless.	Use historical monitoring data; if not available/ adequate, use another forensic technique.

4.1.3 Chiral Fingerprinting

The chiral fingerprinting technique is also based on chemical analysis and targets (measures) the chiral composition of compounds (pollutants) that have chiral or optical isomers.

4.1.3.1 Understanding Chiral Isomers

4.1.3.1.1 Definition, Examples, and Environmental Relevance

As any isomers, the chiral isomers of a compound have the same elemental composition (chemical formula) but a different structure. In this case, the difference in structure relates to the relative order (in 3D space) of different elements or radicals/groups bound to an asymmetric carbon atom (also called a stereocenter or chirality center).[5] Specifically, the chiral isomers are the "mirror" image of each other. This is only possible for compounds that lack an internal symmetry. To imagine chirality, one should consider human hands. Although identical, they cannot be superimposed (unless rotating the hands). In fact, the term *chirality* derives from the Greek name for the hand (*cheir*).

Figure 4.10 provides three examples of chiral compounds (displayed in 2D space), namely (from left to right), a hydroxylamine, an amino acid, and a

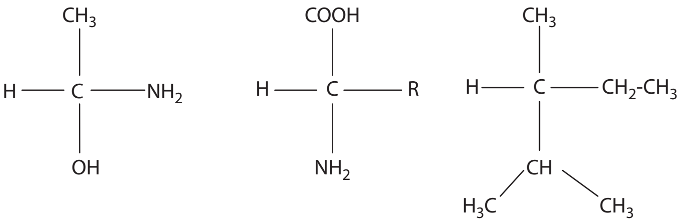

FIGURE 4.10
Examples of compounds with chirality (asymmetric carbon).

branched alkane (SHC). Note that R is used generically to suggest any type of alkyl radical (containing one or more carbons linked to hydrogen atoms). In each case, the asymmetric carbon atom is displayed in the center of the structure. It is easy to see the difference between the four elements/radicals bound to the centrally displayed carbon atom in each situation. Note that in the case of the branched alkane used as an example in Figure 4.10, the centrally displayed carbon is an asymmetric carbon because it is linked to hydrogen and three distinct alkyl radicals, so even if that carbon is immediately bound to three other carbon atoms (from the three alkyl radicals), the fact that the three carbon atoms bound to the asymmetric one belong to three distinct radicals dictates the difference and asymmetry. Note that asymmetry may also be encountered in cyclic structures (not displayed here), which is the case of many cyclic terpenoids, also known as petroleum biomarker compounds.

To synthesize, the compounds that display chiral isomers (also called chiral compounds) are compounds that lack an internal plane of symmetry in their molecular structure. Usually, such compounds are those that contain one or more asymmetric carbon atoms. It should be noted that both organic and inorganic compounds (chemicals) may display chirality:

- For inorganic compounds, many coordination compounds are chiral.
- Examples of chiral organic compounds include at least one or more individual compounds from the following main classes: PCBs, petroleum biomarkers, PAHs, pesticides, pharmaceuticals, dioxins, furans, sterols, amino acids, methamphetamines, alkaloids (e.g., truxilline), and other illicit compounds (e.g., illicitly produced heroin).

Note that many biochemicals (e.g., amino acids, which are the building blocks of proteins) have chiral isomers in certain proportions that dictate their biological function. The concept of chiral isomers or enantiomers (optical isomers) is, in fact, a common one in biochemistry and the pharmaceutical industry. The environmental implications are important since, due to the differences in biodegradation susceptibilities between chiral isomers, some isomers may persist in the environment much more than others. Subsequently, toxicity may be quite distinct between paired chiral isomers. Overall, chiral isometry becomes important when dealing with environmental contamination and provides fingerprinting opportunities, as discussed next.

4.1.3.1.2 Nomenclature of Chiral Isomers

There are different nomenclature systems for chiral isomers. Here, the nomenclature rules for each of these systems are not included as those can be found in chemistry books. Instead, the main nomenclature systems and the general rules for one of the commonly used systems (*R* vs. *S*) are provided. The nomenclature systems for chiral isomers include the following:

- **By configuration *R*- and *S*-:** The chiral isomers are also called optical isomers or enantiomers. The *optical* name relates to the specific property of the solutions of chiral compounds to rotate the plane of polarization of a beam of polarized light in either a clockwise or counterclockwise direction. Thus, the chiral isomers can be considered to have optical activity. Every chiral center in a molecule is, by convention, marked with either *R* (rectus) or *S* (sinister), which has no fixed relation to other nomenclature systems. Assigning the specific *R* or *S* designations is done by a well-known convention system that considers the atomic number of the atoms attached to the stereocenter to assign priorities, including the following main steps (known also as Cahn–Ingold–Prelog priority rules):
    1. Identify the stereocenters (asymmetrical carbon atoms).
    2. Assign priorities to each group attached to the stereocenter (the higher the atomic number of the element bound to the asymmetrical carbon, the higher its priority; the highest priority = 1, while the lowest priority = 4).
    3. Reposition the molecule so that the lowest-priority group is away.
    4. Determine the relative direction of the priority order between the remaining three higher-priority groups (with assigned 1, 2, and 3 priorities).
    5. Assign *R*/*S* designations:
        - If the order between the three high-priority groups is clockwise, then the stereoisomer will be an *R*-stereoisomer (from the Latin term *rectus* for right-handed).
        - If the order between the three high-priority groups is counterclockwise, then the stereoisomer will be an *S*-stereoisomer (from the Latin term *sinister* for left-handed).
- **By optical activity: (+) and (–)** based on property to rotate the plane of polarized light clockwise (+) or counterclockwise (–); note that the (+) and (–) isomers have also been termed *d*- and *l*-, respectively (from dextrorotatory and levorotatory, respectively); this should not be confused with D- and L- terms from a distinct nomenclature system as described in the next bulleted item.
- **By configuration: D- and L-** based on spatial configuration of atoms (used in biochemistry). This nomenclature system is more commonly used in biochemistry.

Note that for cyclic organic compounds, the general convention uses *R* and *S* designations for the chiral centers that are not part of the ring (while α and β are used for the chiral centers within the ring) (Wang et al., 2006a).

4.1.3.2 Method Principle and Steps

The fingerprinting method is based on the fact that chiral compounds are composed of different proportions of individual chiral isomers (two or more isomers depending on how many chiral or stereocenters are in a molecule). The proportion between chiral isomers of a particular compound can be measured to provide an additional line of evidence in forensic cases. Thus, chiral fingerprinting uses the proportion between chiral isomers of a particular compound to evaluate the source and fate and transport of released contaminants.

Chiral fingerprinting is distinct from comprehensive chemical fingerprinting because it focuses on a small number of individual compounds of a mixture. For example, if PCBs are the COCs at a site, chemical fingerprinting could be done both through comprehensive chemical analysis and through chiral analysis. These two types of chemical fingerprints could be seen as independent lines of evidence. While comprehensive chemical fingerprinting would target as many individual compounds from PCB mixtures as analytically feasible (e.g., through congener analysis), chiral fingerprinting may target only one or a few PCB congeners that have chirality. Because the information obtained through chiral fingerprinting is highly specific, similar with the information that would be provided by signature chemicals (another type of chemical fingerprinting), chiral fingerprinting generally does not require the analysis of many individual compounds. One or a few selected individual compounds in a mixture could provide fingerprints as powerful as or even more powerful than hundreds of individual compounds targeted by comprehensive chemical analysis.

Note that chiral fingerprinting is a straightforward method without the higher degree of uncertainty of mathematical modeling, a commonly applied method to distinguish sources of complex pollutant mixtures (such as PCBs).

Chiral fingerprinting may be used in the following main types of forensic investigations:

1. **Source identification and allocation.** A potential forensic application of chiral fingerprinting is source identification and allocation through the comparison of chiral fingerprints of samples with candidate sources. This is dependent on the ability to obtain representative source samples for each source candidate. However, even in the absence of representative source samples, comparison between environmental samples may result in one or more distinct sample clusters, helping evaluate if various analyzed samples come from one or more sources (even when the actual sources remain unidentified).
2. **Relative age-dating.** This type of application refers to manufactured chemicals that are released in the environment (e.g., PCBs). Chiral fingerprinting may allow establishment of whether those chemicals

have been recently released (are fresh) or were released some time ago. Moreover, chiral fingerprinting may allow the relative comparison of the age of chiral compounds in various samples. The principle behind this type of application is based on the following:

a. The fact that manufactured chemicals using nonbiological processes contain equal or close to equal enantiomers (such mixtures being known as *racemic*);
b. The fact that biological processes that occur after contaminants are released into the environment affect differently the individual chiral isomers (Josephs and Barnett, 2005), therefore starting to change the proportion between chiral isomers once racemic compounds are released into the environment;
c. The change in the proportion of chiral isomers due to biodegradation processes increases with the age of the release;
d. The change in the proportion of chiral isomers could be measured using enantioselective GC/MS and captured in the so-called enantiomeric fraction (EF):

$$EF = E1/(E1 + E2),$$

where $E1$ is the first eluting enantiomer, and $E2$ is the second eluting enantiomer

e. For a racemic compound (with equal proportions of the composing enantiomers), the *EF* is 0.5 or close to 0.5. This is the case for commercial formulations of chiral organochlorines such as PCBs (Wong et al., 2001). In contrast, due to biodegradation, the *EF* value changes when these compounds are released in soil (depending on the intensity of degradation processes), varying from 0 to 1 (Aigner et al., 1998). Hence, a comparison of manufactured versus environmentally altered PCBs may be possible (Harner et al., 2000).

In conclusion, chiral fingerprinting may be used[6] to evaluate the degree of biodegradation of a released contaminant and its relative age and to help identify sources and apportion contributions or to distinguish older versus newer releases. Some practical applications are presented in the next section.

The main steps of chiral fingerprinting involve

1. **Selection of one or more targeted individual compounds** that display chirality (from an environmental contaminant mixture).
2. **Determination of the EF** of each selected compound in each sample (a value between 0 and 1 as described previously).

3. **Evaluation of the results based on the type of application:**
    - Comparing the results with candidate sources when representative samples are available and specific source identification is targeted
    - Comparing the results between samples to establish potential common origin
    - Comparing the results between samples to evaluate the relative age of spilled racemic compounds. For example, PCBs are racemic compounds, and their relative age may be evaluated through the EF of targeted chiral congeners. When the EF is close to 0.5, a fresh spill or spill from PCBs used in diverse equipment may be suspected.

Note that another way of using chiral isomery in chemical fingerprinting is to use diagnostic ratios based on chiral isomers (using actual chiral isomer concentrations as reported by the lab). Chiral isomers may provide quite powerful fingerprints which are the basis for using them in many diagnostic ratios (for examples see the biomarker ratios for crude oil and petroleum product forensic differentiation from Tables 4.1 and 4.2).

4.1.3.3 Applications, Limitations, and Recommendations

Although referred to as one of the ultimate fingerprinting techniques, chiral fingerprinting is not a commonly used and reported fingerprinting method yet. So far, chiral fingerprinting has been applied to distinguish the sources of a series of organic environmental pollutants based on their relative age-dating. Examples of practical applications include the following:

- **Source evaluation of atmospheric PCBs** (Robson and Harrad, 2004). The main forensic objective was if the PCBs from air samples originated mostly from emissions from environmental surfaces (such as soils) versus from the remaining stock of PCB-containing materials (such as transformers, capacitors, etc.). A secondary objective was to evaluate biodegradation of various chiral PCB congeners in soil. One urban and one rural location in the United Kingdom were investigated. Soil and air samples (32 samples of each medium) were collected every 2 weeks and analyzed for chiral isomers of the PCB congeners 95, 136, and 149. In addition, the EF of targeted congeners in several fresh Aroclors was investigated to confirm their expected racemic composition. The results denoted that
    - The likely source of PCBs in air was the racemic manufactured PCBs and not the PCBs from soils.

  - Appreciable enantioselective degradation of monitored PCB congeners occurred in soil, providing evidence for aerobic degradation of penta- and hexachlorinated PCBs.
  - The racemic composition of studied congeners in the unspilled Aroclors tested was confirmed.
- **Chiral source apportionment of PCBs to the Hudson River estuary** (Asher et al., 2007). The Hudson River estuary is contaminated with PCBs from multiple sources, including primary sources (atmospheric depositions from surrounding urban areas, such as New York City) and secondary sources such as the upper Hudson River, storm water runoff, and sewer overflows. The main study objective was to apportion PCB sources to the estuary (including food web). The method employed was chiral fingerprinting performed for PCBs (congeners 91, 95, 136, and 149) in air, water, total suspended matter (TSM), phytoplankton, and sediment samples. The results allowed the following conclusions:
  - PCBs 91, 95, 136, and 149 were racemic in the atmosphere of the estuary, suggesting that the predominant atmospheric source of these PCB congeners must be unweathered local pollution and not volatilization from the estuary (which would add nonracemic PCBs since environmental PCBs are expected to show some signs of weathering). This finding is consistent to that of the U.K study described previously (Robson and Harrad, 2004).
  - The source of the estuary PCB congener 95 was consistent among dissolved phase, TSM (total suspended matter), sediments, and phytoplankton. The estuary PCB congener 95 is likely not from atmospheric deposition. This suggested that Upper Hudson discharge seemed to be the source of the dissolved phase and TSM, ultimately controlling sediment and phytoplankton contamination.
  - Similar general trends were observed for the heavier congener PCB 149 with the exception of the dissolved phase, which was not statistically distinct from the atmospheric phase. Several facts may have contributed to this result, including the decreased prevalence of this heavier congener in the predominant Aroclor (Aroclor 1242) from the upper Hudson River, as well as its higher resistance to biodegradation, resulting in a less-discernible difference between chiral isomeric proportions. Thus, this distinction in results may not be significant in changing the overall conclusions based on PCB 95 trends.

  - Note that the differences observed between the results for lighter versus heavier congener were likely due to different proportions in the original Aroclor material from sediments and differences between air and sediment sample chiral composition.
  - A source apportionment was proposed to establish contributions of PCBs from river sediment and air to phytoplankton based on the following equation:

$$f_1 = (EF_{\mathrm{MIX}} - EF_2)/(EF_1 - EF_2),$$

    where f_1 is the fraction of total contaminant contributed by sediment (source 1); EF_1 and EF_2 are the EFs for sediment and air (source 2), respectively; and EF_{MIX} is the EF of the affected medium (phytoplankton).

- **The source investigation of a series of organochlorine compounds** (α-HCH [alpha-hexachlorocyclohexane], heptachlor epoxide, chlordane, o,p′-DDT [o,p′-dichlorodiphenyltrichloroethane]) has also been carried out employing chiral fingerprinting/signatures (Bidleman and Falconer, 1999; Bidleman et al., 1998a,b).
- **Various uses of chiral fingerprinting in forensic toxicology studies** were also pointed out in the literature (Smith, 2009). These types of application include those related to the following:
  - **Source identification for illicit compounds**, of which over half possess at least one chiral center (Smith, 2009). The application of chiral fingerprinting for illicit compounds can provide a manufacturing fingerprint for law enforcement intelligence. Such illicit compounds include heroin (because it is "cut" with sugars), caffeine, phenacetin, amphetamines, methamphetamines, phenylethylamine derivatives such as "ecstasy" (commonly 3,4-methylenedioxymethamphetamine), and *N,N*-dimethylamphetamine. The chiral analysis may provide clues to precursor materials and synthesis pathways. In some cases, some particular drugs are specifically manufactured not as racemic mixtures, but in such a way that they contain predominantly just one chiral isomer. This knowledge would be useful in forensic studies based on chiral fingerprinting.
  - **Screening of athletes for exogenous administration of androgens.** For example, the endogenous steroid profile of testosterone (T) may be screened by using its enantiomer epitestosterone (E) in urine, which is well established. When the E/T glucuronide ratio has certain atypical values (e.g., equal to or exceeding 4 to 1),

exogenous androgenic steroid administration is suspected, and further investigation is required (which may include isotopic analysis). Note that metabolization of various drugs with enantiomeric compounds is done at different rates for the paired enantiomers. This has implication in serum testing for drug use and determination.

- **The general use of chiral analysis for contaminant fingerprinting** was delineated in a fall 2005 EPA Office of Science publication as the "ultimate pollutant speciation" tool (EPA, 2005a).

In the U.S., National Exposure Research Laboratory, Ecological Research Division (NERL-ERD) in Athens, Georgia, has expertise in chiral analyses and chiral contaminants in the environment (Josephs and Barnett, 2005).

It should be mentioned that the proportion of various chiral molecules within an environmental contaminant has particular relevance in forensic studies. While it may not matter what the proportion of chiral isomers of a compound is as far as remediation is concerned, this information becomes important in forensic studies.

Some other publications reported the use of the method, although not necessarily for forensic purposes (Garrison, 2002; Wong and Garrison, 2000; Garrison et al., 1997; Jones et al., 2007).

The main limitations of this technique along with suggested recommendations are given in Table 4.18.

TABLE 4.18

Limitations and Recommendations for Chiral Fingerprinting

Influencing Factors/Limitations	Recommendations
The effect of biodegradation may vary in various environments, affecting the relative age-dating.	This may be tested in experiments following site-specific conditions. Site-specific data should be obtained and consulted.
Effects of other-than-biodegradation fate and transport processes for the studied contaminant (with chiral isomers) should be considered.	Experimental testing of such effects may help understand any potential influence of EF values by processes other than biodegradation. Such potential effects may be defensibly eliminated or, if data indicate potential for such effects, they may be accounted for along with biodegradation.
As with many fingerprinting techniques, commingled contamination will change the original fingerprints and render the method unusable.	Historical data and use of GIS to map the data may help with interpretations (e.g., by determining the likelihood of commingled contamination).
If the site was mitigated, chiral testing is useless.	In this case, another forensic technique should be used (e.g., a technique independent of the physical presence of contaminants at the time of sampling; see Chapter 5).

Hints for Successful Forensic Use of Chiral Fingerprinting

- **In general, chiral fingerprinting may be used in parallel with comprehensive chemical fingerprinting.** The use of more than one chemical fingerprinting technique will provide stronger evidence for a court case.
- **In some cases, however, chiral fingerprinting should be used by itself, and comprehensive chemical fingerprinting should be avoided.** These are the particular cases when the potential sources have a similar chemical composition. In this case, misleading information may be provided by comprehensive chemical analysis. For example, if the comprehensive chemical fingerprints are alike between suspected sources, it might be concluded that they cannot be forensically distinguishable. However, subtle differences may exist and could be reflected in the chiral fingerprints, making the sources distinguishable. Therefore, if suspected sources are known or expected to have similar comprehensive chemical fingerprints, it is recommended just to perform chiral fingerprinting. However, the results should always be interpreted with caution and only after a good understanding of the potential alteration of source and environmental samples due to biodegradation and other processes. Note that if both comprehensive chemical fingerprinting and chiral fingerprinting are performed and conclusions are different, chiral fingerprinting may be assigned a higher priority in providing defensible evidence. However, with this in mind, every case should be analyzed on a specific basis and after careful evaluation of all existing information and data.
- **It may be useful to evaluate biodegradation capacity within the study environment using independent means along with chiral fingerprinting.** Such means could include DNA analysis, as well as checking physical-chemical characteristics of the studied environment. This would provide support in interpreting chiral fingerprints and evaluating comparability between samples in source identification applications.
- While the typical use of chiral fingerprinting involves the evaluation of proportion between paired chiral isomers (through calculation of EF), **the actual concentration of various individual chiral isomers could also be a powerful forensic tool.** The concentration of chiral isomers could provide patterns that are more useful for source identification than all the other individual compounds composing a mixture when comparing samples of common origin and with similar chemical composition (e.g., natural seeps vs. spilled oil extracted from the same rock formation).

- **Chiral fingerprinting provides targeted chemical fingerprints (similar to signature chemicals).** Thus, its application requires fewer analytes to be tested, while providing highly specific information. Overall, the cost of chiral fingerprinting is generally lower than that of classical comprehensive chemical fingerprinting, which is yet another reason for its application at forensic sites.

4.2 Isotopic Fingerprinting

Isotopic fingerprinting involves the use of the proportion between isotopes (also referred to as the isotopic concentration) of a given element from the studied environmental contaminant to trace the source of contamination, identify potential multiple plumes, or establish the age of plumes. In addition, when using stable isotopes, because the stable isotopic composition of released contaminants changes in time as a function of various attenuation mechanisms, the evolution of the isotopic ratio in time can be used to confirm the occurrence of processes such as biodegradation or natural attenuation of released chemicals. Biodegradation has the strongest effect on altering stable isotopic concentrations of released compounds. However, other natural attenuation processes may also affect the stable isotopic composition of released contaminants over a longer time. For example, diffusion may slightly decrease stable isotopic concentrations at plume edges, while sorption may have some effect on stable isotopic concentrations, especially in soils with very high carbon content. There is still uncertainty regarding whether volatilization has no effect or some effect on stable isotopic concentrations (with a potential distinct effect from biodegradation).

Many natural and anthropogenic contaminant sources have a distinct isotopic composition due to the variability in isotopic composition of natural materials and the changes in isotopic compositions induced by manufacturing processes (for anthropogenic sources). This large variability of isotopic composition in source materials provides a powerful forensic opportunity to differentiate sources based on their isotopic composition.[7]

Isotopic fingerprinting provides another dimension of forensic evidence distinct from any type of chemical fingerprinting (discussed in Section 4.1), by capturing another sample characteristic: isotopic composition. There is no correlation between chemical and isotopic data/composition of a sample. Isotopic data are more specific than chemical data and thus are generally considered to provide more in-depth and refined source information.

A good overview of isotopes and forensic application principles was provided by Sueker (2001, 2003). The sampling methods for stable isotopic testing are in general straightforward and similar to those used in usual site sampling, although the amounts of sample needed may be quite different depending on the type of isotopic testing. The analytical costs (for stable isotopic testing) are generally modest, ranging from approximately $75 to $500 to $600 per sample.[8] Yet, the data are usually not available through historical monitoring and thus involve additional collection and analysis of samples during the forensic study. Thus, an overall increase in costs is envisioned compared with using chemical fingerprinting. Such costs are often justified by the higher accuracy and source specificity of the technique compared with chemical fingerprinting and other methods (less specific).

Isotopic versus Chemical Fingerprinting. There is a clear distinction between isotopic and chemical concentrations. For stable isotopic testing (which would be used in this comparison), the isotopic concentration refers simply to the proportion of the two measured stable isotopes (of the chosen element of a released compound) and is unrelated to the chemical concentration. Thus, a sample may have high chemical concentration but low isotopic concentration. So, plotting isotopic concentrations on maps, one can obtain completely different plumes than those based on chemical concentrations. Basically, the isotopic multiple plumes may be interpreted as originating from multiple sources (regardless of whether the original sources may be identified). The isotopic composition is mainly influenced by biodegradation; thus, the various isotopic values of plumes may also be a result of various stages of weathering. This is because microorganisms degrade the lighter isotope first, so the resulting biodegraded plume will be depleted of the lighter isotope.

For better understanding, let us consider investigating the origin of a brick wall. We may consider the brick wall equivalent to an environmental sample, while the individual composing bricks are equivalent to individual contaminants. In such a situation, chemical fingerprinting techniques provide information related to the size/weight of various bricks, while the isotopic fingerprinting provides information related to the color/shade of various bricks. Obviously, if the bricks are of the same color/shade, the information will be of no use, but if the bricks are of different colors or shades, then this extra information could help distinguish bricks of the same size, resulting in a more in-depth source identification. It is hoped this comparison is illustrative of both the distinct nature and the value of isotopic fingerprinting in forensic investigations.

Independent versus Interdependent Use of Chemical and Isotopic Fingerprinting. This general information on isotopic versus chemical fingerprinting also suggests that while these two types of fingerprinting may be seen as independent lines of evidence, in many cases they should be used interdependently for a more reliable and in-depth source identification. Considering our previous example with the brick wall, if two bricks have the same size/weight but distinct colors, conflicting conclusions are drawn; namely, the same source is suggested by size/weight, while distinct sources are suggested by the color information. However, when we combine these two types of information, we understand that distinct sources are likely, and the only way to reach this conclusion is to check the color of the bricks and not just their size/weight. Similarly, if two samples have the same chemical fingerprints but distinct isotopic fingerprints, it may be concluded that the results are conflicting, and something might be wrong. However, an experienced forensic scientist knows that the isotopic fingerprinting provides more in-depth and refined information and thus would consider distinct sources more likely. Of course, such a conclusion becomes more defensible if it is backed up by another line of evidence, such as historical information. Also, potential changes in isotopic fingerprints due to weathering should be considered before a final conclusion is reached.

Application Examples. Isotopic analysis has applications in many sciences. The following are examples of isotopic applications of forensic relevance:[9]

- Distinguishing between biogenic and thermogenic methane (Coleman et al., 1995; Sueker, 2003), which may also be performed using both ^{13}C and ^{2}H isotopic compositions.
- Evaluation of the source of sulfur (Sueker, 2003). The use of stable sulfur isotopic analysis (in conjunction with geochemical and hydrological considerations) to investigate the sources of elevated sulfate in groundwater at a pesticide facility in coastal Florida was also discussed in another study (Sueker et al., 2001).
- Petroleum hydrocarbon studies: Sueker (2001) provided relevant examples of source delineation by isotopic method.
- Differentiating gasoline and diesel spills (EPA, 2010; Kaplan et al., 1997; Wang et al., 2010), which may be done using both ^{13}C and ^{2}H isotopic compositions; note that ^{2}H isotopic concentrations are more source sensitive, with higher variability reported between sources of petroleum hydrocarbons.
- Identification of the source of chlorinated solvents (Beneteau et al., 1999; van Warmerdam et al., 1995).

- Delineation of multiple chlorinated ethane sources (Blessing et al., 2009).
- Identification of the source of biodiesel-derived carbon in motor oil through molecular and isotopic analysis (Peacock et al., 2010).
- Identification of nitrate sources using isotopic data ($\delta^{15}N$ and $\delta^{18}O$) (Liu et al., 2006; Silva et al., 2002).
- Determination of the origin of indigenous natural perchlorate and co-occurring nitrate in southwestern United States (Jackson et al., 2010).
- Evaluation of perchlorate sources (Bohlke et al., 2009; Sturchio et al., 2009) based on distinct isotopic fingerprints reported for manufactured perchlorate versus perchlorate from natural sources, such as the nitrate deposits from the Atacama Desert and natural perchlorate in Southern California. This evaluation may be done using oxygen isotopes (both ^{17}O and ^{18}O isotopic compositions plotted against each other) and chlorine isotopes (both ^{37}Cl and ^{36}Cl[10] isotopic compositions plotted against each other).
- Source attribution of uranium ore concentrates through analysis of lead ($^{207}Pb/^{206}Pb$) and strontium ($^{87}Sr/^{86}Sr$) isotope ratios (Varga et al., 2009).
- Geographical assignment of sources of tap water and beverages. Chesson et al. (2010b) measured the $\delta^{2}H$ and $\delta^{18}O$ values of bottled water, soda, beer, and tap water to evaluate the impact of purchase location on the stable isotope ratios.
- Geographical origin assignment of paired milk and cow drinking water was discussed by Chesson et al. (2010a).
- Differentiation of Pb sources. Main Pb sources (including Pb-based paint and leaded gasoline fallout) may be differentiated based on $^{207}Pb/^{206}Pb$ plotted against ^{208}Pb[11]$/^{206}Pb$ isotopic compositions (Clark et al., 2006).
- Obtaining the proof that natural attenuation occurs and possibly calculating its rate (Heraty et al., 1999; Sturchio et al., 1998; Abe et al., 2009).

4.2.1 Understanding Isotopes

Isotopes are atoms of the same element with the same number of protons but a different number of neutrons in their nuclei. Thus, isotopes of an element have the same atomic number, but they have different masses or mass numbers.

In nature, there are two main types of isotopes:

- Stable and
- Radioactive.

For the purposes of fingerprinting, mostly stable isotopic compositions are used, which is why this discussion focuses on stable isotopic analysis.

Radioisotopes may also be used for age-dating purposes (such as those described by the atmospheric tracer method) and are only briefly reviewed in this section; more information is provided in Section 6.2 related to the atmospheric tracer method (as radioisotopes may be used as atmospheric tracers to help age-date groundwater and establish a minimum age for a contaminated plume).

4.2.1.1 Stable Isotopes

Stable isotopes, as the name suggests, remain unchanged. Most natural elements have two or more stable isotopes. Since these isotopes do not change, they are generally used for source identification. Some commonly used isotopes in environmental studies are listed in Table 4.19.

TABLE 4.19

Examples of Stable Isotopes Commonly Used in Environmental Investigations

Element	Stable Isotopes[a]	Number of Protons (p) and Neutrons (n)	Relative Natural Abundance
Hydrogen	^{1}H	1p, 0n	0.99985
	^{2}H	1p, 1n	0.00015
Carbon	^{12}C	6p, 6n	0.9889
	^{13}C	6p, 7n	0.0111
Chlorine	^{35}Cl	17p, 18n	0.7577
	^{37}Cl	17p,20n	0.2423
Oxygen	^{16}O	8p, 8n	0.9976
	^{17}O	8p, 9n	0.00039
	^{18}O	8p, 10n	0.0020
Sulfur	^{32}S	16p, 16n	0.9502
	^{34}S	16p, 18n	0.0421

Source: Based on Environmental Protection Agency (EPA). 2010. Applications of Stable Isotope Analyses to Environmental Forensics (Part 3) and to Understand Degradation of Chlorinated Organic Compounds. CLU-IN Internet Seminar, October 2010. Presented by Paul Philp.

Note: Not all the stable isotopes for each element displayed in Table 4.19 may be shown here.

[a] Mass number (specific to each isotope) is represented in the upper left of chemical symbol.

As can be seen from Table 4.19, the most abundant stable isotope is generally the one with the lower mass number.

The stable isotopic composition is recorded as a ratio, usually referred to as δ or *delta* and reported relative to a standard, according to the following formula (using sulfur stable isotopes as an example):

$$\left[\frac{\left(\frac{^{34}\mathrm{S}}{^{32}\mathrm{S}}\right)\text{sample}}{\left(\frac{^{34}\mathrm{S}}{^{32}\mathrm{S}}\right)\text{standard}}-1\right]\times 1000 = \text{d or } \delta \text{ (delta) ‰ (per mil).}$$

So, the results of stable isotopic testing are, by convention, calculated as demonstrated in the provided example, and this is how data will be reported by the laboratory (as δ or delta and per mil [see discussion next paragraph]). Note that the more abundant isotope (the one with lower mass number) is always in the denominator. Thus, the higher the result is, the more depleted the sample will be in the lighter isotope, in which case the sample may be referred to as being "heavier." The lower the result is, the more depleted the sample will be in the heavier isotope; thus, the sample may be considered "lighter."

The stable isotopic data-reporting convention shown is meant to identify easily if the tested sample has higher or lower isotopic concentration relative to the standard; specifically, if the value is positive, then the sample isotopic concentration is higher than that of the standard, and the opposite is true for negative values. Note that by convention the results are multiplied by 1,000 and thus are expressed as "per mil" to make them easier to compare and reference (otherwise, the results will be low numbers with multiple decimals).

Based on the natural sources used in their manufacture, the same contaminants may have noticeably different stable isotopic ratios for the component elements, usually referred to as *isotopic signatures*. This stable isotopic variability offers a powerful forensic tool to assess the source of contamination.

Note that while stable isotopes do not change in time (or disintegrate, such as radioisotopes), their proportions may change in the environment due to natural weathering processes. This change in stable isotopic proportions due to weathering is referred to as *isotopic fractionation*. In general, it is considered that biodegradation has the strongest effect on isotopic fractionation, always resulting in a depletion of the lighter isotope (or an enrichment in the heavier isotope) and thus an increased delta value.

The stable isotopic fractionation has been studied, and it involves the process described by the Raleigh equation:

$$R_t/R_0 = f^{(\alpha-1)},$$

where

R_t and R_0 are isotopic ratios at times t and 0 (initial), respectively;

f = fraction of reactant remaining at time t (extent of a reaction);

$f = [\text{Reactant}]_t/[\text{Reactant}]_0$ (referring to concentrations of reactants at the two times);

α = fractionation factor that can be transformed in an enrichment factor (ε):

$$\varepsilon = (\alpha - 1) \times 1{,}000.$$

Using δ (isotopic data as reported by labs), the Raleigh equation becomes

$$\ln[(\delta d + 1{,}000)/(\delta_o + 1{,}000)] = (\alpha - 1) \ln f.$$

While the simple increase of delta value (heavier isotope proportion) in a studied contaminant in time is solid proof that degradation processes are happening, the equation developed by Raleigh can be used to evaluate the extent of that degradation. As shown, to do so and determine the f value (or fraction of contaminant that remains), one needs to know the fractionation factor (alpha or α value), as well as the isotopic composition (delta or δ value) at two times (original time [time zero] and after some time). While the isotopic composition at two distinct times is measured based on collecting field samples (e.g., of groundwater or soil), the fractionation factor is usually determined in the laboratory, and data may be available for the most common contaminants and degradation processes. However, if possible, it is always more reliable to conduct your own microcosm or laboratory study that mimics the natural conditions of the studied environment.

Table 4.20 provides examples of some enrichment factors for common contaminants as published in the literature (please note that the fractionation factor can be calculated from the enrichment factor as shown when

TABLE 4.20

Example of Enrichment Factors for Carbon Isotope Fractionation during Reductive Transformation of Chlorinated Solvents

Degradation Process	ε (‰) Enrichment Factor as Reported in the Literature
PCE → TCE	–2, –2.7, –5.2, –5.5
TCE → *cis*-1,2DCE	–4, –2.5, –6.6, –7.1, –13.8
cis-1,2DCE → VC	–12, –14.1, –16.1, –20.4, –19.9
trans-1,2-DCE → VC	–30.3
1,1-DCE → VC	–7.3
VC → ethene	–26, –21.5, –26.6, –22.4, –31.3
1,1,2-TCA → VC	–2.0
1,2-DCA → ethene	–32.1

Source: Hunkeler, D., Aravena, R., and Cox, E. 2005. Assessment of degradation pathways in an aquifer with mixed chlorinated hydrocarbon contamination using stable isotope analysis. *Environ. Sci. Technol.* **39**: 5975–5981.

discussing the Raleigh equation). Please refer to Sueker's (2001, p. 10) article for an example of such a calculation to determine the fraction of remaining contaminants based on isotopic change measured in time.

4.2.1.2 Radioactive Isotopes

Radioactive isotopes (radioisotopes) are not stable, and they decay (disintegrate), finally resulting into stable isotopes. There are more than 1,700 radioactive isotopes in nature. Many, but not all, elements have radioactive isotopes. Since these isotopes change in time and the time required for them to change is known, they are generally used for age-dating purposes.

Radioactive isotopes are measured as an activity (rate of decay) and reported using the following possible units:

Bq (bequerel) = 27 pCi (picoCuries)

TU (tritium unit) = 1 tritium (T) atom/10^{18} ^{1}H atoms.

Age-dating a contaminant plume using radioisotopes can be done using the decay law and the specific "half-life"[12] for the radioisotope used. Specifically, the following equation may be used to calculate the age of a release:

$$T = t_{1/2}*1.44*\ln(A_0/A),$$

where T is the determined time (age of release); $t_{1/2}$ is the half-life specific for each radioisotope; A_0 is the initial activity; and A is the activity measured at a certain time T.

The half-life is defined by the following equation:

$$t_{1/2} = (\ln 2)/\lambda,$$

where λ is the decay constant (probability that an atom will decay within a stated time).

λ is defined by the decay law described by the following equation:

$$A = A_0 e^{-\lambda t},$$

where A is the activity of radioactive compound at a certain time t, while A_0 is the activity of radioactive compound at time zero (initial activity).

For more details and examples, please refer to the review article by Sueker (2001).

4.2.2 Specific Types of Isotopic Fingerprinting

As with chemical fingerprinting, there are several types of isotopic fingerprinting with relevance to environmental forensics that are discussed further.

Stable isotopic fingerprinting techniques include those based on

- bulk isotopic analysis (BSIA)
- compound-specific isotopic analysis (CSIA)[13]
- position-specific isotopic analysis (PSIA)

Radioisotopic fingerprinting techniques include those related to

- Atmospheric tracers
- Sediment core age-dating.

4.2.3 Bulk Isotopic Fingerprinting

As the name suggests, bulk isotopic fingerprinting is based on bulk stable isotopic analysis (BSIA), which means detection of the isotopic concentration for a targeted stable isotope as a sum of its concentration in all the individual compounds in the sample that contain that element. For example, if the targeted stable isotope is ^{13}C, then the bulk isotopic analysis of a sample containing PCE, TCE, along with *cis*- and *trans*-1,2-DCEs would provide the sum of ^{13}C isotopic concentrations in each of the previously listed composing individual compounds:

Bulk ^{13}C isotopic concentration = ∑(^{13}C isotopic concentrations of PCE, TCE, *cis*-1,2-DCE, *trans*-1,2-DCE).

4.2.3.1 Method Principle and Steps

4.2.3.1.1 Method Principle

The bulk isotopic concentration of a targeted element in an environmental sample should correlate to the bulk isotopic concentration of that element in the release source and thus may be used to identify sources. However, the potential altering of the original bulk composition due to weathering (especially biodegradation processes) should be considered when results are interpreted. Since the changes in isotopic composition due to biodegradation are prevalent and are well defined (biodegradation inducing a depletion in the lighter isotope or an increase in the heavier isotope), even altered results may be used for potential source identification. For example, if the sample bulk isotopic composition is depleted in the lighter isotope versus the candidate source sample, then it might be deduced that the candidate source should not be excluded based on isotopic data. Obviously, in such a situation, more in-depth analysis may be needed to confirm that the candidate source is indeed where the contamination originated (i.e., the source of the biodegraded analyzed material). Such in-depth analysis may be done through more refined isotopic fingerprinting, such as CSIA, that is further described. The source confirmation may also be done through using other fingerprinting techniques described in this book. The more lines of evidence that indicate the suspected source contributions, the stronger the argument will be. In general, at least two independent lines of evidence should corroborate the results for a defensible argument. Apart from biodegradation/weathering, another factor to be considered when using BSIA analysis is the source of composing individual contaminants in the analyzed sample. If it is suspected that multiple sources provided the contaminants (some or all), then the BSIA result may not be representative for source delineation (it may be regarded as an average value resulting from the multiple suspected sources).

When contaminants are composed of more elements that have stable isotopes, the analysis of each stable isotopic composition may be performed to provide multiple bulk fingerprints. For example, in the case of crude oil, bulk stable isotopic compositions for C, H, O, N, and S may all be determined to provide a more comprehensive bulk isotopic fingerprint.

4.2.3.1.2 Method Steps

The following are the main steps that should be followed:

1. **Analysis of environmental samples for the targeted isotope.** Bulk isotopic testing does not require any separation of original compounds in a sample, as the testing is done on the sample as a whole.
2. **Analysis of candidate sources for the targeted isotope** through the same analytical method used to test the samples. The isotopic concentration results are reported relative to a standard and expressed per mil (‰) as described previously.
3. **Comparing results and data interpretation.** The sample data should be compared with that from candidate sources.[14] (Interpretation should consider the effects of possible biodegradation/weathering and multiple source contributions for various individual contaminants as explained in the previous section 4.2.3.1.)
    - If a direct match is found with one source, then that candidate source may be considered likely and the others eliminated.
    - If a direct match is found for more than one candidate source, then more in-depth analysis (e.g., CSIA or other type of testing) should be performed to further distinguish between the candidate sources with a match.
    - If no match is found with any of the candidate sources, then the potential for isotopic alterations in the sample should be evaluated to establish the likelihood of such alteration occurring and predict the alteration; if the alteration might have occurred to change the bulk isotopic composition in a certain direction (e.g., decreasing it), then the candidate sources with the isotopic

composition value in the other direction (e.g., increased value as compared to the sample) may be eliminated, while the other candidate sources should be further evaluated through more in-depth fingerprinting.

- Note that an evaluation of weathering-induced alterations or the lack thereof should be done even if direct matches between sample and candidate sources are found. In such a case, it should be confirmed that any weathering alterations may not have significantly altered the bulk isotopic composition of the sample (in order for the match to be relevant).
- Data display on maps may help data interpretation.
- Plots of bulk isotopic data versus chemical data may help further interpret results.
- In the absence of source candidate samples, samples that may be representative of original sources may be used; if no candidate source representative sample is available, comparison with literature-reported similar isotopic values may help establish general source categories.

4.2.3.2 Applications, Limitations, and Recommendations

General types of applications of bulk isotopic composition include the following:

- **Source identification.** Bulk isotopic composition is an especially effective technique in the case of single contaminants or when only one main contaminant from a mixture contributes to the targeted bulk isotopic result.
- **Proof of biodegradation.** Determination of bulk isotopic values over time may provide proof of biodegradation versus other contaminant transformation processes (e.g., evaporation, dissolution, chemical degradation). Since biodegradation is the major influencing factor of isotopic composition/fractionation (in time), an increase in the bulk isotopic concentration of the targeted compound in time may be an indication that biodegradation did occur.

Typical forensic application examples include the following:

- The use of bulk isotopic composition to differentiate crude oils and gasolines (Kaplan et al., 1997).
- The use of bulk isotopic analysis to evaluate the source of pharmaceuticals and suppress counterfeiting (Jasper et al., 2002). Highly specific isotopic fingerprints were obtained to allow the identification of individual batches of pharmaceutical materials (including

four over-the-counter analgesic drugs and four drug substances), including those counterfeited, which had distinct isotopic composition. The authors pointed out that "The specificity of the technique is analogous to that of DNA identification."

Bulk isotopic composition may be seen as a first isotopic characterization technique that is straightforward and inexpensive. However, bulk isotopic analysis has a series of limitations, including the following:

- Distinct sources could have similar bulk isotopic values.
- The method has low specificity.
- The interpretation accuracy decreases with time since the release occurred.

It is recommended to use this technique as a first "screening" step when contaminant mixtures are present. As described concerning the method steps, depending on the results, more in-depth analysis (e.g., through CSIA) may be performed for refined source fingerprinting. Note that when contaminants are not in mixtures or only one contaminant contains the targeted stable isotope, bulk isotopic data are highly specific as they are the result of only one compound. In such cases, there is no further need for CSIA (compound specific isotopic analysis).

4.2.4 Compound-Specific Isotopic Fingerprinting

Compound-specific isotopic fingerprinting is based on the analysis of targeted stable isotopic concentration in selected individual compounds from a mixed environmental sample (considering that more than one individual compound from the sample contain the targeted isotope). Compound-specific isotopic fingerprinting is done through CSIA.

The analytical technique used for CSIA is GC/IRMS (GC coupled with isotope ratio mass spectrometry). Each individual component is combusted to CO_2 as it exits the chromatographic column. Then, the isotopic proportion is measured by IRMS equipment. The equipment functions under the same principles and is similar to that used for chemical fingerprinting (i.e., GC/MS).

4.2.4.1 Method Principle and Steps

4.2.4.1.1 Method Principle

The stable isotopic concentration of a targeted element in an individual contaminant from a sample should correlate with the stable isotopic concentration of the targeted element in the same individual compound from its release source. This method applies when more than one individual compound (contaminant) in an environmental sample contains the targeted isotope, in which case CSIA distinctively reports the isotopic concentration of the targeted isotope for each individual compound that contains that isomer. If only one compound in a sample contains the targeted stable isotope, the results from bulk isotopic testing of that isotope should be identical with those from CSIA; thus, CSIA is not needed in that case.

The advantages of CSIA over bulk isotopic testing in the case of samples that contain multiple compounds with the targeted stable isotope consists of providing a more in-depth isotopic fingerprint. While bulk isotopic analysis provides only one isotopic concentration as a sum of concentrations from various individual compounds containing the targeted isomer, CSIA provides multiple isotopic concentrations, each corresponding to an individual compound containing the targeted isotope. Thus, CSIA is more specific and provides additional information that can be crucial in source identification.

As in the case of bulk isotopic concentrations, the compound-specific isotopic concentrations start altering once contaminants are released in the environment as a result of various weathering processes (mostly influenced by biodegradation). These alterations are described by isotopic fractionation as discussed in a previous section and are generally predictable. For example, it is well established that microorganisms prefer lighter isotopes; thus, the contaminant molecules with lighter isotopes will be biodegraded at a faster rate than those with heavier isotopes. The result is that when biodegradation occurs, an increase in the heavier isotope (and thus an increased δ value) should be observable in time. Therefore, as in the case of bulk isotopic testing, CSIA may be used to evaluate the occurrence of biodegradation, as well as for source identification and allocation purposes. When source identification is targeted, the weathering and especially biodegradation should be considered and evaluated to help interpret and compare CSIA results from samples and candidate sources. Similar to the discussion included previously related to bulk isotopic analysis, if biodegradation is suspected to have occurred, the CSIA results should be interpreted with caution, and the predicted change in isotopic concentrations should be evaluated on a case-by-case basis.

Also, similar to bulk isotopic analysis, when individual contaminants are composed of more elements that have stable isotopes, the analysis of each stable isotopic composition for each individual compound may be performed, providing multiple CSIA fingerprints. For example, in the case of a chlorinated solvent mixture composed of PCE and TCE, CSIA may target one or more of the following stable isotopic compositions:

- $\delta^{13}C$ in TCE
- $\delta^{13}C$ in PCE
- $\delta^{37}Cl$ in TCE
- $\delta^{37}Cl$ in PCE
- $\delta^{2}H$ in TCE[15]

4.2.4.1.2 Method Steps

The following are the main method steps:

1. **Separation of targeted individual compounds from a sample.** For example, if we want to determine the ^{13}C CSIA composition of TCE and PCE from a chlorinated solvent mixture/plume containing TCE, PCE, 1,1,1-TCA, and CT, the first step would be to extract or separate TCE and PCE from the mixed environmental sample.
2. **Analysis of targeted individual compounds from environmental samples for the targeted isotopes**, usually through IRMS. The isotopic concentration results are reported relative to a standard and expressed per mil (‰) as described previously.
3. **Analysis of the same targeted individual compounds from candidate sources for the same targeted isotopes** through the same analytical method used to test the samples.
4. **Comparison of results and data interpretation.** The sample data should be compared with those from candidate sources[16]:
    - If a match (a general match may be considered when isotopic concentrations are generally within 1 per mil difference) is found with one source for all or most individual compounds, then that candidate source may be considered likely and the others eliminated.
    - If a match is found for all or most individual compounds with more than one candidate source, then all the candidate sources with the match should be retained for further testing (e.g., through other forensic techniques); also, historical data may help further delineate the more likely sources.
    - If matches with candidate sources are found for just a few individual compounds, the potential for differential weathering of the compounds with no match should be considered, as well as any particular information that can help further interpret the results; information from other lines of evidence may also help further interpretation and source delineation.
    - If no match (generally, a difference in isotopic concentrations higher than 2 per mil may be seen as a non-match) is found with any of the candidate sources, then the potential for isotopic alterations in the sample should be evaluated to establish the likelihood of such alteration to occur; if the alteration might have occurred to change the CSIA isotopic composition in a certain direction (e.g., decreasing it), then the candidate sources with the isotopic composition value in the other direction (e.g., increased value as compared to the sample) may be eliminated, while the other candidate sources should be further evaluated through other forensic techniques.

- Note that an evaluation of weathering-induced alterations or the lack thereof should be done even if matches between sample and candidate sources are found. In such a case, it should be confirmed that any weathering alterations may not have significantly altered the CSIA isotopic composition of the sample (for the match to be relevant).
- Data display on maps may help data interpretation.
- Plots of CSIA data versus chemical data may help further interpret results.
- In the absence of source candidate samples, samples that may be representative of original sources may be used; if no candidate source representative sample is available, comparison with literature-reported similar isotopic values may help establish general source categories. Also, relative comparison between samples from various areas may help established if one or more sources exist contributing to the contaminated plume. A better evaluation of contaminant fate and transport mechanisms may also be achieved.

4.2.4.2 Applications, Limitations, and Recommendations

General types of applications of CSIA include the following:

- **Source identification for organic and inorganic contaminants** composed of elements with stable isotopes (e.g., crude oil and refined products, methane, chlorinated solvents, 1,4-dioxane, PCBs, PAHs, perchlorate, metals, nitrates, sulfates, explosives).
- **Source allocation for commingled contaminant plumes,** considering that the CSIA isotopic composition of the contaminant in the plume and in the suspected/candidate sources can be determined or approximated.
- **Detection of multiple releases** in time based on degree of plume degradation (e.g., enrichment in heavier isotopes in various areas of the studied contaminant plume).
- **Estimation of relative time of multiple releases/plumes** using the kinetics of different transformation processes reflected in the change of the original isotopic composition (using measurements of time).
- **Vapor intrusion evaluation** through comparison between isotopic values of compounds in indoor air with the same compounds in underlying soil vapor and groundwater plume.
- **Proof of biodegradation** versus other contaminant transformation processes (e.g., evaporation, dissolution, chemical degradation)

through CSIA testing over time; since biodegradation is the major influencing factor responsible for isotopic composition/fractionation (in time), an increase in the isotopic concentration of the targeted compound in time is an indication that biodegradation did occur.

- **Evaluation of specific degradation pathways** may be done through CSIA. Isotopic data may allow correlation between daughter products (DPs) and potential parent products (PPs) (published enrichment factors should also be considered).

Specific applications of CSIA with forensic relevance include the following literature-published studies:

- Evaluation of the sources of chlorinated solvents, potentially tracking them to the manufacturer (Van Warmerdam et al., 1995; Beneteau et al., 1999), under specific conditions based on measuring both ^{13}C and ^{37}Cl isotopic compositions of targeted chlorinated solvent compounds; however, such tracking to the manufacturer may be questionable due to the high possible variability between batches and years, as well as the lack of enough published data to define such variability. Forensic investigations of the PCE/TCE sources were reported, including revealing multiple sources based on a 3D CSIA approach testing for ^{13}C, ^{37}Cl, and ^{2}H isotopes of targeted chlorinated solvents (Wang et al., 2010).
- Distinguishing manufactured TCE versus TCE coming from degradation of PCE in subsurface may be possible based on the value of the ^{2}H isotopic composition according to Shouakar-Stash et al. (2003).
- Differentiating PCB sources based on congener-specific isotopic composition (EPA, 2010).
- Differentiation of NAPL samples based on CSIA targeting ^{13}C isotopes of individual PAHs (EPA, 2010).
- Differentiation between degrading versus nondegrading DPs (daughter products) of chlorinated solvents based on CSIA isotopic profiles in time of PP (parent product) versus DP (McLoughlin, 2010); the DP starts with a lighter isotopic composition than the PP,[17] and it becomes heavier as heavier PP is degraded. Isotopic data may be used to differentiate between a degrading versus a nondegrading DP in the following manner:
  - A degrading DP will become heavier than the PP (basically, when samples taken at the same time of PP and DP isotopic data are compared, the degrading DP should be heavier than the PP).
  - A nondegrading daughter compound will not become heavier than the PP at any time when testing is done.

CSIA has already proven its utility in many forensic studies and is today a well-established forensic tool. The prices of CSIA vary based on the targeted isotope. Generally, CSIA targeting ^{13}C isotopes is relatively inexpensive, while CSIA targeting other isotopes, such as ^{37}Cl, is more expensive. However, as the technique evolves, it is likely that prices will gradually decrease, making CSIA part of routine site characterization tools. CSIA-based fingerprinting, as most isotopic techniques, has higher source specificity than chemical fingerprinting, with the ability, in many cases, to differentiate between sources with similar chemical fingerprints (see the interdependent use of isotopic and chemical fingerprinting technique discussion from the introductory section related to isotopic fingerprinting). Another advantage of CSIA-based fingerprinting consists of the availability of published fingerprints for main sources of many contaminants (e.g., chlorinated solvents).

Table 4.21 shows some main limitations of CSIA-based fingerprinting and provides subsequent recommendations.

TABLE 4.21

Limitations and Recommendations for CSIA-Based Fingerprinting

Influencing Factors/Limitations	Recommendations
Distinct sources may have the same isotopic signature.	Obtain end members' source samples or samples close to original sources to confirm; if similar isotopic signatures confirmed, then use another fingerprinting technique.
More than one release (in time) occurred at a site involving the same chemical with distinct isotopic composition (for each release).	Evaluate such a possibility during historical review (e.g., Were chemicals purchased from distinct manufacturers, any change in manufacturing or waste treatment and handling? Were multiple spills/accidents recorded?); if potential exists for releases of the same chemical with distinct isotopic composition at various times at a site, then use another fingerprinting technique.
Commingled contamination.	Evaluate the possibility for commingled contamination through other lines of evidence (starting with historical review). If end members' (sources') samples are available, data may be interpreted to see if suspected commingled contamination has an isotopic signature consistent with commingling (in between the end members' signature); in such situation, stable isotopic data may be used for source apportionment.
Altered isotopic composition due to degradation.	Evaluate degradation potential based on environmental conditions and other lines of evidence; compare isotopic results of samples under similar environmental conditions while considering the effects of isotopic fractionation for environments with distinct environmental conditions. Also, evaluate any potential changes in time of environmental conditions.

Overall, CSIA-based fingerprinting has a series of general limitations that should be considered when applying this technique. Such limitations include the following:

- There is a possibility that distinct sources could have similar isotopic fingerprints, thus rendering the method ineffective in some cases.
- As with many forensic techniques, there is a decrease in accuracy with time since the release occurred, especially in environments conducive to biodegradation.
- The technique may not work for contaminants present in small amounts, especially when testing for low molecular weight isotopes such as ^{2}H (deuterium).
- There are still relatively few commercial labs that specialize in performing this analysis, and the costs for certain isotopes other than ^{13}C (e.g., ^{35}Cl, ^{2}H) may be still high.

It is recommended that CSIA data be interpreted within each site-specific context and only after delineation of natural conditions conducive for biodegradation and other weathering processes is performed. CSIA may be done in conjunction with bulk isotopic testing or on its own. While CSIA targeting ^{13}C isotopes is commonly employed and inexpensive, it is not always highly specific to sources, such as in the case of other targeted isotopes, such as ^{37}Cl for chlorinated solvent sources. When source identification is the goal, it is highly recommended to perform CSIA for multiple targeted isotopes of the studied contaminant. However, if the goal is to evaluate biodegradation occurrence, CSIA targeting ^{13}C isotopes should suffice.

4.2.5 Position-Specific Isotopic Fingerprinting

Position-specific isotopic fingerprinting may be seen as the ultimate stable isotopic tool that is based on the analysis of stable isotopic concentration of fragments of a targeted compound in an environmental sample (usually referred to as position-specific isotopic analysis or PSIA). Basically, the technique provides isotopic composition of targeted compounds at an intramolecular level. This provides a more detailed and highly accurate level of source identification, as well as the opportunity for more comprehensive evaluation of fate and transport of contaminants by evaluating natural attenuation mechanisms.

The method, first pointed out in 1961 by Abelson and Hoering, was further developed for biochemical and environmental studies (see, e.g., Corso and Brenna, 1997). The method has long been used for isolation and characterization of biochemical compounds as amino acids (e.g., Wolyniak et al., 2005; Sacks and Brenna, 2003). Although the PSIA technique has existed for a long time, its application in environmental forensics has only been pointed out more recently (Gauchotte et al., 2010). The determination of the isotopic concentration (e.g., $^{13}C/^{12}C$ ratio) at specific positions in a compound provides great forensics opportunities since it reflects highly accurate information related to the origin of a studied compound and may record the status of complex systems, such as environmental or physiological states. It is likely that we will see more use of PSIA in environmental forensics and other environmental studies in the coming years.

PSIA-based fingerprinting versus other types of stable isotopic fingerprinting. If we return to the analogy of a brick wall for an environmental sample, considering that isotopic fingerprinting provides information related to the color of the bricks, the following may be the case for various types of isotopic fingerprinting: BSIA provides an average color resulting from all the bricks in the wall, CSIA provides the color of each brick in the wall, and PSIA provides the color shades associated with various parts within each brick. It is obvious that PSIA provides more detailed information and thus more comprehensive fingerprints; therefore, the use of just PSIA may provide more accurate results (in what concerns the forensic identification of each brick provenience) than both bulk and CSIA analyses.

4.2.5.1 Method Principle and Steps

4.2.5.1.1 Method Principle

The fragments of a targeted contaminant may have distinct isotopic compositions depending on the source material as well as the specific site of attack during natural attenuation processes, such as biodegradation, chemical degradation, or other attenuation processes. Thus, the detection of isotopic composition at the fragment level may result in accurate source identification or evaluation of natural attenuation mechanisms for the targeted compound within the targeted environment.

4.2.5.1.2 Method Steps

PSIA generally involves the use of GC/combustion/IRMS (GC/C/IRMS). The following are the main steps that should be followed to apply the PSIA technique (based on the method proposed by Gauchotte et al., 2009, for MTBE):

1. **Separation of targeted individual compounds from a sample.** For example, if we want to determine the ^{13}C PSIA composition of MTBE fragments from a gasoline sample, we should first separate MTBE from other gasoline components (e.g., usually through GC).
2. **Pyrolysis of the separated targeted compound** should follow using a pyrolysis furnace, resulting in pyrolysis products or fragments (pyrolysates) that are specific to the targeted compound.
3. **Separation of the pyrolysis products/fragments,** usually in a second GC oven, is the next step.

4. **Analysis of targeted individual fragments from the selected compound of an environmental sample for the targeted isotopes**, usually through IRMS. The pyrolysate fragments are oxidized in a combustion furnace, then passed through a water trap before flowing into the IRMS equipment; note that the separated fragments may also be subjected to structural analysis using time-of-flight mass spectrometry (TOFMS).
5. **Analysis of the same targeted individual compounds from candidate sources for the same targeted isotopes** through the same analytical method used to test the sample(s).
6. **Comparison of results and data interpretation.** The sample data should be compared with those from candidate sources.

4.2.5.2 Applications, Limitations, and Recommendations

PSIA has multiple application opportunities in environmental forensics studies as well as in general fate and transport and biochemical studies. The following are the main types of applications with forensic relevance:

- **Highly specific source identification** for contaminants composed of elements with stable isotopes (e.g., MTBE and other oxygenated compounds, halogenated compounds, amino acids) through comparison of the isotopic signature of pyrolysate fragments, which usually preserve the signature of source material even after weathering of an environmental sample; concrete examples include the following:
  - *The use of PSIA for carbon isotope analysis of trichloroacetic acid (TCAA)* of different origins (Breider and Hunkeler, 2011); this information may be used to help distinguish different sources of this environmental contaminant. TCAA was first degraded into chloroform (CF) and carbon dioxide (CO_2) by thermal decarboxylation, a process associated with strong carbon isotope fractionation ($\varepsilon = -34.6 \pm 0.2‰$). Then, the stable carbon isotopic ratio of each resulting fragment (CF and CO_2) was determined. The method quantification limit for TCAA was 18.6 μg/L. The results denoted significant PSIA isotope ratio differences between industrially manufactured TCAA and that produced through chlorination of NOM, proving the forensic applicability of the method for TCAA fate and transport and source evaluation.
  - *The potential use of PSIA for MTBE source identification* was pointed out by Gauchotte et al. (2010), who published a summary of $\delta^{13}C$ values for the two MTBE pyrolysate fragments: the methoxy and the 2-methylpropyl groups from various sources. The isotopic values for the two fragments were distinct between some of the sources.

  - *The use of PSIA to evaluate the present and preindustrial global average N_2O sources in air* (Rockmann et al., 2003); specifically, the ^{18}O and position-dependent ^{15}N isotopic composition of N_2O from Antarctic firn air samples were studied. The study also pointed out the similar changes in ^{15}N composition at both positions (in the N_2O molecule) as a result of the strong increase of global N_2O sources since preindustrial times, which was in contrast to the stratospheric N_2O sinks with a strong fractionation at the central position.
  - *The use of PSIA to characterize amino acids from different sources/vendors*:
    - The natural variability between sources and the potential method use to distinguish different sources of amino acids was pointed out by Wolyniak et al. (2005) in a study of alaninol and phenethylamine, analogues of alanine and phenylalanine, respectively.
    - Large variations in position-specific isotope ratios were observed in samples from different commercial sources of 3-methylthiopropylamine (3MTP) and isoamylamine (IAA), the decarboxylated analogues of methionine and leucine (Sacks and Brenna, 2003); dramatic source isotopic differences were observed for 3MTP.
- **Evaluation of multiple releases and commingled plumes.** The isotopic signatures of pyrolysate fragments would likely vary within the plume without following a similar pattern.
- **Evaluation of specific mechanisms of attenuation processes** for a targeted contaminant through the identification of the first site of attack of microbial or other type of degradation; examples include the following:
  - *The use of the PSIA technique for studying subtle changes in intramolecular isotope ratios of amino acids* due to natural processes was pointed out by Sacks and Brenna (2003).
  - *The use of PSIA for investigation of biomethylation processes in methylcobalamin* was pointed out by Wuerfel et al. (2013), who studied biomethylation of metal(loid) to differentiate between reaction mechanisms and determine the origin of the methyl group; the method was applied to the analysis of the low-boiling partly methylated arsenicals, which are formed in the course of arsenic methylation; this mechanism may be part of natural attenuation mechanisms of MTBE.
- **Obtain proof of biodegradation** versus other attenuation processes for some contaminants, based on the fact that all the targeted pyrolysate fragments may display distinct isotopic composition from the

targeted contaminant in case of abiotic attenuation, while only one pyrolysate may have distinct isotopic composition from the targeted contaminant in case of biodegradation. Concrete examples include MTBE degradation mechanisms studied by Gauchotte et al. (2009, 2010); specifically, the intramolecular location of the first step of the oxidation of MTBE by MNO_4^- was confirmed as being the carbon atom of the methoxy group.

While PSIA holds great promise in forensic investigations, some limitations exist, including the following:

- PSIA is still an emerging forensic technique with limited published environmental forensics applications.
- Commercial availability of PSIA is less common and potentially expensive; this may change as the technology improves, and more practical applications may become as popular as CSIA or other isotopic techniques.
- PSIA may not work for contaminants present in very small amounts.

As the general knowledge and awareness increase, PSIA will undoubtedly gain a preeminent position in the forensic toolbox. This method may be applied by itself or as part of a tiered isotopic fingerprinting approach, including the following:

- Tier 1: BSIA-based fingerprinting.
- Tier 2: CSIA-based fingerprinting if BSIA is not applicable or the results of BSIA are not conclusive. Note that when a contaminant is composed of more than one element with stable isotopes, applying CSIA for each composing element stable isotope provides a more refined source identification.
- Tier 3: PSIA-based fingerprinting if results of BSIA and CSIA are not conclusive. Note that when a contaminant is composed of more than one element with stable isotopes, applying PSIA for each composing element stable isotope provides the highest chance for accurate and reliable source identification. For example, in the case of MTBE, PSIA should target carbon, hydrogen, and oxygen stable isotopes in MTBE fragments, as applicable.

The advantage of the proposed tiered approach for stable isotopic fingerprinting is cost efficiency since the approach starts with the most inexpensive technique and gradually targets more advanced techniques as needed.

4.2.6 Radioisotopic Techniques

Radioisotopic techniques provide useful tools in environmental forensics age-dating studies. Radioisotopes could be used to age-date environmental contamination based on their well-established half-lives. In this section, two radioisotopic techniques are reviewed. More information is provided for one of these techniques (i.e., atmospheric tracers) in Chapter 6.

Two common forensic age-dating techniques using radioisotopes are atmospheric tracers and sediment core age-dating.

1. **Atmospheric tracers technique** consists of the measurement of the activities of certain radioisotopes in the studied environmental media (i.e., groundwater) and the deduction of a minimum contamination age based on well-established atmospheric concentration trends of the tested radioisotopes. Basically, the idea is that the minimum contamination age is the age of the last groundwater recharge, assuming that contamination entered groundwater via leaching from soil when in contact with precipitation water percolating through soil. The age of the most recent groundwater recharge is reflected by the recorded radioisotopic activities of certain elements with known variable trends in the atmosphere over the last century or so. Such radioisotopes (as those of tritium ^{3}H) are, for example, those that have been used and released during nuclear testing during the last century. This method has many challenges and requires particular sampling that may not be easy to achieve. In addition, the method provides a minimum contamination age rather than the exact age and requires sensitive analysis techniques since the radioisotopic activities in the atmosphere and subsequently groundwater are extremely low. The method challenges and requirements are discussed in detail in Chapter 6, Section 6.2, dedicated to the atmospheric tracer[18] age-dating technique. Typical applications of this technique include groundwater age-dating and evaluation of recharge processes (Sueker, 2003; Clark and Fritz, 1997; Fritz et al., 1991; Oudijk 2003, 2005).
2. **Sediment core age-dating** is a well-established technique (EPA, 2008) for age-dating stratified layers of aquatic sediments based on the concentration of radioisotopes such as ^{210}Pb and ^{137}Cs along a sediment core. This method may capture sedimentation occurring during the last century providing that the sediment remained undisturbed (e.g., no dredging or other mechanical disturbance of sediments happened during the period studied). In addition, this method could be used to document contaminant sources over time and space. General applications of this technique include reconstruction of temporal PAH deposition trends

using lake sediment cores dated using ^{210}Pb and 137Cs (Usenko et al., 2010).

4.2.6.1 Sediment Core Age Dating

Also known as **geochronology**, sediment age-dating is a "classic" age-dating technique developed since the 1960s (Goldberg, 1963) that can reconstruct contamination deposited in aquatic sediments (e.g., lakes, rivers, marine environments) as long as they have been mechanically undisturbed. The resulting information may be used for many purposes, including the following:

- Expert witness/litigation support to evaluate sources contributing to sediment contamination during the years and allocate contributions.
- Restoration/remediation of contaminated sites. As with any forensic technique, sediment age-dating help to better understand and address active sources of contamination.
- Dredging operations planning since chronology studies determine the contaminent distributions by depth and whether buried sediment compounds are migrating or degenerating.
- Measurement of sedimentation rates.
- Determination of the sediment mixed layer or the layer actively affected by sedimentation at the time of sampling.
- History tracing in an area in terms of environmental changes. For many watersheds, historic contamination may not be captured by any sampling program since past sources may no longer exist, sources might have changed their discharge/operations, and control systems might have been installed in more recent years. Sediment core age-dating is one of the few techniques that may help reconstruct past contamination in conjunction with historical file review and for as long as the sediment was not significantly disturbed.

4.2.6.1.1 Method Principle and Steps

4.2.6.1.1.1 Method Principle. ^{210}Pb may be classified based on its two main sources:

1. *Autigenic* ^{210}Pb is a product of ^{238}U (uranium) disintegration; specifically, ^{238}U generates a series of radioactive isotopes (decay series), including ^{234}U, ^{230}Th, ^{222}Rn, ^{214}Po, ^{214}Pb, ^{214}Bi, ^{210}Pb, and other isotopes, ultimately ending with ^{206}Pb. In aquatic sediments, autigenic ^{210}Pb is in radioactive equilibrium with the mother isotope and preceding isotope series; thus, the activity of autigenic ^{210}Pb is constant in sediments (known as background value).

2. *Allochthonous* ^{210}Pb is a product of ^{222}Rn decay (being volatile, Rn-222 escapes from sediments into the atmosphere where it results in additional Pb-210 isotope that can be deposed back into sediments) happening outside the sediment environment (typically in the atmosphere). This type of radioactive Pb reaches the sediments through various deposition mechanisms, including fallout from the atmosphere. The activity of this type of radioactive Pb isotope decreases after its deposition in sediments following the radioactive decay law with a half-life of 22.26 years.

The presence of allochthonous lead in sediments with decreasing activities with depth (based on its disintegration until it reaches the background/equilibrium concentration) is used to determine the age of sediments by depth.

4.2.6.1.1.2 Method Steps. The main method steps are as follows:

1. **Collecting sediment core samples** using methods such as gravity or piston coring. The core should be long enough to capture the investigated contamination timeframe. Depending on the sedimentation rates, a typical core covering 100 past years may be 1–7 m long. Cores are often 4–10 cm in diameter. After collection, the cores are extruded and sectioned (typically at 1- to 2-cm intervals) and kept frozen (e.g., 2 cm for each sediment segment that may be 5–10 cm long). Note that grain size measurements may be done for each segment. In addition, samples from each sediment segment may be sent for chemical analysis of contaminants present.
2. **Radioisotopic analysis of each sediment segment.** Analysis of ^{210}Pb may be done by alpha spectroscopy or gamma spectroscopy. Alpha spectroscopy should be preferred for its sensitivity and high resolution. However, gamma spectroscopy provides direct measurements of autigenic Pb. Note that analysis is done on dry subsamples from each core segment after acid digestion followed by plating into silver disks when analysis using alpha counting is used. The results represent ^{210}Pb activity and are reported in disintegration units per minute per gram (dpm/g) (e.g., pCi/g).
3. **Data analysis and age-dating** include the following:
    - *Evaluation of autigenic lead.* The results should be plotted against sediment depth. A typical ^{210}Pb activity profile would decrease with depth until it reaches the so-called background value when it remains constant (at deeper depths). Such representation allows determination of the background level of activity (autigenic Pb), which is important for calculating accurate sedimentation rates. Another way of determining autigenic lead activity is through

gamma ray spectrometry measurement of ^{214}Pb and ^{214}Bi activities in tested sediments, which equal the activity of autigenic lead (since that Pb is in equilibrium with its predecessor isotope series).

- *Age-dating sediment segments* may be done by calculating the sedimentation rate. Different models (Robbins, 1978; Oldfield and Appleby, 1984) may be used to calculate the sedimentation rate and age of various sediment segments:
  - *CF:CS (constant flux:constant sedimentation)* is the simplest model for the constant flux of excess ^{210}Pb from the atmosphere and constant dry mass sedimentation rate. Plots of excess ^{210}Pb activity versus depth should be used. In practice, the logarithm of excess Pb is represented on y axis versus sediment depth on x axis. (Note that the excess Pb is calculated as total ^{210}Pb activity minus the background values of Pb). In fact, there is a linear dependency of radioactive activity and depth in many sediments[19]. The sedimentation rate may be derived from the slope of the line drawn to fit various individual measurements (knowing the radioactive decay coefficient of ^{210}Pb, which is 0.03114) (Jeter, 2000). When base 10 logarithms are used and the depths are expressed in centimeters, the sedimentation rate (in cm/year) would be

    $$\text{Sedimentation rate} = (-0.03114)/\text{Slope}.$$

    Including the slope in the formula, the rate of accumulation is calculated based on the following formula:

    $$C = C(0)e - km/r,$$

    where $C(0)$ is the excess lead-210, m is the cumulative dry mass, k is the decay constant for lead-210 (0.03114), while $-k/r$" is the slope.

    Once the sedimentation rate is known, calendar dates associated with various sediment segments can also be calculated. Specifically, for a given depth, the age would be calculated as follows:

    $$\text{Age} = \text{Year of sampling} - (\text{Sediment segment depth}/\text{Sedimentation rate}).$$

  - *CIC (constant initial concentration).* This model assumes that the sediments have a constant initial excess lead-210 concentration. The age is calculated by the following formula:

    $$T = 1/k \ln(C(0)/C).$$

    See the previous definitions for C, $C(0)$, and k.

  The following conditions need to be met: (1) all particles have the same initial ^{210}Pb activity, and (2) any increase in particle production will proportionally increase the amount of ^{210}Pb from the water column.

  - *CRS (constant rate of supply) of allochthonous ^{210}Pb.* This model assumes a constant ^{210}Pb flux but permits the sediment supply to vary. This may apply to most sedimentary systems in which the sediment supply may vary in response to climatic or anthropogenic changes. The model also requires density measurements; for more information, I recommend the work of Eakins (1983) and Liu et al. (1991).

4. **Facultative supplemental step consisting of determination of ^{137}Cs and/or ^{7}Be activities.** This facultative analysis step may be done for validating sedimentation rates and evaluation of the mixed layer. These analyses should be used in conjunction with ^{210}Pb data. Specifically, the analyses are done by gamma spectroscopy. The two facultative measurements have the following significance/use:
   - ^{7}Be radioisotopes have a short half-life of only 53 days and may be used to determine the depth of the sediment mixed layer; these isotopes are continually produced in the atmosphere by the interaction of cosmic radiation with gas molecules. Note that, in some cases, ^{7}Be may not be detected in surface sediments, which should not necessarily be interpreted by an anomalous result. Rather, the vertical mixing of surface sediments by biological organisms or physical-chemical processes could be the reason for diluting ^{7}Be to the point that it becomes undetectable by a currently available technique (e.g., gamma spectrometry).
   - ^{137}Cs has been deposited on Earth's surface as a fission product from nuclear testing between 1953 and 1964. By analyzing ^{137}Cs in segmented sediment core samples, its detection depth would correspond to the timeframe of its deposition. Note that ^{137}Cs has a half-life of 30 years. ^{137}Cs main peak in most sediments may be linked to a period of maximum aboveground nuclear testing and subsequent Cs fallout, which is generally considered in the early 1960s (e.g., 1963), in advance of the worldwide atmospheric test ban treaty of 1964. Note that other peaks of ^{137}Cs may exist in particular areas linked to nuclear accidents (e.g., the 1986 Chernobyl accident may have left a ^{137}Cs peak in Europe). The information may be used to validate/verify the various sediment segment ages as deduced from ^{210}Pb measurements (while a peak in the early 1960s should appear in any tested sediments covering that time frame, other peaks may also appear, depending on the location, and might be linked to particular events with known dates). This facultative step is especially recommended

in more complex cases for which constant sedimentation rates may not apply.

4.2.6.1.2 Applications, Limitations, and Recommendations

4.2.6.1.2.1 Applications. Specific application examples include the following:

- **Age-dating of sediment at Wyckoff/Eagle Harbor Superfund Site** (Brenner et al., 2002). The sediment was contaminated with creosote from a former wood treatment facility.
- **Sediment age-dating at Lake Hartwell, South Carolina** (Brenner et al., 2004). The study was conducted to evaluate long-term recovery as a result of natural capping of PCB-contaminated surface sediments.
- **Age-dating sediments at a human-made lake in Poland** (Sikorski and Bluszcz, 2003). The sediment cores covering the entire 60-year life span of the lake were analyzed using gamma ray spectrometry in addition to alpha spectrometry. This study accomplished the following: age-dating of sediments, determination of the sedimentation rates, and correlation of changes with modifications of the dam. Data analysis used a modified CRS model.
- **Identification of PAH sources in sediments** (EPA, 2008) at Eagle Harbor Superfund Site, Washington, where large quantities of creosote were used in a historical wood treatment facility. The established PAH sources included the following three primary sources: natural background, urban runoff, and creosote from the wood-processing facility.
- **Age-dating of sediments from three lakes in different regions of China** (Liang, 1998) has been performed using both ^{210}Pb and ^{137}Cs. ^{241}Am has also been measured for one of the lakes. ^{137}Cs profiles denoted two to four distinct peaks in sediments corresponding to the years 1954, 1963, 1974, and 1986. The authors concluded that ^{241}Am profiles may provide an additional age-dating tool to assist in interpretation of the ^{137}Cs record when it is difficult to decide the cause of a ^{137}Cs peak (e.g., Chernobyl explosion).

4.2.6.1.2.2 Limitations. The method relies on two main assumptions:

- The sedimentation rate is relatively constant. Although the method is more exact when sedimentation rate is constant or relatively constant, the results may represent average sedimentation rates over the studied time span.
- Grain-size distribution with depth is relatively uniform.

The limitations of this technique include the following:

- It may not be applied at dredged or otherwise disturbed sites.
- It assumes constant sedimentation rates over time.

4.2.6.1.2.3 Recommendations. It is recommended to apply the ^{210}Pb sediment age-dating technique in systems with little disturbance, such as marshlands, bays, lakes, and the backwaters of river systems. In the case of systems with intermittent sediment deposition patterns such as fast-flowing rivers, the addition of ^{137}Cs measurements could result in more reliable age-dating. Note that when isotopic data are scattered, this might be caused by intermittent sediment deposition, such as during storms, floods, or seasonal events. Such scattered data are often associated with layers of sand found between layers of silt (sand layers usually have low radioactive activities) (Jeter, 2000). If data are scattered, the implication is that greater uncertainty exists concerning calculated sedimentation rates. This might be an indication for performing the facultative ^{137}Cs testing.

Note that often the first few centimeters of sediments produce anomalous ^{210}Pb measurements that may be difficult to interpret. Such anomalous measurements (departing from logarithmic trends) may be caused by the mixing layer and variations in sediment densities for the surface layer. In such a situation, the depth of the mixing layer may be confirmed through the facultative ^{7}Be testing as discussed previously.

The age-dating method described here is usually applied for sedimentation rates greater than 0.1 cm/year.

Hints for Successful Use of Isotopes in Forensic Investigations

- **More is better in the case of isotopic testing. This is valid for both isotopic type and temporal isotopic data:**
    - Temporal additional data may help establish trends and evaluate the potential effect of natural attenuation processes (especially biodegradation) on isotopes.
    - Combined isotopic data for various contaminant composing elements are better than data from only one composing element. Whenever feasible (not prohibited by costs or analytical limitation), test for the isotopic composition of each composing element (having stable isotopes) of a studied compound (e.g., for chlorinated solvents, stable isotopic composition of ^{13}C, ^{37}Cl, and ^{2}H may be checked).
- When two or more composing elements of a certain pollutant are isotopically tested, it is suggested that **the results are plotted for a better comparison and source evaluation.**
- It is recommended to **interpret isotopic data after consulting site general conditions and factors affecting natural attenuation processes.** Factors such as pH, temperature, redox potential, aerobic versus anaerobic conditions, total organic carbon, and microbial activity may have a significant impact on isotopic data.
- While source materials are the best to be used in identifying specific isotopic fingerprints, **relative isotopic differences within**

certain areas usually provide the needed forensic evidence to help differentiate between one or more sources and release times. Such information may become quite powerful when combined with other lines of evidence (such as site historical data).

Notes

1. Typically, this method is referred to simply as *chemical fingerprinting*; this is how it also is mostly referred to in this book
2. Note that sometimes results for air sampling are provided by the labs in parts per million by volume (ppmv) units, which should be converted into milligrams per cubic meter (mg/m^3) using the following formula: ppmv = $mg/m^3 \times (0.08205 \times T)/M$, where T = ambient temperature in kelvin (= 273.15 + °C) and M = the molecular mass of the studied air contaminant; a correction for altitude may be needed for samples taken at higher altitudes.
3. Note that many of the presented techniques may also be applicable to petroleum distillates, as long as the hydrocarbons used (e.g., in diagnostic ratios or other types of evaluation) are present in the particular studied distillate. In addition, some specific fingerprinting techniques for petroleum distillates are discussed in a further section.
4. Note that the presence of 1,1,2,2-TeCA degradation products may not be needed for this age-dating method. Simply the presence of 1,1,2,2-TeCA along with TCE/PCE (within the contaminated plume) may be sufficient to suggest a pre-1978 release.
5. An asymmetric carbon atom is a carbon atom that is bound to four distinct elements or radicals/groups.
6. Please note that although great potential exists, not all the listed applications have been documented in the literature.
7. Usually, stable isotopes are used for source differentiation.
8. Note that prices may vary widely and likely will change in time.
9. Most of these application examples are based on stable isotopic data (bulk or CSIA type of analyses); more specific examples are provided when discussing each main type of isotopic fingerprinting technique in further sections.
10. Note that ^{36}Cl is a radioisotope that may be seen (for the purpose of this forensic evaluation) as a stable isotope since it has a very long half-life.
11. Note that ^{208}Pb is a radioisotope that may be seen (for the purpose of this forensic evaluation) as a stable isotope since it has a very long half-life.
12. Half-life is the time needed for the initial concentration of the radioactive compound to be reduced to half due to disintegration.
13. Note that both BSIA and CSIA can be performed through standardized and relatively inexpensive analytical methods. Usually, for forensic purposes, CSIA is preferred, especially when various co-contaminants in a plume may have suspected distinct sources (that have commingled).

14. Please note that the bullet point discussion related to data comparison and interpretation is intended to provide some general guidance only and is not intended to be used as a decision tree; it is the role and responsibility of each forensic scientist to evaluate data on a site-specific basis, and data interpretation is a complex process that cannot and should not be reduced to a decision tree-type of process.
15. Note that only TCE has H (hydrogen); thus, δ^2H may only be performed for TCE and not for PCE.
16. Please note that the bullet point discussion related to data comparison and interpretation is intended to provide some general guidance only and is not intended to be used as decision tree; it is the role and responsibility of each forensic scientist to evaluate data on a site-specific basis, and data interpretation is a complex process that cannot and should not be reduced to a decision tree-type of process.
17. Note: Parent products always refer to the original manufactured product (if PCE were spilled, then it is considered the parent for TCE, DCEs, and VC).
18. Atmospheric tracers are discussed in more detail in a separate chapter because the method may also use nonradioisotopic compounds (gases) with well-established atmospheric concentration trends over several past decades.
19. Note that, in some cases, two or more logarithmic lines might be described by the results indicating different sedimentation rates. Such cases might be confirmed by historical information suggesting some changes in watershed inputs, for example.

5

Fingerprinting Techniques Targeting the Contaminants within the Environmental Matrix

5.1 Basic Principles

The testing techniques presented in Chapter 4 were based on analysis (chemical or isotopic) of the target contaminant or of a compound linked to the targeted contaminant (e.g., signature chemical or degradation product). In this chapter, testing techniques that are more complex are reviewed. These techniques investigate the target contaminant or associated compounds within the environmental media/matrix where these contaminants occur (at the time of sampling). Thus, two sets of analyses are performed:

1. **Analysis of targeted contaminants and associated compounds** using one of the techniques described in Chapter 4.

II. **Analysis of environmental media where the targeted contaminant and associated compound is found** using lithological characterization or microscopic techniques (for mineralogical characterization) as described in this chapter.

The power of this type of technique consists of linking contaminants to a specific environment with established characteristics. Such association provides more details, resulting in higher source specificity and differentiating power. Using the previous analogy (see discussion of chemical vs. isotopic fingerprinting in Section 4.2) of a brick wall as our sample with individual bricks as individual contaminants within the sample, the following comparisons may apply:

- The contaminant testing techniques described in Chapter 4 provide information on characteristics of component individual bricks (e.g., shape, size, color).

- The techniques described in this chapter provide information on component individual bricks along with the binding patterns of the bricks within the actual wall. It is obvious that this information is more comprehensive, allowing an in-depth source characterization and high defensibility of results.

5.2 Geochemical Fingerprinting

Geochemical[1] fingerprinting can be applied in soil or sediment investigations. The method involves the analysis of contaminants in a sample along with the lithological/hydrogeological characteristics of the contaminant matrix (e.g., soil or sediment) and the interpretation of contaminant data within the specific matrix characteristics. Since soils and sediments are stratified systems, they have a composition layered by depth with distinct lithological/hydrogeological characteristics in each layer.

The lithological[2] soil characterization is usually performed when soil borings are drilled for the collection of soil or water samples. This is typical in environmental projects. However, although the lithological characterization of soil/sediments is available in many cases, contaminant data analysis and interpretations do not necessarily involve the evaluation of contaminant testing data in association with the lithologic context. By not doing this, important forensic information is lost or disregarded. Such information may be critical not only in forensic studies, but also in risk assessment and site remediation.

5.2.1 Method Principle and Steps

5.2.1.1 Method Principle

When contaminant data in soils or sediments are associated with the lithology/hydrogeology of the soil or sediment sample matrices, more in-depth fate and transport evaluations are possible, allowing better data interpretation. Basically, the physical composition of the soil/sediment sample matrix dictates how various contaminants may behave when in contact with that soil/sediment. In addition, the water retention capacity may be evaluated based on sample matrix physical characterization. For example, it is well known that sand particles retain contaminants and water less than silt and clay particles; thus, a sandy soil will have less ability to retain contaminants and water compared with other types of soils.

When contamination could enter subsurface environments via various sources, including surface and subsurface sources as well as transport via contaminated groundwater, the contaminant data (e.g., chemical concentration) patterns interpreted along with the lithological characteristics of the sample matrix across core samples may indicate the likelihood of surface versus subsurface sources. The additional information related to lithological layers would ensure correct interpretations of contaminant data patterns. When looking at vertical and horizontal contamination profiles overlapped on corresponding lithologies, surface sources will be expected to show decreasing contamination versus depth. However, this may not always be true depending on the lithological characteristics of various layers. If a clay layer resides below a sandy layer, the typical decreasing contaminant pattern by depth may not be present or obvious even when contamination sources are exclusively at the surface. On the other hand, if below a confirmed surface source a sandy layer is located below a clay or silt layer, and, instead of decreasing, contamination is increasing in the deeper sandy layer, lateral transport of contaminants along the sandy layer may be suspected, resulting in commingled contamination at that level. Obviously, without evaluation of contaminant data (e.g., concentration) within the lithological/geologic context, such interpretations would not necessarily be reached.

The examples provided in the section on applications demonstrate how the method was applied in a real case study.

5.2.1.2 Method Steps

The main method steps include the following:

1. **Collection of core samples** of soil or sediments within the studied area so that both vertical and horizontal contamination profiles may be evaluated.
2. **Analysis of subsamples from regular depth intervals along the cores for contaminant characterization.** In general, chemical analysis of contaminants and associated compounds is performed. In addition to chemical testing, isotopic data (e.g., stable isotopic composition) may also be performed in each or selected samples.
3. **Analysis of subsamples from regular depth intervals along the cores for physical characteristics** (e.g., grain size analysis), based on which the lithological characteristics may be deduced. An alternative to this step would be to use existing lithological information usually recorded when boring operations take place.
4. **Data evaluation and interpretation.** A typical way to evaluate data is to display the contaminant data (e.g., concentrations) overlaying the lithological data (e.g., soil strata/layers) within a vertical section of the studied area (see example in Figure 5.1). The use of color codes for various concentration ranges and for distinct lithologic layers would make data evaluation easier and more effective. Several vertical sections may be studied to cover all the studied area. The vertical sections should be selected in such way that they cover areas of

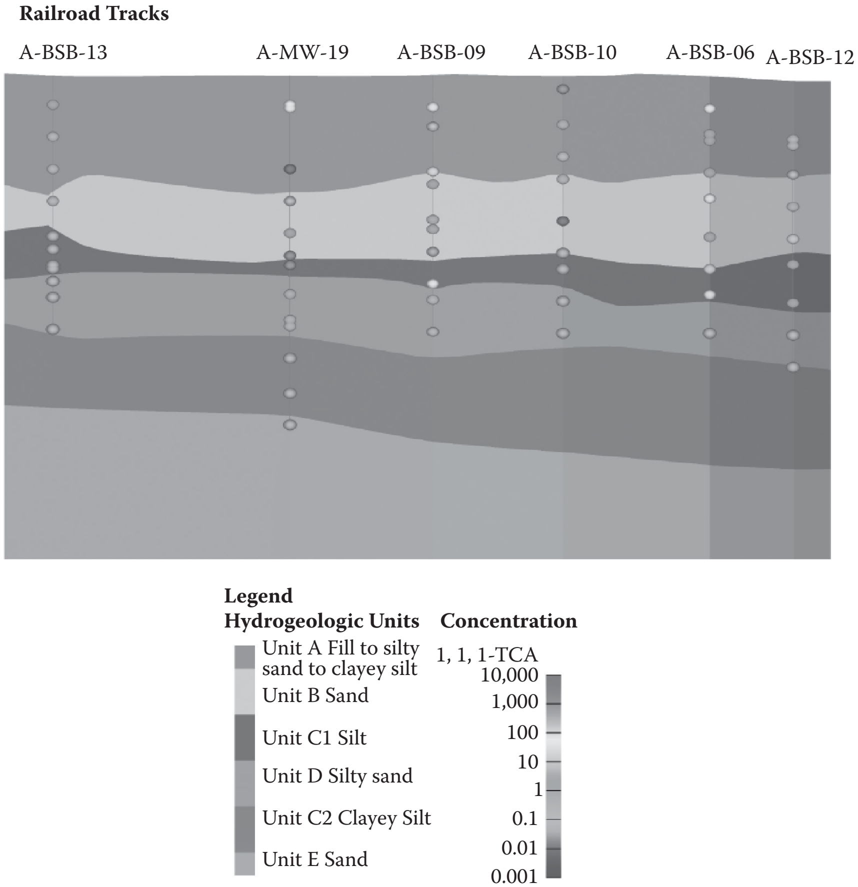

FIGURE 5.1
(See also color insert.) Geochemical fingerprints within a vertical section depicting the area of recorded historical releases at a site in Southern California (southwestern-northeastern section is depicted here from left to right).

suspected releases (e.g., surface or subsurface storage tanks, waste disposal area, areas recorded to have had leaks). A practical application example is provided as Example 5.1.

5. **Supplemental data evaluation.** A supplemental data evaluation may be performed, including comparison of horizontal contamination patterns within various subsurface layers. In this case, horizontal sections at various representative depths should be compared. An alternative evaluation may be performed by comparing horizontal contamination patterns within the same or different depth ranges in distinct sampling media (e.g., soil and soil gas); Example 5.2 demonstrates such an alternative application.

5.2.2 Applications, Limitations, and Recommendations

5.2.2.1 Applications

Two practical applications are presented for a case study in Southern California. The case study is discussed in more detail in Chapter 9. The case involved two neighboring chemical storage and repackaging facilities with recorded historical releases. Geochemical fingerprinting was part of one independent line of evidence developed in this case. The examples provided here relate to using geochemical fingerprinting to evaluate historical sources of contamination at one of the facilities.

EXAMPLE 5.1

Use of Concentration Patterns by Depth and Corresponding Lithological Layers to Evaluate Sources and Commingled Contamination

Figure 5.1 presents the concentration patterns of 1,1,1-TCA (1,1,1-trichloroethane) in soil at a chemical bulk storage and repackaging facility in Southern California (see also overall case discussion in Chapter 9, Case Study 9.1). The displayed area was chosen due to the presence of a historical recorded source of chlorinated solvents, specifically several permanently stationed railroad tanks that stored bulk contaminants (including chlorinated solvents).

Chemical data were interpreted within the lithologic context by overlaying the concentration from various depths on the encountered hydrogeologic layers. As seen from Figure 5.1, a general decreasing 1,1,1-TCA concentration trend with depth is observable in all the displayed soil borings. This is consistent with the main contamination source being at or close to the surface in the displayed studied area, confirming historical evidence related to recorded releases from the railroad tank cars.

An analysis of data displayed in Figure 5.1 also enables interferring that, in a few locations (e.g., A-BSB-06 and A-BSB-12), a subsurface source may have added contamination. Specifically:

- At location A-BSB-06, evidence for commingled contamination from a surface source and from transport along the sand layer (Unit B) is evident since an increase of 1,1,1-TCA concentration is observable within the sand layer, while the precedent concentration recorded at the border of the silty top layer (Unit A) with the sand layer (Unit B) was an order of magnitude lower. Note that silt would be expected to retain more of the original contamination than sand, which would be even more so since the sand layer is below the silty one. Thus, if the contamination would have come exclusively from the surface, the recorded increase in concentration within the sand layer (Unit B) would not be expected. Such concentration increase may be questioned as “abnormal” since it is based on only one data point;

however, when considering the neighboring boring, it becomes more evident that a subsurface source had likely contributed to contamination in that particular zone (see next comment).
- At location A-BSB-12, additional evidence for subsurface contamination consists of the recorded concentration increase within the sand layer (Unit B); this observation strengthens the hypothesis that commingled contamination (from surface and subsurface source, probably transported with shallow groundwater along the sand layer) likely exists in this particular area.

Note that other increases in 1,1,1-TCA concentration observed at deeper depths in other sample locations do not necessarily suggest (by themselves) the presence of commingled contamination. This is because such recorded increases in concentrations happened at the border between a higher permeability layer (Unit B) with a lower permeability unit at the bottom (Unit C1), where some accumulation of original contamination percolating from the surface may be expected. Examples of such increases are in the location A-MW19 and A-BSB-09—at the border between Units B and C1. The final interpretation related to the potential presence of commingled contamination in these locations would depend on hydrogeological information (e.g., historical shallow water flow) and additional neighboring sample location profiles. Such an analysis (not shown here) has been performed, resulting in the conclusion that commingled contamination was likely present in that area.

In this particular example, geochemical fingerprinting allowed establishing the following:

- Historical surface sources of 1,1,1-TCA were confirmed to have had an impact on shallow subsurface areas (generally extending from the surface to Unit D) in the studied zone (railroad track area).
- The impact of surface contamination sources was limited to the shallow subsurface with no contamination reaching the second sand layer (Unit E). This was an important finding since it helped establish the relative limited impact of contamination from surface sources and the lack of impact to the deeper regional groundwater.
- Evidence of commingled contamination was observed in a few locations involving surface and subsurface shallow sources (likely transported along the shallow sand layer).

In brief, the results denoted that not all the subsurface contamination within the depicted area was attributable to historically recorded surface sources.

EXAMPLE 5.2

Use of Concentration Patterns in Different Media and at Distinct Depths to Evaluate Sources and Commingled Contamination

Figure 5.2 presents a supplemental way to evaluate chemical fingerprinting data within the geological context for the same contaminant

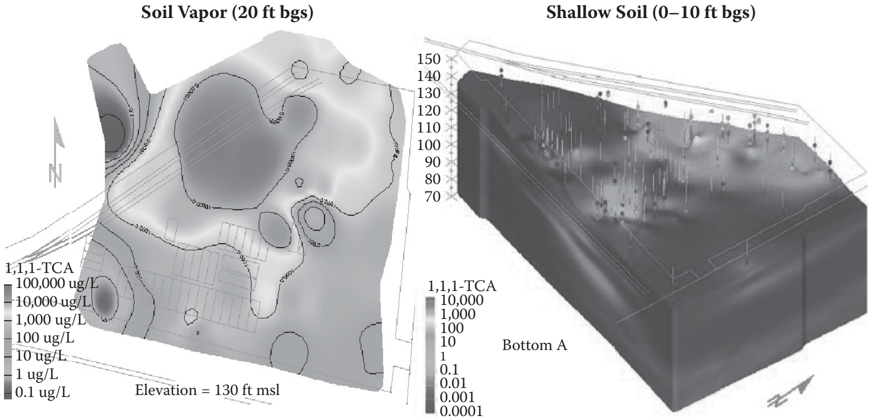

FIGURE 5.2
(See also color insert.) 1,1,1-TCA chemical fingerprints in shallow subsurface at a site in Southern California. Note that north for the left image is toward the top, while for the right image, it is toward the top left corner, so although the same site is depicted in both figures, the orientation is different.

1,1,1-TCA at the same site as in the previous example (chemical storage and repackaging facility in Southern California). Specifically, by comparing contaminant concentration distribution in different media and depths, forensically relevant conclusions may be deduced. Note that the example provided in Figure 5.2 includes images that cover the whole studied site (as compared with Figure 5.1, which depicts a subsurface section from one particular site area, namely the railroad tracks[3]).

The left image of Figure 5.2 depicts a horizontal slice of the whole site at 20 ft bgs (below ground surface), showing the horizontal concentration pattern of 1,1,1-TCA at this depth based on its detection in soil vapor. The right image of Figure 5.2 depicts a horizontal slice of the whole site between the surface and 10 ft bgs, showing the horizontal and vertical concentration patterns of 1,1,1-TCA between 0 and 10 ft bgs based on its detection in soil. Obviously, since the right image depicts a depth interval, the image is in three dimensions (3D) as compared to the left image (in two dimensions, 2D). The concentration color code is similar in both images, with red the highest and blue the lowest (nondetects) recorded concentrations.

In this case, it becomes apparent that overall there is a weak fit between concentration patterns in soil gas (at 20 ft below ground) and in shallow soil (between 0 and 10 ft bgs). In addition, it is evident that shallow soil contamination is of a lower magnitude than deeper soil gas contamination. This indicates that the additional contamination detected in soil gas (as compared to soil) must be due to volatilization from the shallow groundwater from below 20 ft bgs. Indeed, the shallow groundwater recorded regularly at this site was generally between 25 and 30 ft bgs. That water was contaminated, including with 1,1,1-TCA. Overall, such observations suggest the existence of commingled contamination at this site, possibly from both on-site and potentially off-site sources intruding with groundwater. The data displayed in Figure 5.2 also indicate old and depleted on-site surface releases. Note that the interpretation of chemical data displayed in Figure 5.2 confirms the main conclusion reached through the interpretation of the chemical and lithological data from Figure 5.1 related to the likelihood of commingled subsurface contamination at this site.

5.2.2.2 Limitations

This method has few limitations as both chemical and lithological data are largely available at most contaminated sites. The analysis techniques are well established and inexpensive, allowing collection of any additional data as needed. In fact, the only limitation relates to the understanding of the "big picture." In other words, the history of the site as recorded in the historical file should be well understood and considered when interpreting geochemical data/fingerprints. Geochemical fingerprinting should not be used by itself but rather to corroborate a source hypothesis that resulted from the evaluation of the historical file and from other lines of evidence. This type of limitation applies to most fingerprinting techniques. A thorough understanding of site historical context and conditions is the guarantee of successful applications of fingerprinting.

5.2.2.3 Recommendations

In conclusion, the evaluation of chemical patterns within the specific geologic/lithologic context is highly recommended at complex sites with multiple recorded releases and surrounded by neighboring sites with recorded or potential releases. Such evaluation should be performed by plotting data (chemical and lithological) on maps to create 2D and 3D images for the studied areas. Many possibilities for data evaluation exist, two of which were illustrated in the previous two examples.

Hints for Successful Use of Geochemical Fingerprints in Forensic Investigations

- **Always interpret the results within the historical and geographical context** of the investigated site.
- **More is better.** Use all the available data for the investigated area in time and space for more reliable interpretation of geochemical fingerprints; if only limited data are available, collect more data so that they will be representative for the study area.
- **Take advantage of monitoring data.** Both chemical and geologic/lithological data are monitored at many sites. Therefore, the existing monitoring data should be acquired, reducing or eliminating the need for new data collection.

5.3 Mineralogical Fingerprinting

Mineralogical fingerprinting consists of the identification of the size, shape, and chemical composition of particles associated with a contaminant of concern (COC) (usually metal) in a solid environmental sample (soil/sediment or dust). These identifications may provide an accurate indication of the type of source and allow a semiquantitative estimation of contributions.

The method involves two types of testing:

1. A **microscopic evaluation of sample matrix** is performed to evaluate the mineralogical composition along with the size and shape of composing particles (preferably the focus should be on particles associated with the targeted contaminant). Various techniques may be used for microscopic evaluation, including polarized light microscopy (PLM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD).
2. **Determination of the chemical elemental composition** of sample particles associated with the targeted contaminant. Typically, this determination is performed using energy dispersive spectroscopy (EDS). Other techniques, such as inductively coupled plasma mass spectrometry (ICP-MS), may also be used. Note that because the particles for which chemical elemental composition is determined are also characterized for shape, size, and mineralogical composition by the microscopic evaluation, a comprehensive characterization of particles associated with targeted contaminants is achieved.

General information on microscopic techniques that may be used is provided next:

- *PLM* typically involves illumination of samples with polarized light. The technique distinguishes various minerals based on their different refractive indices. PLM is used (in combination with stereobinocular microscopy) to estimate the volume percentage of constituents.
  - Constituents that are readily identified through this technique include kaolinite, montmorillonite, fiberglass, quartz, iron chromite, chrysotile, fly ash, starch, perlite, pumice, hair, titanium dioxide, cotton/paper cellulose fibers, vermiculite, mica, soil minerals, Portland cement, calcium carbonate, calcium and magnesium silicates, gypsum, and sodium silicates.
  - For more details, the book chapter by Millette and Brown (2007) is recommended.
- *TEM* involves the transmission of a beam of electrons through an ultrathin specimen/sample. An image is formed from the interaction of transmitted electrons through the specimen. TEM

provides imaging at significantly higher resolution than light microscopy; thus, the technique is able to examine fine details within a sample matrix.

  - TEM coupled with an energy dispersive X-ray spectrometer is useful for characterizing and identifying very fine particles, including mineral fibers (e.g., asbestos), clays, and pigments.

- *SEM* is one of the most powerful microscopic techniques with many published forensic applications (Kennedy et al., 2002; Kennedy et al., 1996). This technique images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. Based on electron interaction with the sample (atoms at the surface of the sample), signals are produced that provide information about the sample topography, composition, and other properties. These produced signals could be of several types, including the following:
  - Secondary electrons, which are electrons generated as ionization products (by primary radiation or electrons) producing a very-high-resolution image of a sample surface (details < 1 nm) with 3D appearance.
  - Backscattered electrons (BSEs) are reflected from the sample by elastic scattering; the intensity of the BSE signal is related to the atomic number Z of the targeted contaminant in a sample and provides information about the distribution of different elements in the sample, helping locate the targeted element/contaminant.
  - Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, which causes the higher-energy electron to fill the shell and release energy; the characteristic X-ray may be used to identify the composition and measure the abundance of elements in a sample.

  With SEM, a wide range of magnifications is possible, from 10 to 500,000 times.

  The advantages of the SEM technique over other microscopic techniques include better resolution and added three-dimensionality.

In the following sections, the combined use of SEM with EDS techniques is detailed for obtaining forensically relevant mineralogical fingerprints. This method is described in the articles by Kennedy et al. (1996, 2002).

5.3.1 Method Principle and Steps

5.3.1.1 Method Principle

The detailed (microscopic and chemical) characterization of sample particles associated with a targeted contaminant provides highly specific forensic information on contaminant sources. This information may be preserved in solid matrixes (e.g., soils, sediments) for years to decades, depending on the stability of the original source compound and on environmental factors. Even after a contaminant's original composition starts changing in soil, the change may not affect all the released contaminant at once, thus leaving some traces for potential tracking by mineralogical fingerprint testing. Mineralogical fingerprinting is one of the most specific fingerprinting techniques available to date for metals and other inorganic contaminants for which comprehensive or other types of chemical fingerprinting are limited.

5.3.1.2 Method Steps

The main method steps include the following:

1. **Selection of representative samples** (e.g., of soil/sediments or dust). Usually, mineralogical fingerprinting is not performed on a large number of samples; rather, several representative samples are selected. This is because the method is time consuming and expensive, and the highly specific information provided is highly defensible as long as representative samples are tested.
2. **Microscopic analysis** of selected samples using one or more microscopic techniques is performed to target areas of the samples where the targeted contaminant (e.g., metal) is observed. Typically, SEM is the preferred technique; however, other microscopic techniques may be performed, providing additional useful information as needed. After sample preparation (by drying and sieving) and placement into epoxy resin and 1-inch^2 polished mount, the following analyses are performed:
   - Optical analysis for acquiring digital images of samples.
   - Computer-controlled SEM (CCSEM) and manual review are then performed to take advantage of the relative brightness of compositional phases in the backscattered electron image. This allows particles bearing metals with certain atomic number (the higher the number, the brighter the particle) to be distinguished easily. CCSEM may be performed at two magnifications.
3. **Chemical elemental analysis** is then performed on randomly selected particles from those associated with the targeted contaminant; this analysis documents the elemental composition of each elemental particle randomly selected[4] for analysis. Typically, the analysis is automated; however, the option to reanalyze manually selected particles may be performed to confirm the automated results. Resulting images are stored and documented (see Figures 5.3–5.7).

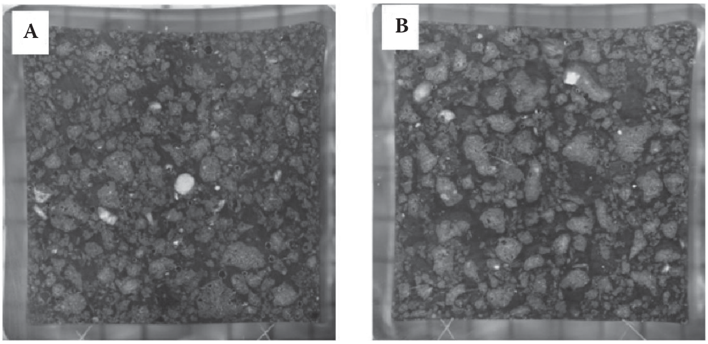

FIGURE 5.3
Example of optical photographs for two prepared samples for the SEM-EDS analysis (namely, epoxy polished 1-inch-square mounts). (Analysis performed by RJ Lee Laboratory.)

4. **Data evaluation and interpretation.** Results may be:
   - Compared with those from samples from potential sources or characteristics of potential sources.
   - Compared with associations characteristic for sources, with some such associations well established and published, while others may be identified on a case-specific basis (see examples under "Hints for Successful Forensic Use of Mineralogical Fingerprinting" at the end of this section).
   - Used for semiquantitative evaluations to allocate contributions between multiple sources based on a count of particles found to be associated with various sources (since in many cases it is not practically feasible to check all the particles associated with a targeted contaminant, the evaluation of randomly selected particles may provide a defensible semiquantitative evaluation).

EXAMPLE 5.3
Method Application for Evaluating Lead Sources in Contaminated Soils

This example is provided to illustrate the use of mineralogical fingerprinting step by step along with representative images captured by this technique. If our focus is to evaluate sources of Pb from contaminated soil, the following steps may be used when performing mineralogical fingerprinting through SEM-EDS analysis:

- Samples of bulk materials are first dried in an oven overnight. Then, representative subsamples may be taken and sieved (e.g., 2-mm screen), separating the fine from the coarse fractions. The coarse material may be archived, while the fines are analyzed by SEM techniques to document their characteristics, with special attention to lead phases present.

- Representative portions of fine fractions are placed into epoxy resin and 1-inch^2 polished mounts are prepared and polished. The prepared polished mounts are documented using a digital optical microscope with a camera (see examples in Figure 5.3). This procedure allows the internal features of particles to be characterized. After the optical photographic documentation, the samples are given a thin coating of carbon to prevent charging when under the electron beam of the SEM.
- The samples are first subjected to automated SEM analysis (also known as CCSEM). In the CCSEM analysis, the sample is imaged in the BE imaging mode, in which the brightness of a particle is proportional to its average atomic number. In this mode, the heavy metal phases are considerably brighter than, and can be distinguished from, the major components of soil that are not of interest. During this analysis, the particles are distinguished from the epoxy matrix and sized. A brightness threshold is employed to disregard the majority of the soil particles that are composed of lighter elements than the targeted element (Pb), such as quartz, aluminosilicates (e.g., feldspars and clays), and carbonates. The analysis will detect particles as bright as or brighter than iron-rich particles. This will allow lead to be detected in the less-bright iron hydroxides, where it may occur in low concentration. Also, the very bright lead-rich phases are easily detected. Figure 5.4 provides an example of a sample "field" with identified targeted features (to be analyzed) indicated by the displayed boxes. Note that in this example the recorded bright particles within the soil sample matrix were complex, consisting of multiple phases, with some above the detect threshold (e.g., iron oxide) and some below it (e.g., quartz).

The CCSEM analysis is typically performed at two magnifications. The first magnification may be ×80 (as in Figure 5.4), and particles larger than 10 μm are characterized. Fields are analyzed until the entire surface is inspected or 3 h have elapsed, whichever comes first. The second magnification[5] that may be used is ×1,600, and particles less than 10 μm but larger than 0.5 μm are characterized. The fields are selected randomly, and the analysis continues for up to 3 h. During the SEM analysis, the targeted particles (e.g., associated with Pb in our example) are distinguished from the epoxy matrix, sized, and photographed.

- EDS analysis follows as part of the automated SEM testing. During this analysis, targeted particle elemental composition is determined using EDS. When a bright (high-Z) particle is detected, its size is determined, and an energy dispersive spectrum is collected to identify the individual elements. For each particle, the physical dimensions and elemental compositions are saved in a file along with location coordinates (see example in Figure 5.5). A small image (i.e., microimage) of the lead-bearing particles and the entire EDS spectrum are also saved, as in the example in Figure 5.5. The obtained spectrum has various

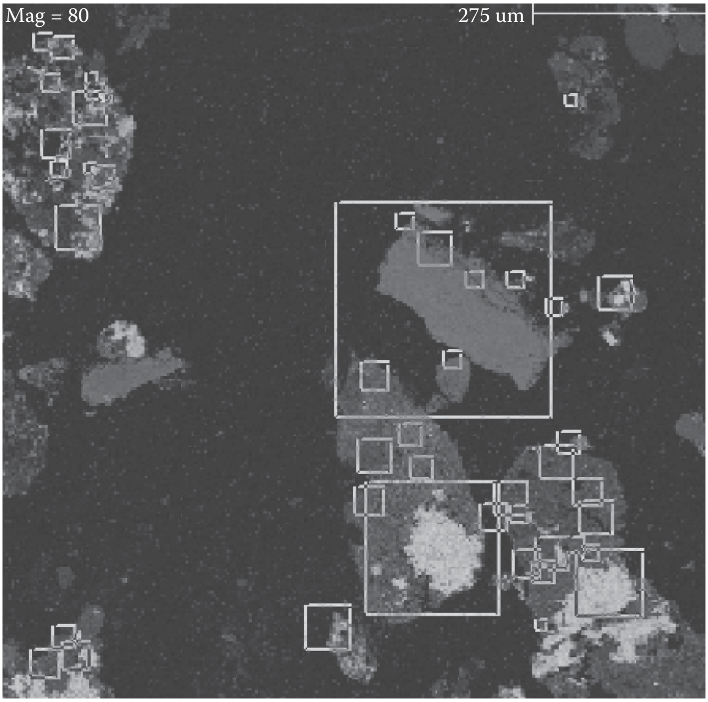

FIGURE 5.4
Example of backscatter electron (BE) of a low-magnification field. The squares indicate potential features of interest identified by the CCSEM analysis. (Analysis performed by RJ Lee Laboratory.)

peaks, each identified by an element. Note that the height of peaks is generally proportional to the amount of that element in the analyzed particle.

- Randomly selected particles identified by the CCSEM analysis as potentially lead containing are relocated and may be analyzed in the manual SEM mode for confirmation of the automatically recorded size, morphology, and chemical elemental composition. Figure 5.5 illustrates the results of a manual relocation and analysis.

The upper left of the image consists of a low-magnification BE image showing the particle of interest in context. Scale information is displayed above the image. The square is a "zoom box" indicating the location of the image shown in the upper right. The scale information is displayed in this case below the image. The small box in the upper right image indicates the position where the EDS spectrum (shown at the bottom of the image) was acquired. The small image at the right side of the spectrum is the microimage acquired during the CCSEM analysis. Note that Figure 5.5 shows several common soil minerals as well as the

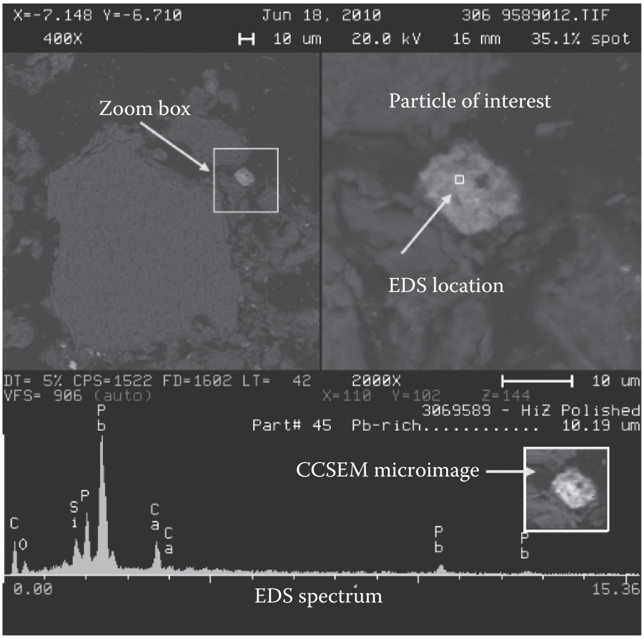

FIGURE 5.5
Example of a composite SEM-EDS image documenting the mineralogical fingerprint of one of the tested particles associated with the targeted element Pb in soil. (Analysis performed by RJ Lee Laboratory.)

bright Pb particle that was analyzed (both microscopically and for its elemental composition).

Another example of a composite SEM-EDS image (from another soil sample) acquired after manual relocation and analysis is given in Figure 5.6. Manual review in this case demonstrates that the particle was compositionally complex with both lead-rich and nearly lead-free areas.

5.3.2 Applications, Limitations, and Recommendations

5.3.2.1 General Applications

Mineralogical fingerprinting is a highly specific forensic technique for solid matrixes. The following are the main forensic applications of this powerful technique:

- **Determination of the contamination sources** may be done by comparing the results with those of suspected sources; also, the size, shape, and chemical composition of particles associated with the COC could be linked to certain sources (such as paint, fly ash, pesticides, foundry, natural minerals, etc.; see examples from Figure 5.7 and related discussions, as well as the hints at the end of this section). In some cases,

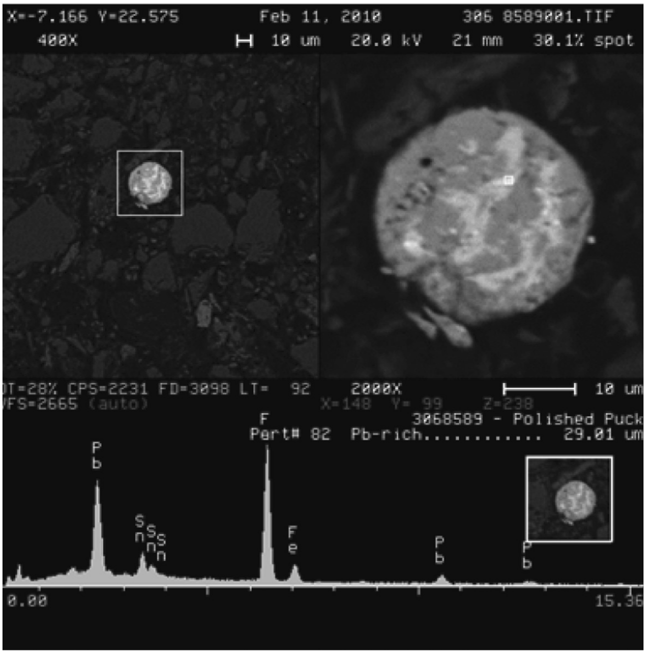

FIGURE 5.6
A second example of a composite SEM-EDS image providing the mineralogical fingerprint of another tested particle associated with Pb in soil. (Analysis performed by RJ Lee Laboratory.)

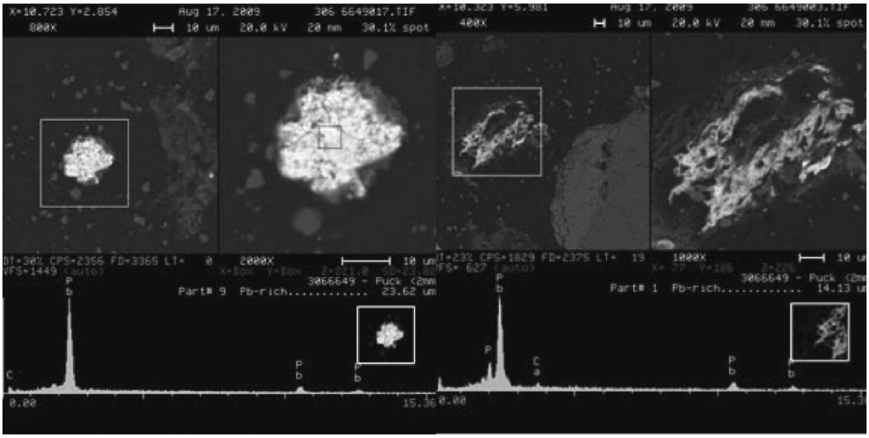

FIGURE 5.7
Examples of composite SEM-EDS images providing mineralogical fingerprints of two particles associated with Pb within the same soil sample. (Analysis performed by RJ Lee Laboratory.)

when secondary phases of metals are discerned (such phases are nonrepresentative for original releases anymore), the method may still be useful for eliminating certain sources, namely, recent sources.

- **Evaluation of background values of metals in soil** may be done by determining the amount of metals associated with natural mineral occurrences as well as with soil characteristic phases. Evaluating site-specific background values could be critical at sites with naturally elevated metals (e.g., mining areas) to establish site-specific cleanup values (which cannot exceed natural background values). In mining and other areas with high metal backgrounds, this could bring substantial cost savings related to site remediation and can help close sites sooner. A real case study example including such an application is given in Section III of this book (Cases 7.1 and 7.2).
- **Source allocation** on a semiquantitative basis could be achieved to help with **cost allocation** at sites with multiple sources/responsible parties.

Two examples follow that provide a demonstration of various general applications of mineralogical fingerprinting and how to evaluate/interpret SEM-EDS results.

Figure 5.7 provides examples of mineralogical fingerprints for two particles associated with Pb from the same soil sample. As seen for the two examples in Figure 5.7, the shape, size, and chemical elemental composition of various particles associated with a targeted element (e.g., Pb in these examples) may vary within the same sample. However, in general, particles may be grouped based on similarity and potential source characteristics.

In the examples from Figure 5.7, the following main associations may be made for each analyzed particle:

- The particle displayed in the left image was almost purely composed of Pb and had a somewhat round shape. This particle may be associated with high-temperature processing since high temperature generates round-shape particles. However, the lack of any other metal except Pb could suggest an undetermined source (e.g., potentially exclusive Pb source or an older release from a predominantly Pb source, such as foundry emissions, in which case other potentially associated metals have separated from the Pb phase). When interpreted within a historical context, the more likely source type may be deduced from a specific mineralogical fingerprint.
- The particle displayed in the right image contained Pb, P, and Ca occurrences. Such associations are typical for stable Pb phases in soils (e.g., associated with phosphates and carbonates), suggesting that Pb associated with this particle may be representative for background soil Pb or could be the result of a very old release (in which

case, it is assumed that enough time passed to allow the dissociation of any released Pb phase and the incorporation of Pb into stable soil compounds such as phosphates and carbonates of Pb, which are naturally present in soils). These deductions based on the chemical elemental composition of the analyzed particle are supported by the lack of shape of the particle itself, which is characteristics for native soil particles (as seen in the right image of Figure 5.7, the analyzed particle was amorphous in shape). Therefore, this mineralogical fingerprint was able to eliminate (with a high level of defensibility) anthropogenic sources of Pb except potentially old ones. Again, this information could provide more exact interpretations within the historical context of the studied site.

Once the main general associations/potential sources are established in each sample, a semiquantitative evaluation of the contribution of various groups/potential sources to the overall Pb fingerprint within the analyzed sample may also be deduced based on the SEM-EDS analysis. The accuracy of such semiquantitative analysis would obviously depend on the Pb concentration in the sample, dictating the representativeness of the Pb particles that end up being analyzed by SEM-EDS. As described previously, generally up to 50–60 individual Pb particles are randomly selected and analyzed for a sample. These analyzed particles may represent 100% or close to 100% of Pb particles in samples with low-to-moderate Pb levels, but only 50% or less of Pb particles in higher contaminated samples. The semiquantitative source apportionment based on established mineralogical fingerprints would thus be more accurate in the first case (samples with low-to-moderate Pb levels).

5.3.2.2 Specific Applications

Mineralogical fingerprinting through SEM-EDS analysis that provides particle-by-particle signatures can be used to assess potential sources, bioavailability, or remediation potential for metals in solid matrices. A common application of the SEM-EDS technique is to determine the relative abundance of metals (e.g., Pb, As, Hg, Cd) and their association with certain particles in the sample. Based on this association, the technique distinguishes different sources and could be extremely useful in historical mining areas with various other metal sources as potential contributors.

Mineralogical fingerprinting can be conducted on solid samples, as reported in the literature:

- In the case of dust, Bern et al. (2009) proved the method's potential to analyze urban dust for the possible presence of World Trade Center constituents.
- Also related to dust investigations, Milette and Brown (2007) used SEM-EDS to evaluate the source of Pb in residential dust as coming

from lead-containing fly ash; in other cases involving concern over Pb particulates, the same authors found that leaded particles were coming from lead paint (Pb-Cr, Pb-Zn associations noted); auto exhaust (Pb-Br associations); industrial Pb (Pb associated with other metals); and soil Pb (Pb-Si, Al, or Ca associations). In addition, some undetermined Pb source (Pb-only occurrences) was also revealed.

- For soil samples, Kennedy et al. (2002) used the SEM-EDS technique for source identification of metals in residential soils. Specifically, two case studies were presented:
    1. One case targeted elevated levels of As in soil, which were attributed to a manufactured product rather than a fugitive source. Most of the particles associated with As in the investigated soil were found to contain arsenic oxide, with occasional traces of Cd, while some of the As particles were found to have been associated with Pb. In addition, most of the As occurrences were in a narrow size range. A manufactured product used for crabgrass control based on arsenic trioxide and lead arsenate was identified as the likely source.
    2. The other case was conducted to identify sources of Pb in soil in the vicinity of an industrial operation involving lead sulfate. SEM-EDS analysis pointed out the occurrence of ash and partially burned coal, suggesting an alternate potential source of Pb other than the industrial site. This alternative source was confirmed by the presence of Mn and Ba associated with Pb particles, which also are associated with coal. Moreover, the spherical shape of some analyzed Pb particles confirmed coal ash as the likely Pb source in the analyzed soil.
- Also related to soil investigations, Kennedy et al. (1996) denoted how the SEM-EDS technique may lead to source apportionment, as in the following cases:
    - Quantification of Cd associated with sphalerite (zinc sulfide) in soils at levels down to a few parts per million;
    - Designation of phases of Pb in soil, including phase sizes.
- An investigation of soils contaminated with Pb, As, and other heavy metals at and surrounding a historical foundry close to the city of Lyon, France (see Case Studies 7.1–7.2 described in Section III of this book), denoted the successful use of the SEM-EDS technique to
    - Define background levels of Pb, As, and other metals in on-site soils to be remediated;
    - Investigate potential foundry contributions to heavy metals in surrounding areas (soil and vegetation).

5.3.2.3 Limitations

Although mineralogical fingerprinting is a highly specific technique with high forensic differentiating power, some limitations exist, including the following:

- The main limitation relates to timing of a release. The longer the timing (age) of a release, the higher the chance that original associations of the targeted element are lost and new associations have been formed in soil. Such new associations are usually referred to as *secondary phases*, which are stable in soil (e.g., common secondary phases for Pb are carbonates and phosphates). When such secondary phases are observed, the original signature is lost, and it is not possible to exactly determine sources or type of potential sources.
- Another limitation relates to the heterogeneity of soil and representativeness of selecting a very small part of a sample and randomly selected particles within the subsample that are associated with a targeted element for SEM-EDS analysis. However, despite such a limitation, SEM-EDS has produced more accurate source evaluations and even semiquantitative estimations than many other available techniques.
- Mineralogical fingerprinting is a generally expensive and time-consuming technique. While this might be a barrier for its routine use in site investigation, its use in forensic investigations could be made reasonable by applying it to selected samples only.

5.3.2.4 Recommendations

Mineralogical fingerprinting should be performed on a reduced number of representative samples. Selection of representative samples may be done based on historical and existing monitoring data and provides the key for defensible conclusions. Generally well-known source characteristics could be used to identify the main types of contributing sources in a given sample (see examples in the hints at the end of this section). However, specific associations based on a case-by-case basis documented within the historical file should be considered and given priority when interpreting results. As with any other forensic technique, data interpretation should be performed within a site-specific context; a general understanding of the type of industry and any applicable potential sources as they relate to the method application (e.g., mineralogical fingerprints known to be generated) should also be accomplished.

Hints for Successful Forensic Use of Mineralogical Fingerprinting

- **The presence of secondary phases may indicate older releases or unstable released compounds.** The phases usually interpreted as secondary phases (transformed from originals) are generally the more stable compounds in soil (such as phosphates), as well as associations with manganese oxides and with calcium. The presence of such phases associated with the contaminant/element of interest suggests either background soil sources or older anthropogenic sources allowing transformation of the original pollutant to have happened in soil. Note that some newer anthropogenic sources may also account for such secondary phases if they are unstable and become transformed soon after the release.

- **Associations of a targeted metal with elements composing natural minerals** for that respective metal defensibly **indicate natural sources** present in the sample.
- **Associations of a targeted metal with iron generally suggest industrial sources**, potentially including foundries and mining activities.
- **Associations of a targeted metal with tin or cadmium suggest industrial sources**.
- **Associations of a targeted metal with several other metals may suggest foundry or mining sources**.
- **Lead halides representative for vehicle emissions** are usually short-lived in the environment and **may transform in secondary phases soon after their release**.
- **Associations of a targeted metal with silicon particles suggest glass or ceramic sources**.
- **Associations of targeted metal (i.e., Pb) with paint pigments** (including Ba, $CaCO_3$, Ti, ZnO, etc.) indicate **paint as the likely source** of that metal (i.e., Pb).
- **Association of a targeted metal with Al and Si may indicate adsorption on clay particles**.
- **The association of a targeted metal with ash** (groundmass usually displays spherical pores) **indicates a likely industrial source**.

5.4 Statistical Evaluation, Contaminant Modeling, and Data Visualization

Statistical techniques and contaminant modeling are distinct forensic methods. They have been grouped together within this chapter since only limited information is provided here related to these techniques. While it is not within the scope of this book to provide a comprehensive review of statistical techniques or contaminant modeling, because these techniques are used in forensic investigations, a brief review is provided here and the reader is directed to some useful references on these topics:

- Recommended references on statistical techniques and their use in forensic investigations include a recently published textbook (Rong, 2011), as well as a few articles related to the use of statistical techniques in environmental forensics (Gauthier and Hawley, 2007; Johnson et al., 2007; Gauthier, 2002).
- Recommended references on contaminant modeling techniques as they pertain to forensic investigations include several chapters from environmental forensics textbooks (Katyal and Morrison, 2007; Egan and Murphy, 2007; Morrison, 2002; Murphy, 2002; Patzek, 2001).

In the following, a brief review of some of the commonly used statistical techniques is provided, emphasizing recommendations related to their forensic use. A general discussion and recommendations related to contaminant transport modeling use in forensic investigations are also included. Finally, a brief discussion related to fingerprinting data visualization is also included.

5.4.1 Brief Review of Statistical Techniques Relevant to Environmental Forensics

Statistical techniques and exploratory data analysis are based on mathematical methods that can be used to identify patterns in groups or mixtures of contaminants. Statistical techniques, by themselves, do not involve contaminant analysis within the environmental matrix as the other methods discussed in this book. However, statistical techniques are included in this chapter to emphasize that there is a strong dependency on interpreting statistical results within site-specific conditions (which may affect statistical use/comparability of data).

5.4.1.1 Types of Statistical Analyses

Statistical analyses include the following:

- Basic statistical techniques such as:
    - Calculation of maximum, minimum, and mean values and methods for:
        - Comparing sample means or populations,[6] including methods such as the Student *t* test, Wilcoxon's rank sum test, paired *t* test, and analysis of variance (ANOVA) (Gauthier, 2002).
        - Evaluating relationships between contaminants, including methods such as Pearson's product moment correlation coefficient or Spearman's rank correlation coefficient (Gauthier and Hawley, 2007).
        - Making predictions, including methods such as linear correlation and linear regression analysis and associated methods

(Gauthier, 2002); a correlation coefficient is usually calculated through these methods.
    - Testing distributions, including methods such as chi-square goodness-of-fit test (Gauthier and Hawley, 2007).
- More complex techniques, such as multivariate statistics, including some common statistical methods used in forensic investigations such as: principal component analysis (PCA), hierarchical cluster analysis (HCA), discriminative analysis, neural networks, and polytopic vector analysis (PVA). A recent study (Henry and Christensen, 2010) pointed out the power of the application of two multivariate source apportionment models in any given forensic case.

5.4.1.2 General Applications, Limitations, and Recommendations

5.4.1.2.1 Applications

Statistical techniques may be applied in conjunction with chemical or other type of fingerprinting data for multiple purposes, including the following:

- To demonstrate a point or determine the statistical significance of a conclusion. An example would be assessing contamination at a site by comparing contaminant values with background values in the area.
- To identify relationships among contaminants at a site (e.g., ratios between contaminants correlation coefficients that provide a simple measure of the linear association between two variables, or correlation matrices when more than two contaminants are present).
- To evaluate larger patterns of contamination or environmental footprints and help with source identification and allocation.
- To test the significance and validity of environmental models using site-specific data.

5.4.1.2.2 Limitations

Statistics may be misleading if the data are not analyzed with site-specific physical meanings. Examples of potential pitfalls associated with application of several basic statistical methods in real case studies include (Rong, 2011) the following:

- The automatic assumption of a normal distribution to environmental data for estimation of percentile and confidence interval; in many cases, data may show a log-normal distribution instead, resulting in a different percentile and confidence interval values.
- The use of a wide range of data in which the maximum data points may trivialize other smaller data points, changing the correlation

coefficient; this is the problem when a large amount of data is collected and available for analysis.

- The propagation of uncertainties of input variables to the regression model prediction, resulting in an even more uncertain model when using regression analysis.
- The acceptance of a hypothesis as a weak argument to imply a strong conclusion when using the ANOVA technique.
- The analysis of a data trend without looking into the magnitude of the data values and the meanings of the values.

5.4.1.2.3 Recommendations and Checklist for Data Comparability

A key point for using defensible statistical techniques, generating reliable conclusions, relates to having "comparable" datasets. In other words, we need to make sure that the data used in various mathematical statistical programs are comparable. Comparability of the data has a strong influence on the results of statistical analysis, which typically consist of grouping similar data into clusters usually associated with distinct sources. If the differences in the data itself may be due to other factors (e.g., environmental weathering, changing in site conditions) instead of the hypothesized distinct sources, the statistical approach becomes flawed, and results may be misleading. Therefore, it is absolutely necessary that the forensic scientist carefully examine the data within each case-specific context to evaluate the comparability of various data before using them in statistical analyses. If multiple environmental data were collected during the years, things to check to establish comparability of the data before the statistical analysis include the following:

- *How were the data collected*? Were the collection methods similar, and if not, could the differences have influenced the results (and how much)?
- *How were the data analyzed and generated*? Were different labs used? Were different analytical methods used? Were different qualifiers (flags) assigned to the data? If the answer is yes to any of these questions, the scientist needs to use his or her judgment and experience to evaluate whether any recorded differences could have had an impact on the data in such a way to render it less comparable (e.g., samples collected in different years could provide distinct results due to differences in analytical techniques or lab used, distinctions that may mislead in source or fate and transport evaluations).
- *Did any site conditions change during the years (between sampling and data-generating events)*? For example, did any construction work happen during some sampling events but not during others? How about weather conditions? Did any other site-specific external factors potentially influence contaminant fate and transport and weathering between sampling events? For example, if we are investigating a site with known

chlorinated solvent releases and a petroleum spill happened at the site at some point, the release of petroleum products (light nonaqueous phase liquids, LNAPLs) could have two main types of influence on the subsurface chlorinated solvent plumes: (1) Petroleum compounds may accelerate the biodegradation of chlorinated solvents by serving as microbial food and by contributing to more anaerobic environments; (2) petroleum LNAPL free product, if present, would slow or even prevent the vertical movement of chlorinated compounds (dense nonaqueous phase liquids, DNAPLs) due to preferential partitioning of chlorinated compounds into the petroleum organic phase. In such a hypothetical situation, the data collected before the petroleum spill event cannot and should not be compared with the data collected after the spill through the statistical analysis. Statistical analysis could be separately employed to compare the two sets of data, but the general forensic evaluation should not be based on the statistical results unless either more recent or older data are considered representative for the question at hand.

Even when only one main sampling event is to be used in the statistical analysis, the spatial distribution of data may influence its comparability; therefore, the data should also be evaluated for comparability before any statistical analysis is performed. Things to check related to spatially distinct data (collected within the same sampling event) include the following:

- *Is there any difference in the spatial location of data that could influence the analysis result*? For example, were some of the samples collected below structures (or from where structures were still present at some point in time following a suspected spill)? In such a case, the weathering of contaminants from those locations could be altered due to the presence of structures (e.g., buildings), reducing the oxygen supply.
- *Could the sample depth render data less comparable*? If a sample were collected above versus below the groundwater table, distinct results may be due to differential weathering patterns and may not necessarily be associated with distinct sources.

Therefore, it is always wise to carefully review the data first and make sure they are comparable and relevant. For statistical analysis, it is preferable to use fewer data (only representative data) rather than all data, with some perhaps less-representative or "noise" data, which may influence the overall evaluation.

It is also recommended that more than one statistical method be applied, and that the forensic investigator should carefully consult the existing data (e.g., check sample means and standard deviations) to become familiar with the data distribution and variation range. Finally, as with any forensic investigation, it is recommended to use at least one more independent line of evidence to confirm and validate the results.

Since multivariate statistics are becoming increasingly popular in forensic and other environmental investigations, two such commonly used techniques are briefly reviewed.

5.4.1.3 Principal Component Analysis

Principal component analysis (PCA) reduces the dimensionality of a given dataset and may objectively and defensibly distinguish subtle variations of the most diagnostically powerful chemical ratios. PCA also provides information about similarity between samples and potential sources. Within a given dataset, PCA may be used to identify the number of fingerprints, the composition of each fingerprint, and their relative contribution in each analyzed sample without *a priori* knowledge about sources. Moreover, when differences between samples are subtle, PCA may help distinguish them and could be used to select diagnostic ratios with the highest discriminatory power for certain datasets. An excellent review of PCA was provided by Johnson et al. (2007).

PCA is commonly used to evaluate fingerprinting data for complex compound mixtures, such as crude oil and petroleum products. Each environmental trajectory related to a marine oil spill, for example, may have its particularities, and no diagnostic ratio may necessarily work well for all trajectories. Therefore, PCA may be used at various steps of an oil spill investigation to evaluate the data and select relevant parameters.

Note that apart from the score plot used to visualize (in two dimensions [2D] or three dimensions [3D]) the results of PCA, the associated loading plot is also useful in identifying the features (e.g., ratios) with the highest diagnostic power (accounting for most of the variability in this system) to be used in the forensic investigation (e.g., double-ratio plots).

5.4.1.4 Hierarchical Cluster Analysis

Hierarchical cluster analysis (HCA) sorts various environmental samples and groups them in clusters based on their characteristics and similarities. HCA finds relatively homogeneous clusters of samples based on measured characteristics (e.g., diagnostic ratios). A hierarchy or tree-like structure is constructed to see the relationship among entities (observations or individuals).

This analysis starts with each sample in a separate cluster and then combines the clusters sequentially, reducing the number of clusters until only one cluster is left. This hierarchical clustering process can be represented as a tree, or dendrogram, with each step in the clustering process illustrated by a joint of the tree (for more information, consulthttp://www.clustan.com/hierarchical_cluster_analysis.html).

HCA may be used with the enhanced *k*-means algorithm for the clustering, which is suitable for very large datasets. The goal of *k*-means clustering is to partition the data into *k* groups such that the within-group sum of squares is minimized.

The gap statistic method may be used for estimating the number of clusters in a dataset. This methodology applies to any technique used for grouping the data and compares the within-cluster dispersion with what one might expect given a reference null distribution (i.e., no clusters). Two-way hierarchical cluster diagrams may be produced to better visualize the similarity between samples from any given area.

5.4.2 Brief Review of Contaminant Modeling Relevant to Environmental Forensics

Contaminant transport modeling uses contaminant and site-specific data to calculate and reconstruct (model) contaminant transport in time and space. Both contaminant characteristics and environmental matrix characteristics need to be considered in modeling of contaminant transport. Obviously, the more, the better—in other words, sites that are thoroughly characterized would enable the generation of more accurate models. However, even for well-characterized sites, since not everything is known about site and release characteristics, a series of assumptions is usually incorporated into the model design. For example, the period during which a contaminant was released into an aquifer is required for modeling but is many times not available (e.g., through historical information). The ultimate reliability of model predictions relies with the forensic expert's skills and knowledge.

5.4.2.1 Method Types and Steps

There are many contaminant modeling programs applicable to groundwater, air, and other environmental media. The use of any of these models may be easily challenged in the court, and it may be hard to defend modeling results and conclusions. This is because it is hard to develop a model that will fit with all existing monitoring data, and many subsurface parameters may change in time and are hard to adjust within the model.

The main types of contaminant transport models applicable to environmental forensics include

- liquid and vapor contaminant transport models through paved surfaces and soil;
- contaminant transport models in groundwater;
- air dispersion modeling.

A few examples of general types of models applicable to environmental forensics are provided along with associated basic equations to point out the type of parameters that need to be considered when building/using models.

Some of the most commonly employed models in forensic investigations include liquid and vapor transport models through paved surfaces and soil. An excellent overview of the mathematical basis and forensic applications of such models can be found in the book chapter by Katyal and Morrison (2007). A representative example for modeling fluid transport through soil is SESOIL, which is a one-dimensional vertical transport code for the unsaturated zone, simultaneously modeling water and contaminant sediment transport. SESOIL uses soil, chemical, and meteorological input values to describe the depth reached by a chemical, with a linear equilibrium partitioning between its vapor, liquid, and adsorbed phases (Jury and Farmer, 1984):

$$D = (V_w\, t_c)/[(\theta + \rho_b K_d) + (f_a H)/R(T + 273)]$$

where
D = depth
V_w = water velocity
t_c = convective time
θ = water content of soil
ρ_b = soil bulk density
K_d = contaminant partitioning coefficient
f_a = air-filled porosity
H = Henry's law constant
R = universal gas constant
T = soil temperature (^{o}C)

Other types of commonly employed forensic models are those related to contaminant transport in groundwater. A multitude of groundwater flow (advective) and contaminant transport models is available based on many mathematical approaches, including probabilistic and geostatistical simulations, heat transport inversion, and direct methods. Of these models, the most frequently used in forensic investigations are classified as follows (Katyal and Morrison, 2007):

- Instantaneous point source solutions for contaminants injected into groundwater
- Continuous injection of contaminants in groundwater
- Transient injection of contaminants in groundwater
- Transient injection of multiple sources of contaminants in groundwater
- Multiphase models
- Multiphase inverse models

For models of contaminant transport in groundwater, the most appropriate mathematical expression is the standard 2D convection-dispersion-adsorption (CDA) model for solute transport. A series of assumptions includes that the porous medium is homogeneous and isotropic, that the pore space is saturated with a fluid, and that Darcy's law is valid. If these assumptions are not met, the defensibility of the model may be compromised. A general equation used to describe the flow of a conservative solute in a homogeneous, isotropic medium is as follows (Katyal and Morrison, 2007):

$$\partial/\partial t(R(x, y, t)c) + V(x, y, t)\, \partial c/\partial x - \partial/\partial x(D_L(x, y, t)\, \partial c/\partial x)\, \partial/\partial y(D_T(x, y, t)\, \partial c/\partial y) = q,$$

where

q = volumetric solute source or sink term
c = vertically averaged solute concentration
V = linear solute velocity = $U_x(x,y,t)/\varphi(x,y)$
U_x = Darcy velocity for one-dimensional flow along the x-axis
D_L = longitudinal dispersion coefficient = $D^* + \alpha_L(x,y)V(x,y,t)$ (where D^* = coefficient of molecular diffusion of the contaminant in water; α_L = longitudinal dispersivity)
D_T = transverse dispersion coefficient = $D^* + \alpha_T(x,y)V(x,y,t)$ (where D^* = coefficient of molecular diffusion of the contaminant in water; α_T = transverse dispersivity)
t = time
x, y = 2D coordinates
R = retardation factor

The retardation factor may be calculated according to the following equation:

$$R = 1 + \rho_b K_d(x, y, t)/\varphi\,(x, y)$$

where $\rho_b = (1 - \varphi)\, \rho_{\text{grain}}$, K_d is the distribution coefficient as a function of organic carbon partition coefficient (K_{OC}), and weight fraction of organic carbon in soil (f_{OC}); specifically:

$$K_d = K_{OC} f_{OC}.$$

Apart from releases to soil and groundwater, contaminant emissions to the atmosphere may disperse over large areas and affect a large number of people. Sources for contaminant releases into air include power plants, smelters, refineries, chemical plants, and other industries that would use chimneys or vents for the discharge of air emissions. Although the amount of releases from these sources under normal operational conditions is not sufficient to alter the overall air quality, in special situations, when accidents happen, air dispersion models may be useful for understanding the impact of contaminants released to the air. Such models may also help confirm the suspected air contamination sources and allocate between sources (e.g., air emission source vs. other sources of contaminants in soil). Air dispersion models use meteorological records and emissions rate as input information to mathematical models to calculate or simulate the effect of atmospheric motions in transporting, diluting, and dispersing pollutants released into air and predict their concentrations at studied receptor locations. A good review of air dispersion modeling as it relates to environmental forensics was provided by Egan and Murphy (2007).

Input parameters for air dispersion modeling include source emission parameters, such as the emission rate for the chemical of concern, the emission rate for stack releases, exit velocity, temperature of the exhaust gases, as well as the physical dimensions of the stack (e.g., inside stack diameter and stack height). This information may often be available from state environmental agencies. In addition, air dispersion models should account for the influence of meteorology. Terrain and water bodies include factors such as wind speeds and directions (for downwind transport of contaminants), the wind and temperature gradients in the vertical direction, the atmospheric turbulence mixing rates, as well as local topographical features. Meteorological data needed for air modeling may be obtained from a number of governmental and private sources, including the National Climatic Data Center (NCDC) in Ashville, North Carolina; the National Weather Service (NWS), the Federal Aviation Administration (FAA), universities, agricultural facilities, as well as the U.S. Environmental Protection Agency (USEPA; through the Support Center for Regulatory Air Modeling [SCRAM], which may be accessed through the EPA website, http://www.epa.gov).

Of note is that air dispersion models may be based on patterns of contaminants left in soil for historical emission sources no longer in use. However, often, historical source emission parameters needed for modeling are unknown and must be estimated. Techniques for estimating such source emission parameters exist and are discussed in the book chapter by Egan and Murphy (2007).

Air dispersion models with applicability in forensic investigations include the following main types (Egan and Murphy, 2007):

- *Models based on the Gaussian plume equation,* including models such as SCREEN3; the Industrial Source Complex (ISC3) model; the American Meteorological Society and EPA Regulatory Model Improvement Committee Model (AERMOD); the California Puff (CALPUFF) model; and the Offshore and Coastal Dispersion (OCD) model. The Gaussian equation is provided and briefly discussed further in this chapter.
- *Numerical simulation models,* such as the Meteorological Model Version 5 (MM5) and computational fluid dynamics (CFD) models. These models are capable of simulating the detailed airflow of both large and small physical scales on finite difference-type computational grids.

The Gaussian dispersion equation calculates downwind concentration c as follows (Egan and Murphy, 2007):

$$c = Q/2\pi u\sigma_y\sigma_z * \exp(-y^2/2\sigma^2{}_y)\{\exp(-(h-z)^2/2\sigma^2{}_z) + [\exp[-(h+z)^2/2\sigma^2{}_z]]\},$$

where

Q = mass per unit time emitted by the source
y = the cross wind horizontal distance from the plume center line
z = the height above the ground
σ_y = the horizontal dispersion parameter
σ_z = the vertical dispersion parameter
h = the plume centerline height
u = the wind speed at that height

5.4.2.1.1 Modeling Steps

Regardless of the type of release and environmental characteristics, the main steps of a modeling process include the following (Patzek, 2001):

1. Define the purpose of developing a model.
2. Define the model scope by reviewing available site data.
3. Develop a conceptual site model through data review and analysis.
4. Select a suitable mathematical model to describe contaminant transport.
5. Verify that the employed numerical algorithm is correct.
6. Use of the developed conceptual model as inputs to the computer model.
7. Calibrate the computer model through input adjustment.
8. Verify the results of the computer model.
9. Present the results.

The purpose of the model may be defined using a few sentences that describe the intent for model use. Related to defining the scope, the following site data should be reviewed (in case of a groundwater model) (Patzek, 2001):

- Triangulated X, Y surface locations of groundwater monitoring wells
- Groundwater levels measured for the years in question
- Aquifer thickness measured and recorded in geological logs
- Contaminant concentrations measured in groundwater for the years of concern
- Measured concentrations for any sulfate and chloride ions (which do not adsorb and can be used as plume calibration tracers), an important step in creating a defensible model
- Aquifer conductivity as measured by well test data
- History of site operations for the years in question

- Recorded volumes of waste streams
- Geological logs, soil types, and layering
- Approximate surface locations for contaminant entry points
- Regional geological information

Following the review of all relevant site data, a conceptual model should be reached, including the contamination sources, historical discharges, contaminant retardation coefficients, contaminant plume shapes in space and time, ranges for groundwater flow velocities, and various aquifer characteristics (influencing contaminant fate and transport).

Once these preliminary steps are completed, selecting a suitable mathematical model is crucial for the defensibility and reliability of the model results. As mentioned, there are many available models for different types of contaminant transport. It is the role of the forensic expert to evaluate available models and select the most appropriate ones for a particular site. In the case of groundwater flow models, for example, the mathematical model appropriate in most cases is the standard CDA model briefly discussed previously. However, in some situations, a more sophisticated 3D compositional simulator may be needed. When, to distinguish between various contaminant sources, the model area needs to be subdivided into many small elements (composing the model grid), typical groundwater flow models such as MODFLOW may not be suitable (e.g., the analysis may take too long). In such situations, suitable numerical algorithms should be developed. Once this is accomplished, a computer implementation of the conceptual model should be designed and calibrated (e.g., the parameters established through the site conceptual model should be adjusted so that the calculated plume concentrations agree with the concentrations measured in groundwater at various monitoring wells in time). Finally, the developed and calibrated model may be implemented in MATLAB, a general computing environment for engineers and scientists.

5.4.2.2 General Applications, Limitations, and Recommendations

5.4.2.2.1 Applications

Contaminant transport models may be applied in many types of forensic investigations to do the following:

- Indicate the age of contamination. For example, the age of a contaminant plume may be back-calculated through modeling of the plume behavior/transport in subsurface; also, the time required for a liquid to migrate through paved or compacted surfaces may be estimated.
- Evaluate/confirm the source. Environmental models may provide the evidence of historical contributions from suspected contaminant

sources by evaluating the feasibility of a contaminant released from suspected sources to travel and reach the investigated end points (e.g., residential properties). What is remarkable about modeling the line of evidence is the fact that it could provide convincing evidence related to historical releases in the absence of direct historical measurements or data. However, the results may, and usually do, end up being challenged in litigation cases, going through strict scrutiny, which is why the modeling output should always be backed up by another independent line of evidence or, at the very least, should not be significantly contradicted by any direct evidence (e.g., measurements). A representative example of the effective use of environmental modeling confirmed by other independent forensic lines of evidence is provided in Chapter 9, Case Study 9.1.

- Simulate contaminant fate and migration and estimate the average contaminant concentration in groundwater.

5.4.2.2.2 Limitations

The main issue with modeling techniques is that environmental data are hardly homogeneous and perfectly comparable, and many unknown factors could make modeling less defensible and more vulnerable in the court of law. It is especially difficult to apply models to large contaminant plumes. Small errors during model calculations could result in significantly different outcomes of the model. According to a well-known saying by George Box, "Essentially, all models are wrong, but some are useful" (1987, p. 424). It is the role of the forensic expert to decide when to employ models and, more importantly, to interpret modeling data within a site-specific context and use other lines of evidence to confirm modeling results.

Some specific challenges for contaminant transport models include the following:

- Potential existence of preferential pathways of transport in soil (e.g., natural and artificial features, colloidal transport or cosolvent transport);
- The general lack of use of statistical methods to determine the precision of the release parameters;
- The assumption that soil is homogeneous could render modeling of contaminant passage through soil less reliable;
- For groundwater models, sufficient data should be collected to define heterogeneity in hydraulic conductivity;
- Temporal variation of the internal groundwater recharge should be considered along with various factors that may affect this when modeling contaminant transport in groundwater;

- In the case of groundwater models, the nature of flow during the period of interest may be distinct from the current nature of flow or what is included in the model;
- The effect of retardation factors when modeling groundwater flow could be important (Patzek, 2001); also, small systematic errors may significantly affect the aquifer transport velocity; all these factors may influence the quality of the model results and their defensibility.

A detailed review of these and other challenges along with recommended solutions were provided by Katyal and Morrison (2007).

5.4.2.2.3 *Recommendations*

Overall, in spite of their considerable applicability in forensic investigations, it might be preferable not to use contaminant transport models in court cases facing tough scrutiny unless no other forensic approach works and available information allows building a reliable model. If information is missing, the forensic expert may consider collecting it before starting the modeling exercise. However, in no way should a forensic expert compromise building models without sufficient or adequate information.

When applying contaminant modeling, a good understanding of contaminant fate and transport (e.g., hydrolysis, sorption, biodegradation, and other processes that may change the contaminants after their release) and physicochemical properties (e.g., liquid density, solubility, viscosity, vapor pressure, vapor density, boiling point, and Henry's law constant) is a must. Also, a good understanding of environmental media properties such as hydraulic conductivity and total organic carbon (TOC) content in the case of soil is needed for modeling contaminant transport. For example, equations for contaminant migration though soil may be used to identify when the contaminant entered the groundwater or migrated into another property. However, before using modeling techniques, the forensic investigator should identify whether the fluid was transported as a vapor or as a liquid and whether its transport occurred under saturated or unsaturated subsurface conditions.

A good understanding of the mathematical equations and algorithms on which the employed model is based is also necessary for building defensible forensic evidence. The forensic experts often pay little attention to the mathematical basis of a model, assuming this must be sound and applicable to the case at hand. However, lawyers often challenge experts in depositions and in the trial court related not only to the modeling outcome but also to their understanding of the mathematical basis of the models. Obviously, even if the model results are sound and backed up by other lines of evidence, the case may be damaged if the expert shows a lack of understanding of how the model was built.

5.4.3 Fingerprinting Data Visualization

Data visualization involves displaying fingerprinting data on maps (2D or 3D maps) that ideally may also show matrix information, specific site features, and historical operations. Since data visualization involves displaying contaminant information along with contaminant matrix information and other types of site information, various displaying techniques are briefly reviewed in this chapter (some were used and discussed also when the geochemical fingerprinting method was presented at the beginning of this chapter). In addition, most model results are displayed on maps for easier interpretation and communication.

Usually, a geographical information system (GIS) is used for data visualization on maps. Data representation on maps helps with interpretation and communication of results to peers, clients, a jury, and so on. The most effective way to use data visualization in forensic investigations consists of displaying multiple layers of data on maps. For example, overlaying chemical concentration data on lithological data within vertical soil profiling representations is used for a technique referred to in this book as "geochemical fingerprinting." Moreover, the site information can be displayed on top of historical site photos showing features relevant for the time when the releases occurred. Multiple layers of information, including various types of available fingerprinting data, environmental matrix characterization data, site features, site topography, and subsurface stratigraphy, can be displayed on maps at the same time.

Note that data visualization is not a stand-alone technique since it is based on information resulting from a multitude of other techniques, and it is generally associated with various individual fingerprinting techniques. However, data visualization is briefly reviewed, by itself, in this section to emphasize its important role in forensic studies and illustrate its value in source investigation through some concrete examples presented in this section (other examples were provided in a previous section in the discussion of geochemical fingerprinting).

The examples related to chemical fingerprinting data visualization as it was used in a real forensic investigation[7] are displayed in Figures 5.8 through 5.13. Specifically, soil vapor, groundwater, and soil plumes are depicted in 3D or 2D images for two COCs: 1,1,1-TCA and methylene chloride (MC). These examples demonstrate how data visualization helps interpret chemical fingerprinting and evaluate the source and age of contaminants.

Soil vapor, groundwater, and soil plumes are shown for each of the two contaminants, namely:

1. Figures 5.8 and 5.11 display a 3D image of the overall soil vapor plume between the surface and 20 ft bgs for each of the selected contaminants: 1,1,1-TCA and MC, respectively. These 3D images also display various soil boring logs with collected deeper soil data

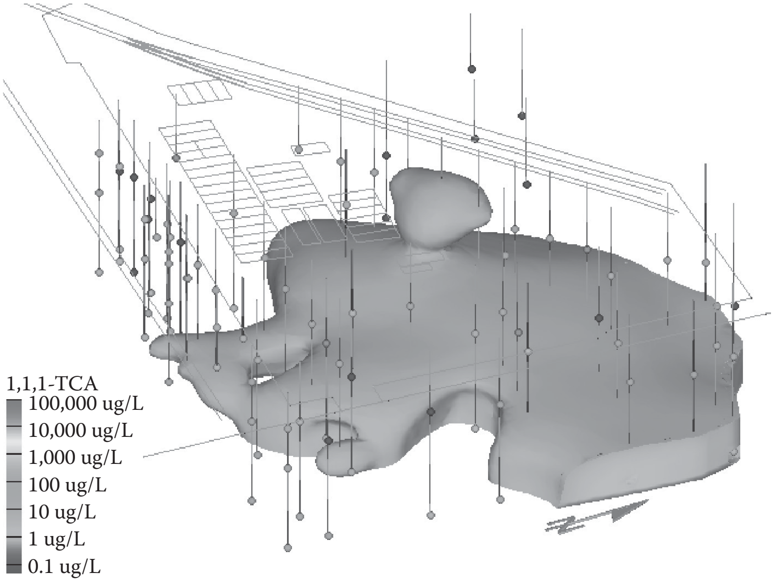

FIGURE 5.8
Example of a 3D representation of a contaminant (1,1,1-TCA) soil vapor plume at a site with recorded releases in Southern California. The soil vapor plume is shown based on all collected data between the surface and 20 ft bgs; contaminant concentrations in soil borings at various depths are shown in circles. Note: This was originally a color figure; thus, the 1,1,1-TCA original color concentration scale (toward the left of the image) is now provided in shades of gray. Although for the purposes of this example the exact concentrations are less relevant, the concentration range of the plume itself was between 10 and above 1,000 (but below 5,000) μg/L. The circles representing 1,1,1-TCA concentrations in borings vary between nondetects (dark circles) up to 1,000 μg/L (lighter circles).

(concentrations) shown as color-coded circles at various depths within each boring (represented by a line). Note that these 3D images of soil vapor plumes with overlaying soil boring logs also display representative site structures (e.g., location of underground storage tanks and operations) as the shown rectangles.

2. Figures 5.9 and 5.12 (each) display two 2D-images of the soil vapor plumes at 10 and 20 ft bgs (left images in each figure) and two 2D images of the shallow and deeper groundwater plumes (right images in each figure) for each of the selected contaminants (1,1,1-TCA and MC, respectively). These 2D images also show representative site structures and location of some of the monitoring wells (for the groundwater plume images).
3. Figures 5.10 and 5.13 display four 3D images of soil plumes at different depths for each of the selected contaminants (1,1,1-TCA and MC, respectively). These 3D images also show soil boring logs with collected soil data (concentrations) at all depths and times (from

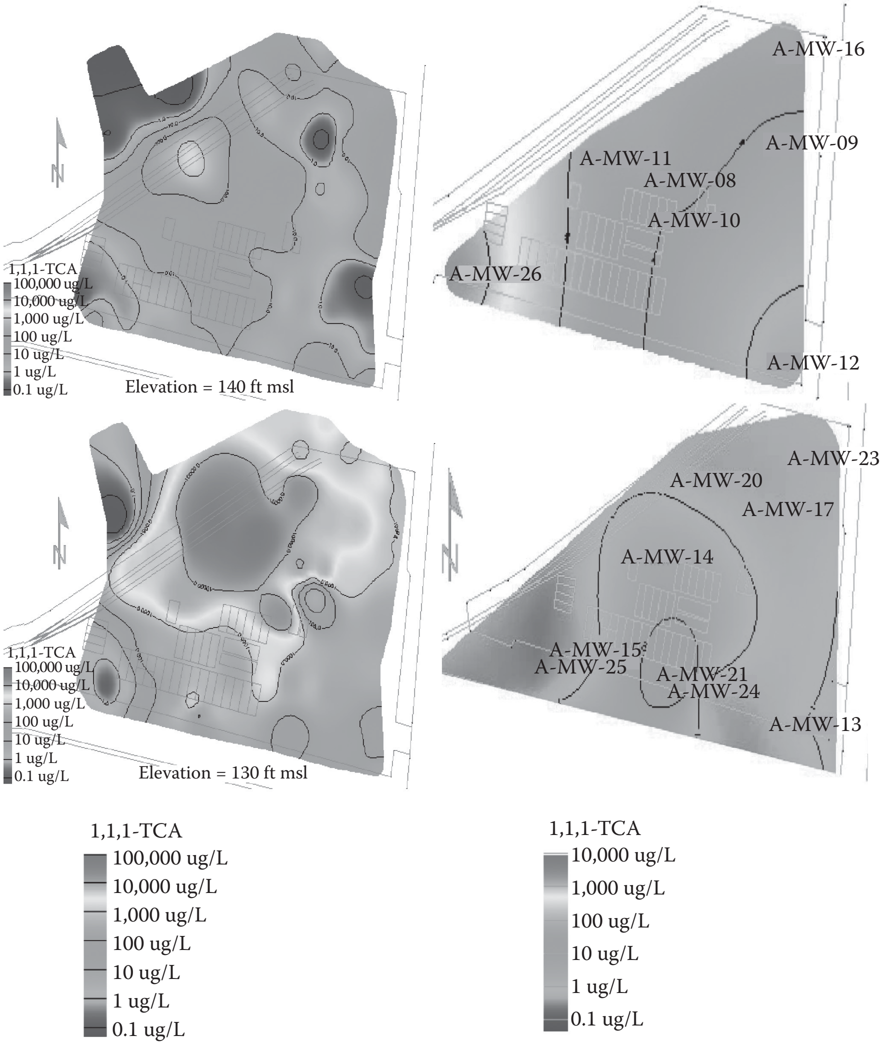

FIGURE 5.9

(See also color insert.) Examples of 2D representations of soil vapor plumes (left images) and groundwater plumes (right images) of a contaminant (1,1,1-TCA) at a site with recorded releases in Southern California. The top left image shows 1,1,1-TCA soil vapor plume at 10 ft bgs; the bottom left image shows 1,1,1-TCA soil vapor plume at 20 ft bgs. The top right image shows the 1,1,1-TCA shallow groundwater plume; the bottom right image shows the 1,1,1-TCA deeper groundwater plume. Note the differences between soil vapor and groundwater scales.

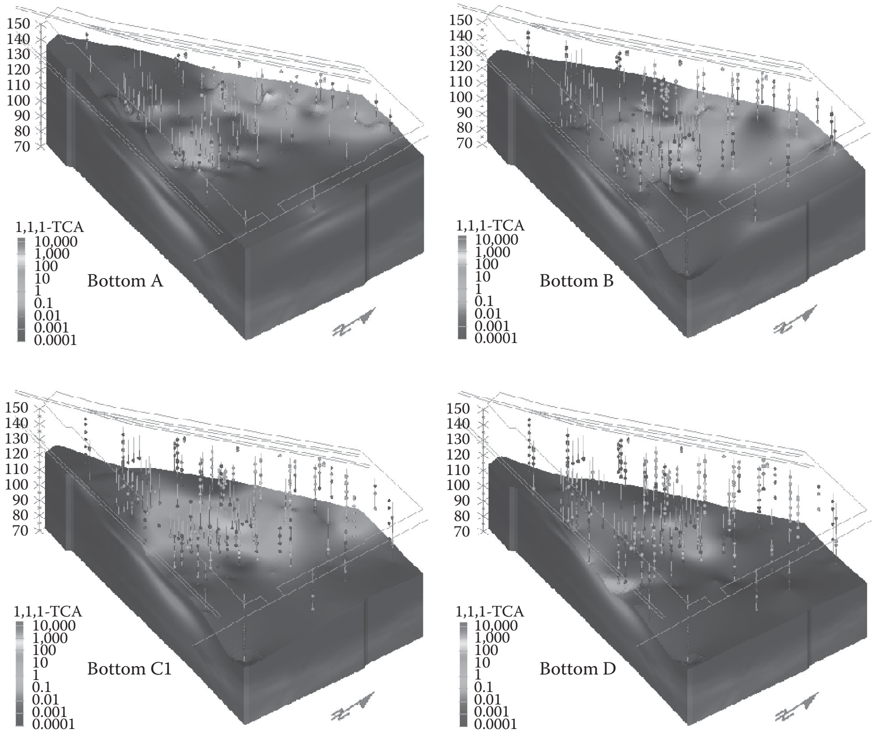

FIGURE 5.10
(See also color insert.) Examples of 3D representations of a contaminant (1,1,1-TCA) soil plumes within distinct lithological layers at a site with recorded releases in Southern California. The soil plumes are shown within the same soil "slice," expanding from the surface to approximately 80 ft bgs. Specifically, the four images show color-coded 1,1,1-TCA soil plumes at the bottom depth of four distinct lithological layers expanding from the surface down (from top left toward bottom right, with layer A being the surface layer and layer D being the deepest layer). Note that the color code scale in each individual image ranges from 10,000 to 0.0001 µg/kg as color changes from red to blue (nondetects).

> the surface down) shown as color-coded circles within each boring (represented by a line). Note that the same slice of soil from the surface to approximately 80 ft bgs is shown in each of the individual four images of each of the two figures; however, what differs between the four individual images in each figure relates to the color-coded soil plume that is based on soil data collected on the bottom of four distinct individual lithological layers (i.e., from the surface down: A through D). This is part of the chemical fingerprinting technique.

Useful forensic information can be deduced from the data displayed in Figures 5.9 through 5.13. Here is selected forensically representative information:

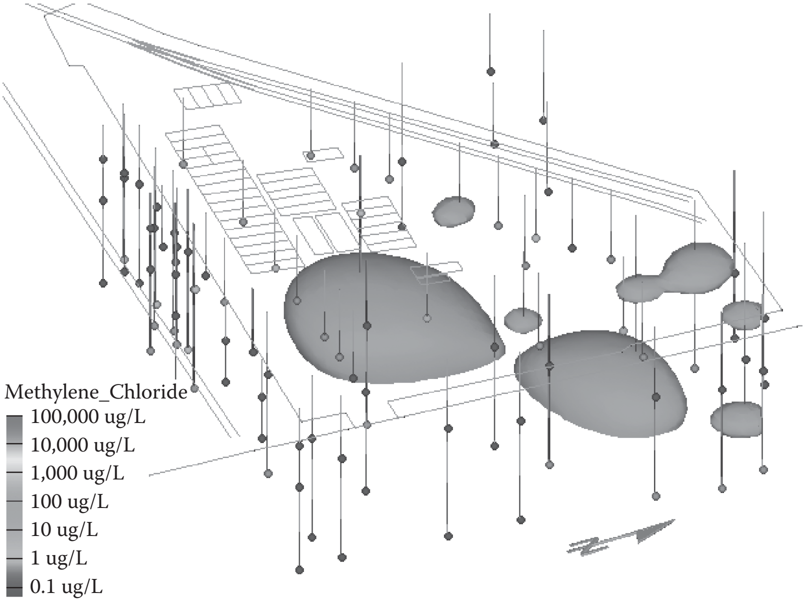

FIGURE 5.11
Example of a 3D representation of another contaminant (methylene chloride, MC) soil vapor plume at the site with recorded releases in Southern California shown in previous figures. The soil vapor plume is shown based on all collected data between the surface and 20 ft bgs. Contaminant concentrations in soil borings at various depths are shown in colored circles. *Note*: This originally was a color figure; thus, the MC original color concentration scale (toward the left of image) is now provided in shades of gray. Although for the purpose of this example the exact concentrations are less relevant, the concentration range of the plume itself was between 10 and below 1,000 µg/L, while the circles representing MC concentrations in borings vary between nondetects (dark circles) up to between 1 and 10 µg/L (lighter circles).

- For both 1,1,1-TCA and MC, surface or close-to-surface on-site sources were confirmed and likely responsible for most of the soil vapor detections; this is due to the detection of these contaminants in soil and soil vapor from the surface toward deeper depths. In soil and soil vapor, the detections were continuous from the surface to the deepest depth tested for 1,1,1-TCA, while the detections were not continuous for MC. One main surface source (toward the northwest) and a potentially secondary deeper source (south of the main one) are suggested for 1,1,1-TCA by the 3D image of soil and soil vapor plumes, while potentially multiple less-prevalent surface sources along with a deeper source toward the south (potentially from off site) are suggested for MC. Also, older MC releases from surface sources are suggested by the discontinuity of its detections. The final conclusion should be taken after reviewing data from other lines of evidence.

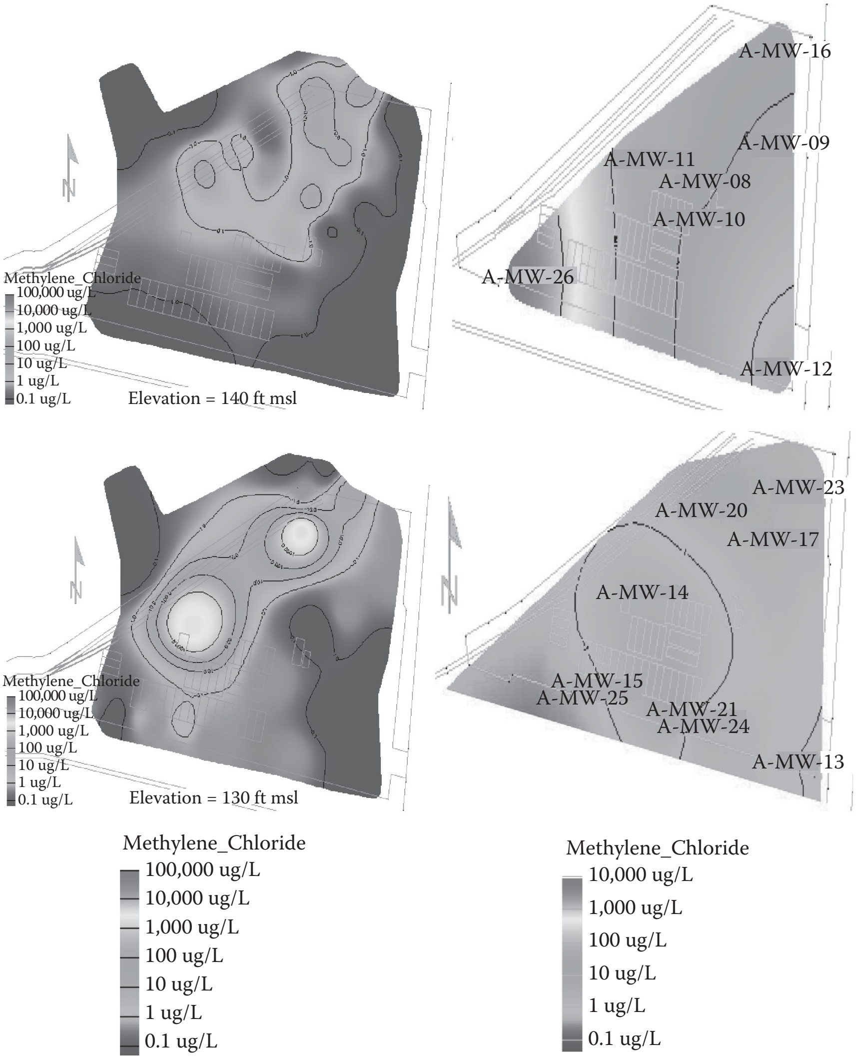

FIGURE 5.12
(See also color insert.) Examples of 2D representations of soil vapor plumes (left images) and groundwater plumes (right images) of another contaminant (methylene chloride, MC) at the site with recorded releases in Southern California also displayed in previous figures. The top left image shows the MC soil vapor plume at 10 ft bgs; the bottom left image shows the MC soil vapor plume at 20 ft bgs. The top right image shows the MC shallow groundwater plume; the bottom right image shows the MC deeper groundwater plume. Note the differences between soil vapor and groundwater scales.

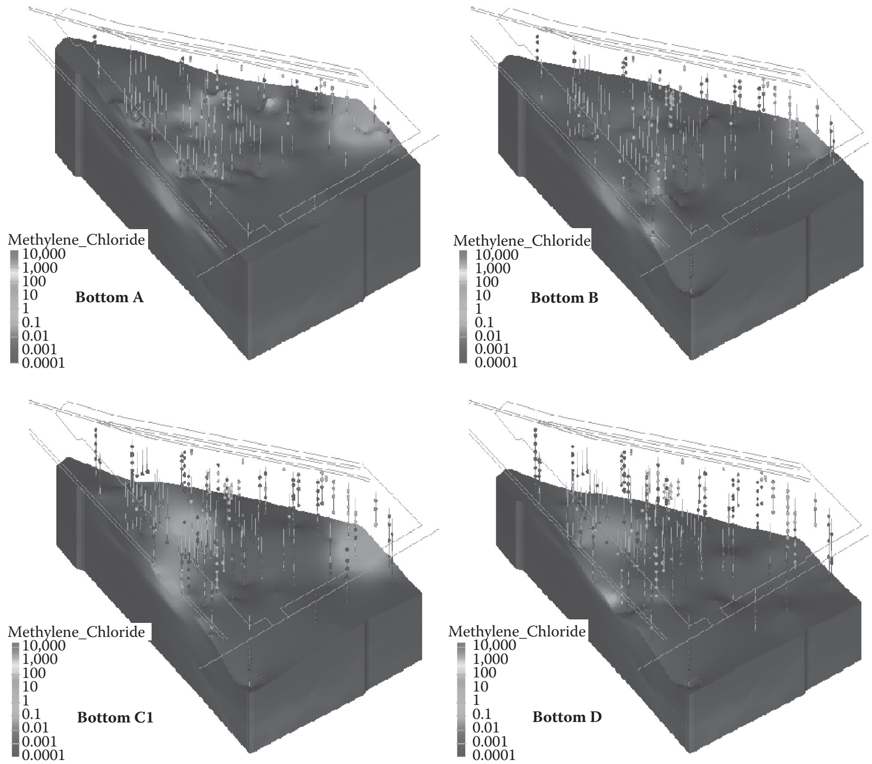

FIGURE 5.13
(See also color insert.) Examples of 3D representations of another contaminant (methylene chloride, MC) soil plumes within distinct lithological layers at the site with recorded releases in Southern California shown in previous figures. The soil plumes are shown within the same soil slice, expanding from the surface to approximately 80 ft bgs. Specifically, the four images show color-coded MC soil plumes at the bottom depth of four distinct lithological layers expanding from the surface down (from top left toward bottom right, with layer A being the surface layer and layer D being the deepest layer); note that the color code scale in each individual image ranges from 10,000 to 0.0001 μg/kg as color changes from red (highest concentration) to blue (nondetects).

- For both 1,1,1-TCA and MC, the confirmed surface sources did not affect either the shallow or the deeper groundwater since there is no correlation between either of the corresponding groundwater plumes and the shallower soil and soil vapor ones. However, for both 1,1,1-TCA and MC, there is some correlation of the deeper soil plumes (bottom of layers D and C to some extent), with the deeper groundwater suggesting a potential influence from a common deeper source (including potentially off site toward the south-southwest).

- Of note is the fact that, in this particular case, soil vapor surveys and soil samplings were conducted years before the displayed groundwater data were collected. Typically, it is preferred to compare data collected from the same time or year. However, for this case, more recent groundwater data were displayed (as compared with the available soil and soil vapor data) to point out that the recorded historical releases at this site (with still some traces in soil vapor and soil at the time when data were collected) were no longer affecting the shallow or deeper groundwater.
- For both contaminants (1,1,1-TCA and MC), there was a general correlation between shallow and deeper soil vapor plumes, suggesting historical surface sources. However, while soil data for these contaminants did correlate with the main shallower soil vapor detections, some of the shallow soil data (the detections toward the north), especially in the case of MC, did not correlate well with shallower soil vapor data, suggesting potentially additional deeper (possibly off site) sources.
- For both contaminants (1,1,1-TCA and MC), there was no correlation between contaminant patterns in shallow versus deeper groundwater, suggesting distinct sources of these contaminants in the two aquifers with a likely common source for both contaminants toward the southwest and one toward the south for shallow and deeper groundwater, respectively.
- For this site, there does not seem to be any significant correlation between contaminant patterns in the vadose zone (soil and soil vapor) and the main displayed site features. The same comment is valid for shallow groundwater. However, other potential on-site sources not displayed on these maps existed for this site (e.g., permanently stationed railroad tank cars toward the northwest) and were recorded release sources (see more information in the discussion of Case Study 9.1 in Chapter 9 of this book).
- Overall, the displayed data confirmed the existence of several on-site historical contaminant sources, in accordance with the historical evidence. The data also showed the lack of influence of the historical sources on shallow and deeper groundwater quality. Furthermore, potentially additional deeper contaminant sources are suggested for both contaminants, including potential off-site sources toward the south, southwest, and north. Such contamination from suspected deeper sources might have commingled with that from surface sources, resulting in the complex fingerprints displayed here.

Related to data visualization, a recent forensic application was published by Fernandez-Varela et al. (2010), who demonstrated how a new method based on self-organizing maps (SOMs) can be used for analysis of complex data on polycyclic aromatic hydrocarbons (PAHs) from spilled oils. Weathering differentiation was also possible.

In addition, a variety of animations is possible today due to the rapid progress of computer programming. Recently, animations of environmental data may allow the creation of a 3D site simulator environment (on the computer), including detailed site features that allow navigation within this 3D created environment (similar to navigating within a 3D space of a computer game). When contaminant data are included, it is easy to associate the data with potential source areas/site features and to envision hypothesized contaminant fate and transport. Lithological and hydrogeological data are also usually included and help to better evaluate various fingerprinting data.

In conclusion, data visualization is a powerful forensic method when associated with fingerprinting data, as it accomplishes two main objectives:

1. Evaluating the data to distinguish sources and contributions;
2. Communicating the data for successful trial testimony and client communication. It is well established that the most efficient form of communication is visual.

Also, remote sensing data visualization is a powerful forensic tool that may be applied to oil spill monitoring. The tool can be seen as a "green" technique as it does not require the physical disturbance of soil or water while extracting samples. Basically, it uses spectral measurements and a spectroradiometer for remote monitoring (see, e.g., the study by Ma et al., 2009).

Hints for Successful Forensic Application of Data Visualization

- **It is recommended to overlay the chemical analysis data on top of the lithological layers/composition (see the geochemical fingerprinting technique presented in this chapter)**. Chemical data from boring logs may be shown overlaying the lithological layers. By doing this, one can investigate correlations between the chemical and lithological data. For example, if a correlation of contamination with fine particles is not seen (such as clay and silt) or higher concentrations are observed in association with larger particles (such as sand), this may indicate an additional source of contamination contributing to the higher concentrations observed in sand layers. Also, for example, if the main source of contamination is at the surface of a boring, then it is expected that soil contamination will continuously decrease from the top toward the bottom of the boring. However, when higher contamination is observed in a deeper layer versus a shallow one (of comparable lithologies), then it should be suspected that an additional source has affected that area.

- **Where available, the slope of the lithologic layers of lower permeability (on top of which groundwater may flow) should also be depicted** and taken into consideration when interpreting chemical or isotopic data/fingerprinting.
- **Useful forensic information may be gained by comparing shallow soil (0–10 ft bgs) with subsurface soil vapor data** (see Case Study 9.1 in Chapter 9 of this book). Such comparison allows distinguishing if surface sources (seen in the surface soil data) account for subsurface contamination. This is because (for volatile organic compounds [VOCs] and semivolatile organic compounds [SVOCs]) although surface soil is affected by a surface source or shallow subsurface source, the soil vapor data are a result of both the surface source and any groundwater source potentially bringing pollutants from upgradient (on-site and/or off-site) sources.

Notes

1. Note that the term *geochemical fingerprinting* is used here in the strict context of the forensic investigations of soil/sediment contamination. In a broader sense, geochemical fingerprinting encompasses various testing techniques that help establish the composition and source of minerals and rocks (Hoefs, 2009); other uses of the term may be recorded in some forensic investigations, such as those related to the origin of crude oil and its formation conditions.
2. Lithological soil/sediment characterization refers to the physical characteristics of soil/sediment sample matrix, including the type and preponderance of particles composing the soil matrix (e.g., soil, silt, clay).
3. The railroad track area (from the previous example) is located in the northeast of the site, where the higher concentration is observed in soil (the right image in Figure 5.2).
4. Generally, 50–60 randomly selected particles (from those associated with the targeted contaminant) are analyzed for chemical elemental analysis. Depending on the concentration of targeted contaminant, a sample may have less than 50 particles associated with the contaminant of concern. In such a situation, all associated particles may be analyzed.
5. Note that these magnifications are provided here as examples; many other magnifications may be used on a case-by-case basis.
6. The population may consist of all conceivable items, observations, or measurements in a group; the population parameter of interest may be the arithmetic mean of a contaminant measurement/concentration.
7. This forensic investigation is further discussed in Section III of this book (Chapter 9) as Case Study 9.1.

6

Fingerprinting Techniques Targeting Traces Left by Contaminants in the Environment

6.1 Basic Principles

So far, two main types of experimental fingerprinting techniques have been presented: (1) techniques based on testing the contaminants or associated compounds (e.g., signature chemicals or degradation products) and (2) techniques based on testing both the contaminants and the environmental matrix in which they are found.

A third main type of fingerprinting techniques relates to testing the traces that the contaminants leave within the environment through which they pass after the release. While the techniques from this third main category of testing are generally indirect techniques measuring one aspect (i.e., traces left from contaminants), they are considered advanced forensic techniques due to the following advantages over the first two types of testing techniques:

- They are not affected or only little affected by the passage of time since the release occurred; in many cases the contaminant traces left in the environment are stable for a long time after the original contaminants have passed or have been degraded or transformed from their original forms.
- Some may be applied at mitigated sites where contamination is no longer present (detectable) in the tested environment.
- In general, they are quite sensitive to tiny amounts of contamination.
- Some may be applicable at sites with multiple releases of the same contaminant.

Using the previous brick wall analogy (see the analogy from Chapters 4 and 5) considering a brick wall as our environmental sample, with individual bricks being individual contaminants within the sample, the following comparisons apply:

- The first category of forensic testing techniques based on measuring the contaminants or associated chemicals (described in Chapter 4) would provide information on characteristics of component individual bricks (e.g., shape, size, color).
- The second category of forensic testing techniques measuring the contaminants within their environmental matrix (described in Chapter 5) would provide information on component individual bricks along with the binding patterns of the bricks within the actual wall.
- The third category of forensic techniques measuring traces left by contaminants in the environment (described in this chapter) would provide information on tiny (microscopic) fragments of bricks from the wall that are left in the soil surrounding the wall location after the wall was destroyed and no longer exists at the time of sampling. Such small fragments may not be seen by the naked eye, but they might alter the chemical composition of soil. The soil analysis thus may reveal specific characteristics associated with the tiny brick fragments that would help identify the source and characteristics of the original wall. While the information from this category of techniques is not as exact as that provided by the previous two categories of techniques, it has the advantage of being potentially available long after the original brick wall is destroyed—when no other technique would work.

If the first two categories of testing techniques investigate the cause of the contamination (i.e., the contaminants themselves, their degradation products, or some other chemicals released along with the targeted contaminants), this third category of techniques targets the effects that contaminants leave in the release environment, which are referred to in this book as *traces*. Such traces could be various measurable parameters depending on the specific technique. However, such traces are caused by the passage of contaminants and would not be there if contamination had not existed. To be more specific, these measurable parameters referred to as traces include the following:

- *Tiny amounts of certain atmospheric gases or radioactive atmospheric compounds that enter into an aquifer via precipitation water.* These are the measured parameters in the case of the atmospheric tracer technique; this technique estimates the most recent recharge of a groundwater within the leading edge of a contaminant plume as a measure of the minimum age for the contaminant plume (assuming the contaminants got in the groundwater via precipitation water).
- *Microbial DNA composition from the studied environments.* This is the parameter measured when applying DNA fingerprinting; the DNA

composition of the studied environment is the representative trace for contamination in two major situations: (1) when contamination is caused by microorganisms (e.g., bacteria, fungi), in which case the microbial source may be tracked through the DNA composition of the studied environment; and (2) when the passage of chemical contaminants through the studied environment determined changes in the composition of environmental microbial communities, these changes are reflected in the environmental DNA composition, which may help establish contaminant passage after contaminants are long gone from the studied environment.

- *Tiny amounts of contaminant composing elements left in tree tissue (growth rings).* These are the measured parameters in the case of the tree-ring fingerprinting (dendroecology) technique; when contaminants pass within tree root zones, they would inevitably be absorbed into trees, leaving elemental markers in the trees' wooden tissue formed in the year when contamination entered the tree. Note that while small amounts of the contaminants may be retained in tree wooden tissue, the dendroecology technique is based on measuring one or more of the composing elements of the original contaminant (or metals when contaminants are metals) in the tree's wooden tissue. This technique provides a reliable and sensitive way for age-dating a large variety of contaminants and for confirming sources.

This chapter reviews each of the three techniques mentioned. As in previous chapters, the material is organized as a practical guide to help professionals understand the available techniques and decide when to use them in forensic and other investigations.

6.2 Atmospheric Tracers

The forensic technique based on the use of atmospheric tracers consists of testing the groundwater concentration of a series of compounds (i.e., radioactive elements and anthropogenic gases) present in the atmosphere in trace amounts to determine the age of a dissolved groundwater contaminant plume. A minimum plume age is inferred based on groundwater age. Specifically, the groundwater age is deduced based on the groundwater concentrations of atmospheric tracers, which are considered to be representative of their concentrations in rainwater (and thus in atmosphere) at the time of the last groundwater recharge. When the tested groundwater sample is taken from within the leading edge of a dissolved contaminant plume, that age is considered representative for a minimum age of the contaminant plume.

The age of the contaminant plume is not exact but rather reflective of a minimum age because the released contaminant transport to groundwater may be affected by natural processes such as biodegradation, dispersion, or adsorption to aquifer matrix, which may ultimately delay the contaminant transport into the aquifer as compared to the transporting rainwater. Obviously, several assumptions are made, and a series of conditions needs to be met for this age-dating technique to work properly. The many limitations and factors affecting this technique, including specific types of sampling, should be carefully considered before its practical application and are discussed in detail in a following section.

Recommended readings related to the use of the atmospheric tracer technique in environmental forensics include the following:

- The materials by Balouet et al. (2007a), Oudijk (2003, 2005), and Oudijk and Schmitt (2000)
- Articles and materials from the U.S. Geological Survey (USGS) website:
  - For a method overview, http://water.usgs.gov/lab/presentations/dating_young_groundwater
  - For tritium/helium analysis, including details on sampling and analysis, http://water.usgs.gov/lab/3h3he/
  - For the chlorofluorocarbon [CFC] analysis, including details on sampling and analysis, http://water.usgs.gov/lab/chlorofluorocarbons/
  - For SF_6 [sulfur hexafluoride] analysis, including details on sampling, http://water.usgs.gov/lab/sf6/)

6.2.1 Understanding Atmospheric Tracers

Atmospheric tracers are atmospheric radioisotopes or anthropogenic gaseous compounds that have stability and persistence once released into the atmosphere. Regardless of the type, for a compound to be used as an atmospheric tracer, it needs to have well-established atmospheric concentration trends recorded over the last century or so.

Note that atmospheric tracers are typically present in tiny amounts in the atmosphere. However, the advancement in testing technology makes it possible to analyze for tiny amounts of these compounds in the atmosphere and corresponding rainwater and groundwater.

Commonly used atmospheric tracers for groundwater and contaminant age-dating include the following:

1. **Radioisotopes such as tritium (^{3}H), helium (^{3}He), and krypton-85 (^{85}Kr).** Tritium was introduced into the atmosphere in the 1950s through the hydrogen bomb detonation/testing. Based on recorded trends as shown in Figure 6.1 and as recorded in the literature (Oudijk, 2005):

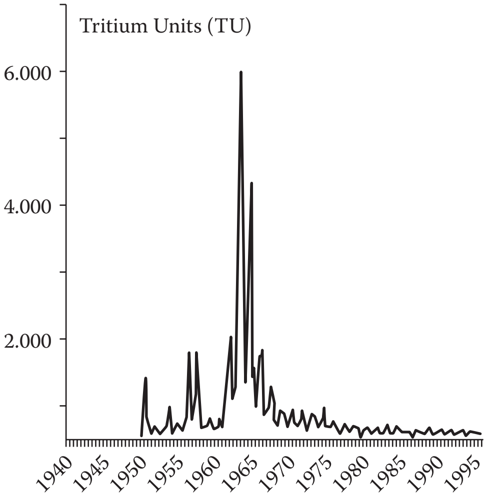

FIGURE 6.1
Tritium concentrations in the atmosphere. Tritium patterns are provided for general information only. (Adapted from Balouet, J.C., and Oudijk, G. 2006. *Claims J.* **18**(1): 1–18; and Cook, P., and Herzog, A. 2000. *Environmental Tracers in Subsurface Hydrology*. Kluwer Academic Press, Norwell, MA. Please consult original references for a more detailed representation.)

- Prior to 1953, rainwater and groundwater contained very little tritium concentrations, less than 0.5 tritium units (TU); note that 1 TU corresponds to 1 tritium atom per 10^{18} hydrogen atoms).
- Post-1953, rainwater- and groundwater-recorded tritium concentrations were higher than 10 TU.
- Water with tritium concentration between 0.5 TU and 10 TU may be a mixture of pre- and post-1953 water.
- Tritium concentration in rainwater and groundwater reached a peak in the mid-1960s, after which its concentration sharply decreased; thus, tritium may not be used to age-date more recent plumes (within the last decade, for example).

2. **Anthropogenic gaseous compounds such as CFCs** (also known as "freons") **and SF_6** (sulfur hexafluoride). The CFCs and SF_6 increased steadily in concentrations through the mid- to late twentieth century, as shown in Figure 6.2:
    - CFCs are stable synthetic (manufactured)[1] chemicals formulated in the United States since the 1930s. CFCs appeared in the atmosphere in the first half of the last century and then increased until the 1990s (see more on the USGS website: http://water.usgs.gov/lab/software/air_curve/). The following observations apply:

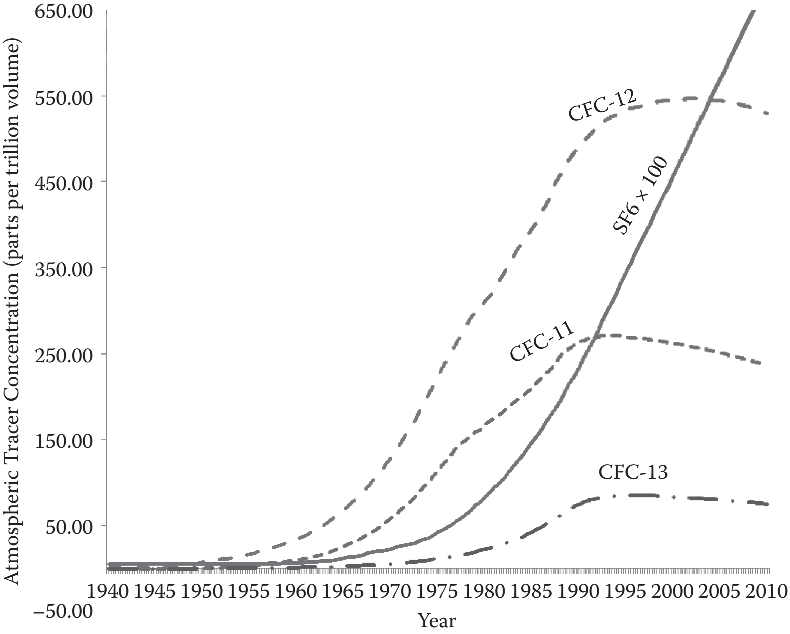

FIGURE 6.2
Atmospheric concentrations of anthropogenic gaseous compounds. (Drawing based on data provided on USGS website: http://water.usgs.gov/lab/software/air_curve/.)

  - CFCs started being produced in the 1930s (e.g., CFC-12 started being produced in 1931, while CFC-11 started being produced in 1936).
  - After 1940, the atmospheric and corresponding groundwater concentrations of all CFCs increased (with an abrupt increase recorded after 1960) until the 1990s. Then, their concentrations started a slowly decreasing trend likely due to their decreased use.
- SF_6 is also a manufactured product; its atmospheric and corresponding groundwater concentrations also had sharp increases after the 1960s; however, compared to CFCs, SF_6 atmospheric concentrations are about 100 times lower, but keep increasing.

6.2.2 Method Principle and Steps

6.2.2.1 Method Principle

By testing the groundwater concentrations of atmospheric tracers, the age of the groundwater can be calculated based on the recorded atmospheric tracer's concentrations in air with well-established patterns during previous years. The idea is that the groundwater concentrations of atmospheric tracers should be reflective of the rainwater concentrations at the time of the last groundwater recharge (Ekwurzel et al., 1994; Cook and Herzog, 2000; Rademacher et al., 2001). Moreover, the rainwater concentrations of atmospheric tracers should be reflective of their atmospheric concentrations at the time when rain was formed and fell on the ground. Therefore, by determining the atmospheric tracer's concentration in a dissolved groundwater plume, the age of the contaminant plume would be no older than the age of the groundwater if the tested sample is taken for the very leading edge of the plume. So, the age of a dissolved contaminant plume should be considered equal to or older than the age of transporting groundwater, which can be inferred based on the atmospheric tracer's concentrations (the year corresponding to their corresponding atmospheric concentrations). Of course, a main condition is that the main pathway through which the contaminant reached the groundwater table was via infiltration with precipitation water.

6.2.2.2 Affecting Factors and Conditions

For an accurate dissolved plume age calculation, the atmospheric tracers should be determined in the very leading edge (both horizontally and vertically) of the dissolved groundwater plume, and a series of other conditions should be met, including the following (Balouet et al., 2007a):

- The groundwater sample should not be collected from within a fractured rock system (which may contain water of different ages mixed within the fractures) to avoid mixing of groundwater of different ages in the collected sample.
- The groundwater aquifer should not be impacted by local sources of the atmospheric contaminant used.
- Cross-contamination of the groundwater sample during collection and transport should not occur.
- The collected groundwater sample should be representative for the rest of the aquifer.
- The atmospheric contaminants should not have been affected by any processes that could have occurred in the aquifer and resulted in any significant change of their rainwater concentrations.
- Sampling should be done with adequate equipment, which may be different from that used for typical groundwater sampling.
- The analytical technique used for atmospheric tracer chemical analysis should be sensitive enough at the tiny contamination amounts expected to be associated with rainwater and the atmosphere.

As mentioned, even when groundwater plume samples are correctly collected from the leading edge and the conditions mentioned are considered to have been met, the calculated plume age is reflective of a minimum age and not necessarily of an absolute age. Although not as precise as other age-dating methods, this technique may be all that is needed at sites where the following is the question: Is the release more recent or older than a certain number of years?

More details related to method limitations and influencing factors to be considered when applying this technique are included in the next section.

Note that if such tracers are not found while employing a sensitive method (e.g., with detection limits within the parts-per-trillion range), then the groundwater's last recharge date is deduced as before the known date of introduction into the global atmosphere of the used tracers. On the contrary, if some amounts are found, then one can use published trends to check what timeframe best fits the amounts found. It should be noted that the timing deduced is the timeframe when the tested groundwater was last recharged.

6.2.2.3 Method Steps

From a practical perspective, the atmospheric tracer's age-dating method for dissolved groundwater plumes involves the following steps:

1. **Screening for method feasibility and detailed planning for adequate sampling and analysis.** This technique requires particular sampling and analyses, and even small deviations from the method requirements could result in inaccurate time estimates or unusable results. More than with many forensic techniques, this one needs a lot of planning and consideration before the actual field sampling can occur. It is recommended to go through two preliminary steps before the actual method deployment:
    a. First, the forensic scientist should screen the particular site conditions to evaluate if the atmospheric tracer's age-dating is feasible for any particular case/site. At this stage, the scientist needs to have a profound understanding of method principle, limitations, and potentially affecting factors as well as of the environmental conditions and history of the site where the method is considered to be deployed. A bullet point checklist may be helpful in this respect. The list should ideally contain every limitation and potentially affecting factors (as described/listed previously and in more detail in sections on limitations that follow). "Red flags" should be raised for any condition that is not met in any particular case. Ideally, all conditions have to be met for the atmospheric tracer method to be deployable. However, in some cases, exceptions may be allowed as long as the overall effect of a certain condition/factor that is not met would not have a significant impact on the resulting age-date calculation. As with many forensic techniques, the scientist's judgment, knowledge, and

experience should be used to evaluate the impact of potentially limiting factors on the overall method results. For example,[2] a site located near a nuclear power plant will certainly not be feasible for groundwater plume age-dating using tritium since higher tritium background levels in groundwater would likely be elevated in such a situation. Such red flags cannot be overcome and will have a significant impact on overall results. The anthropogenic gases might be used in that case, as long as other limiting conditions are met. However, when both local sources of tritium and anthropogenic gases (e.g., CFCs and SF_6) are suspected to affect the aquifer to be tested, the atmospheric tracer technique will simply not work and should not be attempted. On the other hand, if potential issues with sample representativeness for the overall aquifer conditions are raised based on evaluation of site-specific conditions, the atmospheric tracer method may not be immediately dismissed. Collection of multiple samples and further evaluation of specific ways to increase sample representativeness should be considered before dismissing the atmospheric tracer application. The same might apply if there are issues related to identification of the leading edge of the plume (both vertically and horizontally). In this case, one can perform additional groundwater testing to confirm the location of the leading edge before planning and deploying the atmospheric tracer's age-dating method.

b. Second, once the method feasibility is established, detailed planning should ensure that a series of conditions is met, including, but not limited to, the following:

    (1) The leading edge of the plume is identified and targeted.

    (2) Adequate sampling devices and containers are used. Note that depending on the exact atmospheric tracer to be tested, distinct sampling devices may need to be used. To ensure adequate equipment and devices are used, it is recommended to contact the specialized laboratory to be used and check with them to make sure adequate sampling is performed; also, useful information for sampling of each main type of atmospheric contaminant is provided on the USGS website (see specific web addresses provided previously in the recommended readings section).

    (3) Cross-contamination during sampling or transport is minimized, and blank indicator samples should always be included to confirm that no cross-contamination occurred.

    (4) Adequate laboratory and analytical testing techniques are used. It is especially important to check with the laboratory

concerning the detection limits for the targeted atmospheric tracers and compare them with value ranges of respective tracers in the atmosphere and corresponding groundwater (if a certain timeframe is targeted or expected, that may also help define acceptable detection limits).

    (5) Potential interferences are considered. This should be applicable for any testing technique but might be more stringent in this case since the analysis deals with extremely low levels. The scientist needs to consider what other contaminants are present in the tested water and evaluate if their presence could affect the result of tracer analysis. Consulting with laboratory personnel may also help in this situation.

2. **Collection of adequate groundwater samples** is the next step once the feasibility study and the detailed planning are performed. As discussed in the following, once the specific atmospheric tracer to be tested is established, information on the adequate sampling and analysis can be found on the USGS website and literature sources and should always be double-checked with the laboratory that will perform the actual analyses. For example,[3] consider the following:

    a. When tritium is the targeted atmospheric tracer, the following sampling devices are recommended: a special copper sample tube[4] (used in duplicate) along with two 500-cc bottles (either safety coated with polycone seals or high-density polyethylene bottles with polycone seals) for each sample to be tested (see specific indications at http://water.usgs.gov/lab/3h3he/sampling/). The water collected in the duplicate copper sample tubes would be tested for helium and neon, and the ^{3}He/^{4}He isotope ratio (δ^3He) of dissolved helium determined. (Note that, as detailed in the discussion of data evaluation and interpretation, all these analyses are needed for an accurate calculation of the total atmospheric tritium. Regarding the two 500-cc bottles, these are actually used for tritium determination by helium ingrowth.) Detailed instructions related to sampling requirements, handling, storage, and shipment of collected samples, as well as analysis and communication of results, are provided on the USGS website (http://water.usgs.gov/lab/3h3he/sampling/).

    b. When CFCs are the targeted atmospheric tracers, the recommended sampling devices may differ depending on the analytical method to be used, including the following:

        (1) CFC bottle method: Water samples may be collected in glass bottles with a special foil-lined cap (see more details on the USGS website, http://water.usgs.gov/lab/chlorofluorocarbons/sampling/bottles/); useful sampling tips are also provided on

    the USGS website (http://water.usgs.gov/lab/sf6/sampling/tips/index.html).

    (2) CFC ampoules method (old method): Fused borosilicate ampoules may be recommended if archiving of water samples for CFCs or other volatile organic compound (VOC) analysis for periods of more than 6 months is required (more information on groundwater sampling, including detailed field instructions and apparatus setup, can be found on the USGS website: http://water.usgs.gov/lab/chlorofluorocarbons/sampling/ampoules/); in addition, useful information on troubleshooting CFC sampling may also be found on the USGS website (http://water.usgs.gov/lab/chlorofluorocarbons/sampling/troubleshooting/).

    (3) Note that the USGS website also provides adequate information related to the use of SF_6 as a tracer (see, for example, the following: http://water.usgs.gov/lab/sf6/lab/analytical_procedures/index.html).

3. **Analysis** of the collected groundwater samples using adequate analytical testing.[5] Once the samples are collected and shipped to an adequate laboratory, the actual analyses are performed using adequate analytical techniques (with very low detection limits) and equipment. For example, an analytical laboratory listed on the USGS website (for tritium analysis) is Lamont-Doherty Earth Observatory (with the following address: Corner Building, 61 Route 9W, Palisades, NY 10964, USA). Note that this laboratory is provided here as an example; other laboratories may also perform atmospheric tracer analyses, and information may also change with time. Therefore, it is recommended to check the USGS website and other suitable Internet and literature sources to determine the most suitable analytical laboratory for use in any particular situation.
4. **Data evaluation and interpretation.** As with most forensic techniques, the last but not least step involves the evaluation and interpretation of results. For this particular technique, the results evaluation uses different strategies based on the type of tracer used. Next, we provide more information on data use for estimating the age of a groundwater dissolved plume when tritium and CFCs, respectively, are used as tracers.

6.2.2.3.1 Data Evaluation When Tritium Is the Atmospheric Tracer Used for Age-Dating

Tritium (^3H) is the radioactive isotope of hydrogen. Being radioactive, tritium disintegrates into the helium isotope (^3He). The recorded half-life of tritium is 12.43 years. Thus, to accurately determine the original tritium concentrations in the atmosphere and corresponding rainwater, the concentrations of both tritium and ^{3}He should be measured in groundwater. However, these measurements are not enough because ^{3}He is also introduced into the atmosphere by the radioactive decay of uranium and lithium from rocks or rock fragments. Therefore, to evaluate the total original tritium in the atmosphere the ^{3}He that originates from tritium decay versus the other ^{3}He sources needs to be distinguished. To do this, the concentrations of another helium isotope (^{4}He) along with the concentration of another gas, neon (Ne), must also be determined in the groundwater sample. These measurements are needed for the calculation of the ^{3}He derived from tritium decay (also known as tritiogenic helium or $^{3}He_{tri}$) using the known Ne/^{3}He and ^{4}He/^{3}He ratios in the atmosphere. Specific methods to estimate the $^{3}He_{tri}$ concentrations using the groundwater concentrations of ^{3}He, ^{4}He, and Ne are provided in the literature (Schlosser et al., 1988; Szabo et al., 1996).

When tritium is used as an atmospheric tracer, the concentrations of tritium, along with the concentrations of two isotopes of helium (^{3}He and ^{4}He) and the concentration of neon (Ne) should all be measured in groundwater. Therefore, the laboratory should provide all these results. These results provided by the laboratory should be entered in the following equation (based on the radioactive decay equation; see Chapter 4) to calculate the groundwater age:

$$t = (T_{1/2}/\ln 2)\ \ln(1 + {}^{3}He_{tri}/{}^{3}H),$$

where t is groundwater estimated age, $T_{1/2}$ is the half-life of tritium (i.e., 12.43 years), $^{3}He_{tri}$ is the concentration of helium that resulted from the radioactive decay of tritium,[6] and ^{3}H is the concentration of tritium measured from the groundwater.

Note that it may not always be necessary to calculate the $^{3}He_{tri}$ concentration (considered a corrected ^{3}He concentration) for age-dating groundwater. In some cases, when the ^{3}He originating from other sources than tritium is indicated to be low, the uncorrected and corrected groundwater ages would be similar or very close (Balouet et al., 2007a). Obviously, the uncorrected age assumes that all the ^{3}He in the sample is derived from tritium (and this should be equal to $^{3}He_{tri}$). To determine the potential presence of ^{3}He originating from sources other than tritium (also known as terrigenic helium), one can compare the ^{3}He and ^{4}He concentrations in the tested groundwater sample with the known value of the ^{3}He/^{4}He ratio of the terrigenic helium of 2×10^{-8} (Balouet et al., 2007a).

6.2.2.3.2 *Data Evaluation When CFCs Are the Atmospheric Tracers Used for Age-Dating*

The detected groundwater CFC concentrations reported by the laboratory should be converted to their corresponding atmospheric concentrations based on the known recharge temperature for the area of the site (Busenberg and Plummer, 1992). If specific recharge temperature is not tested for, the mean annual temperature in the study area may be used instead.

Thus, in the case of CFCs, the recharge temperature should always be considered as it affects the amount of CFCs that transfer into rainwater from the atmosphere. The lower the recharge temperature, the lower the amount of atmospheric CFCs transferred into rainwater will be. Published graphs exist for various CFCs showing the relation between their groundwater detected concentrations and recharge temperature along with corresponding years (see, e.g., Busenberg and Plummer, 1992, or Balouet et al., 2007a). Such graphs may be used to convert the detected groundwater concentrations of CFCs into their likely atmospheric concentrations and corresponding year for the respective atmospheric concentration. That year should be extracted from the year of sampling to calculate groundwater age as a minimum age for the dissolved contaminant plume. For example, according to the graph presented by Balouet et al. (2007a) (after Busenberg and Plummer, 1992), the following holds:

- If the groundwater concentration of CFC-11 is determined to be 600 pg/kg, for a recharge temperature of 2°C, the corresponding year of recharge would be approximately 1975; if the groundwater sample was collected in 2012, then 2012 – 1975 = 37 years would be the age of the groundwater and also the minimum age of the plume.
- For the same groundwater concentration of 600 pg/kg obtained at a different site with a recharge temperature of 16°C, the corresponding recharge year would be approximately 1990; if the sample was collected in 2012, then 2012 – 1990 = 22 years would be the resulting groundwater age and also the minimum age of the contaminant plume.

The hypothetical example provided denoted how important it is to consider the correct recharge temperature when calculating the minimum contaminant plume age based on concentrations of CFCs detected in groundwater.

Note also that calculating and comparing the ratios of the three main CFCs in groundwater may provide insights regarding whether the sample contains water of different ages (Balouet et al., 2007a).

6.2.3 Applications, Limitations, and Recommendations

6.2.3.1 Applications

While the atmospheric tracer method has many applications in hydrogeology (e.g., determining groundwater flow paths, recharge dates,[7] residence times, and susceptibility to contamination, as well as calibrating groundwater flow models), the main application in environmental forensics relates to age-dating dissolved contaminant plumes. Although this is an indirect age-dating method that results in a minimum age rather than the exact age of the contaminant plume studied, this method is particularly powerful for contaminants such as chlorinated solvents, for which few techniques are available for age-dating (e.g., historical document review, chemical fingerprinting in the case of 1,1,1-TCA (1,1,1-trichloroethane) [see Chapter 4], or modeling).

Published case studies that deal with the application of the atmospheric tracer technique in environmental forensics include the following:

- estimating the minimum age of a chlorinated solvent plume in groundwater with CFC and tritium methodologies (Oudijk, 2003);
- a minimum age estimate for a contaminated groundwater (Oudijk, 2005);
- application of SF_6 age-dating of groundwater, along with concentration data (of this tracer) for natural and anthropogenic sources (Busenberg and Plummer, 2000).

Two hypothetical case studies are presented next to exemplify typical environmental forensics applications of the atmospheric tracer technique. While these case studies are not real, the general settings and type of results may be expected in real case studies, and I have observed them in real cases.

HYPOTHETICAL CASE STUDY 6.1
Investigating Dry Cleaner Contributions to a Regional Groundwater Plume

In this hypothetical case study, let us consider a large PCE (perchloroethane)/TCE (trichloroethane) plume in the regional aquifer at about 100 ft below ground. The plume originated at a Superfund site located upgradient of many industrial establishments within a heavily industrialized area of a big city. Many of the downgradient facilities with recorded releases of PCE or TCE were overlying the regional plume and were considered as potentially responsible parties (PRPs) to the regional PCE/TCE plume. Within these PRPs, it was a dry cleaner that operated within the last 30 years and had recorded PCE releases and contamination of shallow soil and groundwater (at about 30 ft bgs [below ground surface]) above the regional groundwater plume as shown in Figure 6.3. The dry cleaner is our hypothetical client that hired us to conduct a forensic investigation to determine if indeed its shallow releases could have reached the deeper aquifer contributing to the regional water plume.

We could not use contaminant distribution patterns since PCE offers limited chemical fingerprinting possibilities, especially in the absence of degradation products other than TCE (as in this hypothetical case). Even if more degradation products would have been present in the plume, it would have been difficult to fingerprint the dry cleaner PCE versus the PCE in the regional plume. Limited historical evidence from the dry

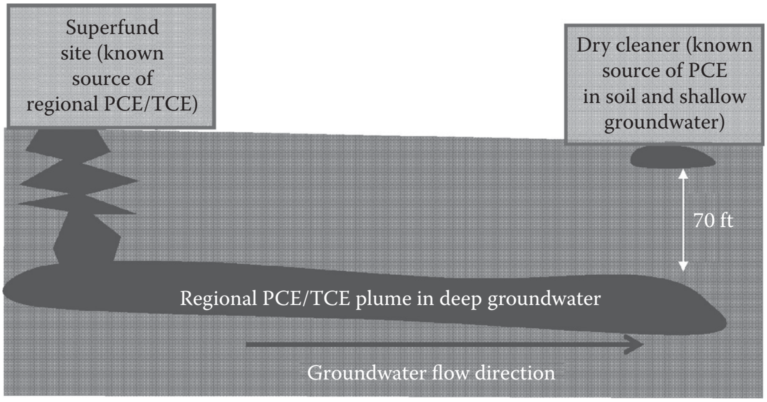

FIGURE 6.3
Schematic representation of a hypothetical case study investigating potential contributions to a regional PCE plume from a dry cleaner with recorded shallow releases.

cleaner's operation also restricted our potential use of signature chemicals to establish any potential contributions.

In this situation, the atmospheric tracer method seemed the only viable alternative to evaluate the dry cleaner's contributions. The idea was to take samples from the leading edge of both regional and shallow groundwater plumes and determine their minimum ages. If the ages would not match or would indicate that the regional groundwater plume was older than the shallow plume, we would gain defensible evidence related to the lack of client contributions to the regional plume. Thus, we first conducted a thorough screening for method feasibility and noticed that all the conditions required for reliable application of atmospheric tracers were met. In addition, both the regional and the shallow plumes were thoroughly characterized during the years, enabling us to determine the exact location of the plume's leading edges. Once the method feasibility was established, we planned the use of CFC groundwater concentrations and prepared the field activities accordingly. Triplicate samples[8] were collected for each main CFC analysis (CFC-11, CFC-12, and CFC-13) and were sent to a specialized laboratory using adequate sampling, storage, transport, and shipping procedures.

The results are shown[9] in Figure 6.4. From data shown in this figure, it is clear that the shallow and regional groundwater plume minimum ages are significantly distinct. Specifically, the shallow groundwater that contained our client's PCE plume was last recharged in about 1995, while the deeper groundwater with the regional PCE/TCE plume (originating at the Superfund site) was last recharged in circa 1965, therefore about 30 years apart from the dry cleaner's plume. It is obvious that the client's much younger plume could not have contributed to the older regional plume. Note that no evidence for dense nonaqueous phase liquid (DNAPL) releases (which could have reached the deeper aquifer without the need of rainwater) at the dry cleaner were found.

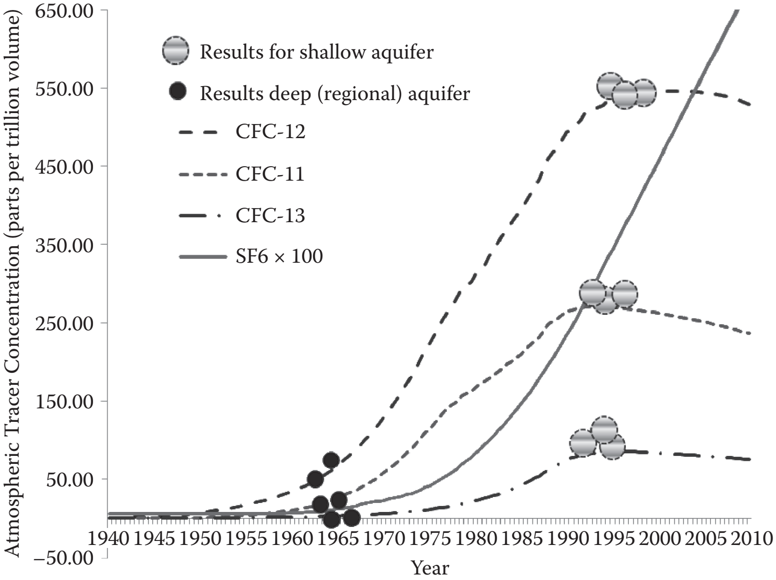

FIGURE 6.4
Example of atmospheric tracer data from a hypothetical case study. (The curves for CFCs and SF6 were drawn based on data provided on the USGS website, http://water.usgs.gov/lab/software/air_curve/.) Sample results (circles) were chosen to demonstrate the presented hypothetical case study.

Based on our findings, the client's property was removed from the PRP list. Overall, the study cost was approximately $20,000, while the results provided the means to avoid litigation and potential costs of millions of dollars in contributions to complex remediation of the large regional plume.

HYPOTHETICAL CASE STUDY 6.2
Establishing Contributions at an Electronic Manufacturing Site Operated by Distinct Owners for the Years in Question

Let us now imagine a hypothetical situation in which two electronic manufacturing companies operated at a site: one from 1976 until 1992 and the other one from 1992 until 2003. TCE and its degradation products were the main groundwater and soil contaminants at the site. Their presence (as traces) in shallow soil denoted that at least some of groundwater contamination was released at the site. The question was when the contamination was released; this would establish liability with one (or both) of the companies.

Historical file review, chemical fingerprinting, and modeling were attempted but did not reveal the answer, mainly due to insufficient data. Therefore, we decided to check the groundwater for atmospheric tracers (specifically tritium and helium) with the idea that the minimum plume age could potentially exclude one of the companies (the more recent one). We first conducted a thorough feasibility study to make sure the atmospheric tracer technique was applicable. While no particular limitations were found, the leading edge of the plume was not known with certainty. Therefore, we first collected additional groundwater samples to evaluate the location (vertical and horizontal) of the plume's leading edge. Once we did this, we were able to apply the atmospheric tracer method. We collected samples in triplicates from the leading edge of the plume. The sampling was planned carefully, consulting with a specialized laboratory. Using the equation presented previously, we were able to calculate the groundwater and minimum plume age, respectively. The results denoted that the last groundwater recharge happened in the mid-1980s. Such data reliably eliminated the second company operating at the site as a contributor to the currently observed groundwater plume. Note that both companies had confirmed historical releases to soil. However, based on atmospheric tracer data, releases from only one company (the first one) did reach the groundwater table, resulting in the currently observed groundwater dissolved plume.

6.2.3.2 Limitations and Recommendations

6.2.3.2.1 Limitations

The following limitations apply to the atmospheric tracer method:

- The method does not provide an absolute contaminant plume age, but rather only a minimum age. However, as shown in the two hypothetical cases presented and supported by the cited literature applications (in this section), obtaining the minimum plume age may be sufficient to solve forensic puzzles in many practical situations. Moreover, the atmospheric tracer method is one of the very few options for age-dating chlorinated solvent plumes.
- Sampling is challenging and quite vulnerable to cross-contamination. For example:
  - Sample cross-contamination with the atmosphere may be common, requiring duplicate or triplicate sampling. This method measures tiny amounts of contaminants in water, which is why the results may be easily changed even when traces of cross-contamination occur.
  - The sampling equipment itself may contain CFCs (from plastic).
  - A series of devices that may be used or worn by the samplers may cross-contaminate the samples, for example (Balouet et al., 2007a):
    - Wristwatches, especially the "glow-in-the-dark" types, may contain tritium and cross-contaminate samples when tritium is used as a tracer (Balouet et al., 2007a).
    - Compasses or similar devices with luminescent dials should be avoided when sampling for tritium in groundwater as these devices may also cross-contaminate the samples.

- Collecting adequate groundwater samples may be difficult or impossible in some cases, such as the following:
    - The leading edge of the plume may not be correctly identified vertically or horizontally, in which case inexact or misleading results may be obtained.
    - Samples should be collected from the deepest portions of the plume, which is not always practically possible. Monitoring wells with very short screens are needed to evaluate the very leading edge of the plume only. However, this creates problems as sufficient sampling volume may not be easily achievable or may be practically impossible.
- Any mechanisms that may transport contaminants to the groundwater table without the need of percolating rainwater will render the method inapplicable. For example, the following situations will likely not be feasible for the use of the atmospheric tracer method:
    - The contaminant was released in the subsurface at the water table level or below the water table.
    - The contaminant is a DNAPL (e.g., chlorinated solvent) and free-phase DNAPL was observed at the site or is suspected based on contaminant concentrations in the groundwater plume (e.g., general rule of thumb related to the fact that when contaminant concentration in groundwater exceeds 1% of its effective solubility, DNAPLs might be present and are suspected; see EPA [Environmental Protection Agency], 1992).
- Any subsurface process resulting in the change of the original tracer concentration (from rainwater) after it reaches the aquifer could invalidate the method application resulting in inaccurate results. For example:
    - Potential biodegradation of the tracer compounds, such as CFCs in groundwater, especially under anaerobic conditions, may alter the results and should be considered on a case-by-case basis.
    - Other factors that may determine a decrease in tracer concentration in studied groundwater include raising the water table (which could result in mixing water from two aquifers).
    - Mixing of groundwater of distinct ages may occur in subsurface environments depending on specific geologic and hydrologic conditions.
- Any factor that may influence the groundwater recharge process may affect the method results. For example, the recharge process may not be uniform in urban settings.
- The presence within the sample collection area of localized potential sources[10] of the tracer to be used may render the method unusable

since it would change the local atmospheric tracer's concentration as compared to the generally recorded trends used for age calculations. Examples of potential localized sources of atmospheric tracers include the following:

  - Nuclear power plants are potential sources of some of the atmospheric tritium.
  - Some rocks, especially those with significant lithium concentrations, exhibit tritium concentrations not related to thermonuclear explosions; this tritium is known as geogenic tritium, which might be a concern when concentrations are above 0.1 TU (generally not commonly recorded).
  - Some igneous rocks, in particular granites, contain higher-than-usual ^{3}He concentrations with potential to have an impact on the age calculations.
  - Urban environments (especially highly populated areas or industrial regions) may have higher amounts of atmospheric CFCs.
  - Septic systems may provide sources of CFCs (e.g., from household plastics).
- The method would not be valid under extreme flow velocities or dispersion coefficients (Schlosser et al., 1989).
- The method may not be applicable for more recent and future releases. Tritium concentrations, for example, have been declining since the ban on atmospheric thermonuclear explosions in the 1960s (after about 1964).
- Certain subsurface geologies may not be conducive for method application, including sites underlain by heterogeneous formations such as glacial tills or fractured rocks.

6.2.3.2.2 General Recommendations

As just discussed, the atmospheric tracer technique has many limitations and should be applied after extensive review and understanding of each site's potential influencing factors. As mentioned when presenting method steps, a feasibility assessment for method applicability should be initially performed through careful consideration of various potential limiting factors and evaluation of their impact on the overall results. In addition, once the method is found to be applicable, a careful evaluation of sampling devices and techniques needs to be performed, preferably by consultation with a specialized laboratory to perform the analyses. Careful sampling planning and adequate preparation will ensure method reliability and, ultimately, its defensibility under the scrutiny of the court of law. These are the main recommendations for the successful application of atmospheric tracers in age-dating dissolved groundwater plumes.

6.2.3.2.3 Specific Recommendations

Additional specific recommendations include the following:

- Having an open mind for potential influencing factors that may not be listed in textbooks but could occur in a specific case; understanding the method principle and the main reasons behind each main type of limiting factors could help determine site-specific factors that may not be captured within a textbook. The way the information is presented here is designed to enable the understanding of listed and unlisted potential influencing factors. New processes and mechanisms related to contaminant fate and transport are discovered; therefore, the limiting factors listed in this or other books may not be exhaustive. The forensic scientist should always filter the information and obtain decisions on a case-by-case basis based on both knowledge and experience.
- When sampling is to be done in urban environments, a detailed understanding of site settings is needed to evaluate any potential influence on the groundwater recharge. Factors such as underground utilities, foundations, or hydraulic controls should be understood in the method feasibility step.
- A thorough understanding of geologic and hydrologic conditions within an area is also recommended at the feasibility step level.
- Any devices that may result in sample cross-contamination should be avoided during sampling and for at least a week in advance of sampling because some devices can cross-contaminate with tritium (e.g., glow-in-the-dark wristwatches) (Balouet et al., 2007a).
- Using accurate recharge temperatures is key when CFCs are used as tracers, and direct measurements should be preferred rather than the reported mean annual temperature.
- When bubbles are observed during sampling, the samples may not be usable because such bubbles may strip the helium from the sample, thus rendering any results based on tritium concentrations inaccurate.
- Generally, sites more conductive to the use of the atmospheric tracer technique are those underlain by high-permeability, well-sorted, well-rounded sands.

Hints for Effective Forensic Deployment of the Atmospheric Tracer Technique

- **A thorough understanding of site conditions and potential limiting factors** is necessary before deciding if this method is feasible in a particular case.

- **Extremely careful planning and execution of sampling are necessary** since the method deals with extremely low amounts of contamination that may be easily significantly changed via cross-contamination or other influencing factors.
- **The groundwater samples should be collected from the very front edge of the contaminant plume.** This includes both vertical and horizontal planes; typically the farthest away (from the main source) and the deepest plume regions should be used.
- If radioisotopes are used as tracers, the method may not be applied near a nuclear powerhouse; similarly, when other tracers are used, **the method may not be applied in areas with an elevated background of the tracers.**
- **The recharge temperature and elevation may be considered for data interpretation** since the solubility of tracers is influenced by such factors (Solomon et al., 1998). The same is true for geology/lithology conditions.
- **The formation of air bubbles** (e.g., in fine-grained sediments and fractured rock) **may affect the age calculations** and should be carefully looked for; specifically, isotopic fractionation may occur (for isotopic tracers) if bubbles are formed (during the sampling) and should be considered.
- Atmospheric recorded **concentrations of tracers may be higher in urban areas.**
- **Groundwater recharge may not be uniform** and therefore could affect the age estimate.

6.3 DNA Fingerprinting

DNA fingerprinting is a generic term referring to a series of techniques that investigate the compositional patterns of the genetic material (deoxyribonucleic acid or DNA) extracted from environmental samples (e.g., soil/sediment, water, or dust) to track the source of microbial pollution or to evaluate the microbial population within certain contaminated environments. Typically, the extracted DNA derives from all the microorganisms (both dead and alive) present in the examined sample. Usually, a large number of microbial species (e.g., bacteria, fungi) are present in a sample (most of which may not be isolated/cultured in the lab), resulting in a large variety of DNA patterns/sequences. The community of microorganisms from a certain environment is referred to as its *microbiota*.

In environmental forensics, DNA fingerprinting techniques have two main areas of application:

1. **Microbial source tracking**. Referring to the use of DNA fingerprints to identify the source of microorganisms in a sample, microbial source tracking is typically of interest when pathogen microorganisms contaminate a water source or other environmental media that may ultimately affect human health.
2. **Contaminant source tracking.** This refers to the evaluation of the source and passage of contaminants through the environment based on expected changes in microbial populations reflected in the DNA fingerprints of sampled media. Note that while this application holds great promise, there have not been published cases.[11]

Recommended readings providing useful reviews of DNA fingerprinting techniques and their proven and potential use in environmental forensics include several publications (Petrisor et al., 2006; Balouet et al., 2007a; Cano, 2010) and an editorial (Petrisor and Kitts, 2004).

6.3.1 Method Principles

Microbial source tracking is a straightforward application. DNA fingerprints from environments contaminated with pathogen microorganisms are compared with suspected sources or known microbial fingerprints of species of interest. Matches between samples indicate a common source, and matches with one or more suspected sources help to defensibly identify the actual source(s).

The potential forensic application of DNA fingerprinting methods to track the source and passage of environmental contaminants should be based on the following main principles and observations:

- *Microorganisms are ubiquitous in the environment.* Microorganisms were found even in the most inhospitable environments with extreme conditions (under high pollution, salinity, acidity, etc.)—where no other living beings can survive.
- *Microbial diversity is huge.* This means that the type and proportion of various microbial communities are extremely diverse in differing environments and may be influenced by a large variety of factors. At the same time, there is a degree of similarity in areas with similar conditions (e.g., similar soils).
- *Microbial species have distinct DNA sequences*, which are used as "biomarkers" for species identification. The overall DNA sequence of an environmental sample is a reflection of the type and preponderance of various microbial species present in the sample, resulting in a particular DNA fingerprint.
- *Microorganisms respond to the presence of environmental contaminants.* When pollution is released, it triggers changes in the surrounding

microbial communities in favor of those species that are able to better survive (e.g., by degrading or transforming the released contaminant).

- *Changes in microbial community patterns are reflected in the microbial DNA.* The changes in microbial community structure induced by the presence of contaminants determine distinct DNA fingerprints (sequences) in contaminated versus uncontaminated environments within the same area. These changes may be captured by DNA fingerprinting techniques. Thus, by extracting and analyzing the DNA from environmental samples, distinct patterns may be observed when contamination occurs.
- *Generally, the microbial DNA changes induced by contaminants may be preserved* long after contaminants are gone or degraded. The stability in time of DNA fingerprints has been experimentally pointed out (Horswell et al., 2002). Note that the genetic material continues to be preserved in a sample even after the microbial cells die and are destroyed. Namely, the freed DNA fragments usually adsorb to soil particles, where they can persist for a long time. This is a significant observation for environmental forensics since it may make possible the distinction between an environmental matrix (e.g., soil) that was never polluted versus a medium that was polluted at some point in time. Moreover, DNA fingerprinting techniques should be independent of the physical presence of pollution at the time of sampling because changes in microbial DNA while environmental pollutants were present in the sampled matrix should be preserved after the contaminants passed or are degraded (i.e., not detectable anymore). Thus, the method may be applied at sites that were mitigated, as well as at sites still to be remediated.

Thus, DNA fingerprinting employs a series of experimental techniques that examine microbial DNA extracted from an environmental sample. The resulting DNA fingerprint could be compared between samples and with suspected sources for tracking the origin of microorganisms from the studied environmental sample. In the case of tracking contaminant passage through the studied environment, the resulting DNA fingerprints may be compared with soil from the area artificially contaminated (in the laboratory) with the contaminant source material to establish if contaminants have passed through the studied environment. This may help identify sources and understand the fate and transport of released contaminants.

6.3.2 Method Steps and Examples

There are many individual methods all aiming to obtain the DNA fingerprint of a certain environment. Most of the methods take advantage of automated PCR (polymerase chain reaction), which requires only tiny amounts of sample. Thus, traces (potentially invisible to the naked eye) of pollutants are amenable to DNA fingerprint testing. This highly increases the forensics applicability of DNA fingerprinting, especially in criminal forensics.

The general main steps of many DNA fingerprinting techniques include the following:

- **DNA extraction step.** In most cases, this is the first step of DNA fingerprinting. In a few cases, a step for cultivation of the microorganisms of interest precedes DNA extraction. However, this is a quite restrictive step and usually applies when certain well-characterized microbial groups are targeted for analysis. Thus, in that case, only their DNA would generate the fingerprints.
- **DNA amplification step.** After extraction, DNA may be amplified using PCR, which is a fully automated process, easy to conduct and relatively inexpensive; this step is especially important when the extracted DNA is in such tiny amounts that it cannot be analyzed unless amplified. For PCR to occur, so-called primers are needed. Primers are small snippets of DNA homologous to certain regions in a target gene. For any targeted DNA gene, at least two primers are necessary to delimit a DNA segment targeted for amplification. Note that various primers may be used in the PCR process, depending on which various regions (segments) of DNA will be amplified; thus, various genes may be targeted and amplified as long as adequate primers are identified and used.
- **DNA processing step.** This step usually varies between methods; the aim is to create specific smaller fragments from the DNA to be tested (thereby generating the fingerprints), which is typically done by digestion with so-called restriction enzymes. These enzymes cut the DNA strand between certain base pairs, so the type of restriction enzyme used will dictate where the DNA strand will be cut and thus the type of generated fragments. In some cases, this processing step consists of so-called denaturation of the DNA strand, which splits the double DNA helix into single strands; denaturation may be done by various methods, including heat or enzyme attack.
- **Resulting DNA fragment separation and visualization step.** This is typically performed through a technique called electrophoresis, which separates the various resulting DNA fragments and produces the so-called DNA fingerprints.
- **Data evaluation and interpretation step.** As with any forensic methods, results should be evaluated and interpreted keeping in mind the goal of the forensic investigation. In many cases, evaluation of results consists of comparing resulting fingerprints, which could be done qualitatively (visually, similar to visual comparison of chemical fingerprints resulting from chromatographic data) or quantitatively

(using statistical techniques). For example, DNA fingerprints are compared between samples and with suspected sources. This provides the answers for many microbial source-tracking cases. For contaminant source tracking, comparison of DNA fingerprints may provide indirect evidence related to contaminant passage and sources.

Some commonly employed DNA fingerprinting techniques and their specific uses and main steps are further presented in brief. The goal is to familiarize you with some available DNA fingerprinting techniques and point out their main uses and steps without providing details or explanations related to specific terms that are used when describing the methods. For more information on any of the listed techniques and specific terms used, consult the recommended readings (Petrisor et al., 2006; Balouet et al., 2007a). This book focuses on providing principles so that the reader understands how and when to apply a specific method. Also, the book is intended as a practical guide for understanding how the method results are evaluated and used (or may be used) to solve real-world forensics puzzles. It is, however, recognized that DNA fingerprinting techniques are unique and based on processes with which the typical environmental practitioner may not be familiar. So, more than with other methods presented in this book, for DNA fingerprinting techniques it is highly recommended to consult the specified references to become familiar with various specific terms, processes, and challenges related to microbial DNA testing.

The **terminal restriction fragment length polymorphism (TRFLP)** method is perhaps the most commonly used DNA fingerprinting technique in environmental studies to monitor the type and changes in microbial communities during bioremediation or monitored natural attenuation (MNA). The method is also used in criminal forensics for matching samples of soils from a crime scene with soil traces from a shoe or the clothing of suspects. This method may be fully automated, allowing analysis of large amounts of information in short time. The method steps include the following:

- DNA is extracted from the environmental sample.
- PCR with fluorescently labeled primers is performed. Conserved portions of the 16S rRNA[12] gene are typically targeted for amplification; this may be done with universal or species-specific primers.
- Digestion of the amplified DNA with one or more restriction enzymes is next. Note that problems with incomplete digestion may arise, influencing the resulting fingerprints.
- Resulting fragments (TRFs, terminal restriction fragments) of varying length are separated and detected (the fluorescently labeled fragments only) on an automated capillary-based electrophoresis system. Note that the possibility of TRFs of similar length overlapping exists, resulting in less-accurate patterns.
- The last step is data analysis for peak and potential microbial species identification.

The **amplified fragment length polymorphism (AFLP**) method is typically used in basic diversity and genetic variation studies, as well as in detecting molecular markers, with application in paternity analyses. This method has high resolution and reproducibility and is time efficient. The method steps include the following:

- DNA extraction from the environmental sample
- Extracted DNA digestion using (typically) two restriction enzymes
- Ligation of so-called adapters to the resulting restriction fragments
- PCR selective amplification of the resulting restriction fragments using primers complimentary to the adapter's sequences
- Separation and visualization of the resulting AFLP fragments based on their polymorphism[13]

The **single-stranded conformation polymorphism (SSCP)** analysis method has many applications in microbial ecology and environmental biotechnology, with high potential for environmental forensics applications. The method involves denaturation of DNA and analysis of single strands of DNA. It is simple, inexpensive, and sensitive. Basically, the method has 3D (three-dimensional) features that make it possible to distinguish between DNA molecules of the same size based on their distinct nucleotide sequences and 3D arrangements (structures).[14] The method steps include the following:

- DNA extraction from the environmental sample
- Amplification of extracted DNA by PCR using a phosphorylated and a nonphosphorylated primer (typically targeting a ribosomal RNA [rRNA] gene)
- Denaturation of the amplified fragments by exonuclease digestion
- Separation of the resulting denaturated fragments based on their polymorphism
- Visualization (by silver staining) and interpretation of the resulting patterns via hybridization with DNA fragments or RNA copies (synthesized on each strand)

The **temperature and denaturating gradient gel electrophoresis (TGGE, DGGE)** methods are typically used in microbial ecology and general genetic variations. These techniques are also used to evaluate the impact of environmental contaminants (e.g., metals) on the microbial communities from the studied environment. These methods involve the incomplete denaturation of the amplified DNA fragments, resulting in DNA differentiation based on thermal behavior of fragments with different sequences. These techniques are powerful tools for analyzing complex microbial communities. The method steps include:

- DNA extraction from the environmental sample
- Amplification of extracted DNA by PCR using primers from the targeted gene, which may be 16S rRNA, 23S rRNA, or a species-/genera-specific gene
- Incomplete denaturation of the amplified fragments using
  - a linearly increasing temperature gradient (for TGGE) or
  - a linearly increasing gradient of formaldehyde and urea (for DGGE)
- Separation of resulting denaturated DNA fragments based on fragment polymorphism, with this separation performed in gels containing a linear gradient of:
  - temperature or
  - DNA denaturating agent
- Visualization of the separated fragments

The **randomly amplified polymorphic DNA (RAPD**) method is typically applied to create the "biochemical fingerprint" of an organism and has applications in genetic mapping and studies of population genetic structure. This method has potential for forensic applications and has already been applied in criminal forensic studies to permit quick identification of arthropods and support classical morphological and medicolegal analysis of maggots on a human corpse. For this method, PCR amplification is done using randomly chosen primers. The method is relatively fast (a complete analysis is done in 1 day) and inexpensive. The method steps include:

- DNA extraction from the environmental sample
- Amplification of extracted DNA by PCR with randomly chosen primers (this method "fishes" for potentially relevant genes by amplifying DNA sequences not a priori known)
- Separation of the amplified DNA fragments based on their polymorphism
- Visualization of the separated fragments
- Possible cloning and sequencing of the DNA band of interest

The **restriction fragment length polymorphism (RFLP)** method is typically used for inferring evolutionary trees or assessing the phylogeographic structure of populations. This is one of the few DNA fingerprinting techniques that does not use PCR for amplification of extracted DNA (so it requires large amounts of extracted DNA). Basically, RFLP is a non-PCR alternative to the AFLP method discussed previously. This method involves laborious steps, and not only is it expensive (not amenable to automation), but it also has some advantages, such as high stability and reproducibility. The method steps include:

- DNA extraction from the environmental sample
- Digestion of extracted DNA using endonuclease restriction
- Separation of the resulting restriction fragments
- Transfer of restriction fragments to a nylon filter by Southern blotting
- Hybridization of transferred fragments to a locus-specific radiolabeled DNA probe
- Visualization of DNA fragments using autoradiography

The **ribotyping**, with or without PCR, method has widespread use in microbial source tracking, with well-established applications in tracking the source of fecal pollution in water by discriminating between human and nonhuman forms of *Escherichia coli,* as well as distinguishing between *E. coli* from major animal groups. This is one of the few techniques in which initial cultivation of targeted microorganisms (in the lab) is needed (which subsequently limits applicability to only the well-characterized microbial groups). The method is commercially available and relatively inexpensive (with costs in the ballpark of $250–$500 per sample[15]). However, it is also a time-consuming procedure requiring highly skilled technical staff and specialized equipment. Ribotyping main steps are as follows:

- The microbial isolate is cultured, targeting the organisms to be studied.
- Culture DNA is extracted.
- The extracted DNA is digested with one or more restriction enzymes.
- The digested DNA fragments are separated and analyzed by Southern blotting or PCR followed by a gel electrophoresis.
- DNA patterns are analyzed by cluster analysis; species identification is based on a sample pattern's degree of matching to the source species' patterns.

6.3.3 Applications, Limitations, and Recommendations

6.3.3.1 General Applications

DNA fingerprints obtained from the studied environment through various fingerprinting techniques may be used for the following general forensic purposes:

- **Microbial source tracking** applies when pollutants are represented by microorganisms themselves (e.g., fecal contamination of water or food or microorganisms used in bioterrorism). The basis for this particular application is straightforward: As with chemical fingerprints, one can compare the DNA fingerprints from polluted environments with those from suspected sources. Moreover, due to some well-established DNA patterns, the results may be interpreted even without comparison with suspected sources (e.g., distinguishing human vs. animal fecal pollution based on well-established patterns).

- **Contaminant source tracking** applies when the pollutants are represented by chemical contaminants.[16] Contaminant source tracking may be done by comparing the DNA fingerprints of polluted environments with those from suspected sources. In addition, even in the absence of materials from suspected sources, by comparing the DNA profiles from a study area one may be able to determine if they are consistent with one or more sources.
- **Criminal investigations** refer to human crimes when suspects are identified based on matching DNA fingerprints from their clothes or shoes with DNA fingerprints of soil from a crime scene or from where the victim is found. DNA fingerprinting was accepted as evidence in criminal forensics. A typical example consists of using the TRFLP method to match crime scene soil with soil (or traces of soil in stains) from the clothes or shoes of a suspect (Horswell et al., 2002). Another typical example is the use of RAPD for medicolegal analysis of maggots on a human corpse (Benecke, 1998).

6.3.3.2 Specific Applications

Specific applications of DNA fingerprinting methods with relevance for environmental forensic investigations include the following selected examples:

- Tracking the sources of fecal pollution in a South Carolina watershed was performed using the ribotyping method by Scott et al. (2004).
- Differentiation between human and nonhuman sources of fecal pollution (mostly represented by *E. coli)* in water was performed by the ribotyping method (Parveen et al., 1999; Scott et al., 2003).
- Forensics soil comparison was made through the TRFLP method as published by Horswell et al. (2002). These authors tested various scenarios likely to occur in criminal forensics. For example, at a hypothetical crime scene, they compared the DNA fingerprints of a soil sample from the study area with a shoe print and a knee print on jeans made in that soil. They have also looked into the preservation of DNA fingerprints in time, finding out that the fingerprints were mostly preserved over an 8-month period. Sorenson's Index was used to compare resulting soil profiles.

- Source identification of bacteria isolated from amber and age-dating amber was performed through the TRFLP method (Cano and Borucki, 1995).
- Investigation of bacterial community structure and dynamics during a bioremediation experiment in a land treatment unit of soil contaminated with weathered petroleum hydrocarbons at Guadelupe Oil Field, California, was performed using the TRFLP technique as published by Kaplan and Kitts (2004). This study denoted that the TRFLP patterns of pristine versus oil-contaminated sand dune were distinct, proving the effect that contamination had by switching the original composition of indigenous microbial community in those soils; therefore, this application indicates the potential for contaminant passage and source tracking.
- Comparison of surface and subsurface soil bacterial communities was reported using the TRFLP method (LaMontagne et al., 2003).
- Monitoring microbial communities in a series of metal contaminated environments (Petrisor et al., 2006) and detection and monitoring of actinomycetes in different soils (Heuer et al., 1997) was performed using TGGE and DGGE methods.
- Investigation of variations between bovine strains of microorganisms from various areas (Shianna et al., 1998), as well as the study of correlation of profile-based measures of genetic diversity in crayfish from areas with environmental impacts (Krane et al., 1999), were performed using the RAPD method.
- The analysis of microbial community diversity in environmental samples was performed using SSCP (Wagner, 2002).

There are several forensic application possibilities for DNA fingerprinting techniques. Rapid development of the techniques and increased applications in environmental forensics are predicted for the near future.

6.3.3.3 Limitations

The main limitations of DNA fingerprinting methods as they relate to environmental forensics applications include the following:

- The lack of proven applications in contaminant source tracking. Such applications may need proof of concept in the laboratory first, which could substantially add to the overall costs and timing of the forensic investigation.
- The limited commercial availability of many DNA fingerprinting methods.

- The complexity of microbial community structure in various environments with hard-to-predict variations based on potentially many other factors than the contamination sources and passage.
- The limited available "library" of DNA fingerprints from microbial species in various contaminated and uncontaminated environments.
- The limited knowledge of the genetic profiles of genes involved in the metabolization of environmental contaminants could make it hard to develop specific primers to be used in the PCR process to amplify those particular genes; while relevant forensic results may be obtained with primers of typically used genes such as 16S rRNA, targeting the DNA fingerprints of specific genes involved in the metabolization of the contaminants of concern would result in the most reliable and defensible forensic evidence.
- Specific limitations related to various individual methods (see Petrisor et al., 2006) may influence the reliability and defensibility of the obtained evidence and should be considered on a case-by-case basis.

6.3.3.4 Recommendations

The use of source comparison samples is recommended for microbial source tracking. In what concerns contaminant source tracking, apart from typical source comparison samples, the proof of concept on a case-by-case basis is highly recommended. For example, if the investigation relates to tracking the source of PCE at a residential site surrounded by a dry cleaner and other potential PCE sources, DNA fingerprints from the residential site soils and off-site potential sources, along with those from soil (from the residential location studied) artificially contaminated (in the laboratory) with PCE from various potential sources should be obtained and compared. Note that the historical file review along with good knowledge and understanding of contaminant fate and transport should guide in the selection of soil locations to be sampled for representative DNA fingerprints (which would show changes in DNA fingerprints based on contaminant passage).

Another recommendation is to find an adequate laboratory with experience in deploying the DNA testing method of choice and making sure to comply with all the laboratory requirements related to sampling, preservation, and shipping conditions. Since we are dealing with less-common and quite sophisticated testing techniques, it is important to make sure an adequate laboratory exists and is available to test the required samples within the project-specific timeframe. This needs to be established up front, before any other planning occurs. In addition, since these techniques evolve rapidly, it is highly recommended to keep pace with new findings and potential development of a new technique.

Hints for Effective Use of DNA Fingerprinting in Environmental Forensic Investigations

- **For microbial source tracking, comparison samples should be collected from any potential contaminant source in a given area.** This would increase the reliability and defensibility of the forensic evidence even when general knowledge allows the source identification without comparison samples; for example, if the lab assures you that it can distinguish between human and animal DNA fingerprints of a fecal-contaminated water source, it is still recommended to provide comparison samples from sources of both human and animal fecal contamination (e.g., sewage contamination and animal fecal waste from any given farm in the area).
- **For contaminant source tracking in a litigation context, it is recommended not to use the DNA fingerprinting technique unless funds and timing permit the proof of concept in the laboratory** first; as tempting as they may look, DNA fingerprints have not been used in contaminant source tracking, and there is limited published material in this respect. Therefore, the method and the results may be easily challenged in court and possibly eliminated as evidence.
- **Always find the right laboratory and consult with it** before planning DNA fingerprint sampling. Some methods may not be commercially available, while for those that are, the available laboratories may be overwhelmed and not able to perform the analysis in the required time. In addition, sampling requirements may include specific important details that, if not considered, could render the forensic evidence invalid in a court of law.
- **Always check specific limitations and advantages associated with various DNA fingerprinting methods** before deciding which one is better in a given situation.
- **It is highly recommended to have the DNA fingerprinting evidence backed up** by at least another independent line of evidence.

6.4 Tree-Ring Fingerprinting (Dendroecology)

Tree-ring fingerprinting uses the information stored in tree growth rings to forensically evaluate contaminants that get within the tree root zone. Specifically, the technique measures two main parameters of tree rings: (the width and the chemical elemental composition. These two parameters were shown to be affected by various factors, including the presence of contaminants within the root zone, as further explained in the overview of the technique and its principles.

Tree-ring fingerprinting is one of the few “ultimate” contaminant fingerprinting techniques with rare forensic capabilities, including the following:

- High age-dating precision (within 1 year or less)
- Ability to distinguish multiple releases (in time) of the same contaminant at one site
- Lack of effect of the passage of time
- Independence of the physical presence of contaminants at the time of sampling
- High sensitivity to small amounts of contamination
- Straightforward and easy-to-explain evidence provided

This technique also has a series of limitations (especially related to its application feasibility) that are discussed in detail further in this section. However, whenever it can be applied, it provides some of the most accurate and straightforward forensic evidence that can be obtained by any testing techniques to date.

Note that tree-ring fingerprinting is the term used in this book for the emerging environmental forensics application of dendroecology/dendrochronology, which has been published under the generic name of *dendroecology* (Balouet et al., 2007a,b; Balouet, 2005). The term *dendrochemistry* was also used to refer to the forensic application of this technique. The *phytoscreening* and *dendrochemistry* terms refer to specific testing types as part of phytoforensics (discussed further in the section on application). An international research program was initiated aiming to test phytoscreening and dendrochemical methods on halogenated VOCs, fossil fuels, polycyclic aromatic hydrocarbons (PAHs), metals, polychlorinated biphenyls (PCBs), and dioxins. This program was funded by ADEME (the French Agency of Environment and Energy Management) starting in 2010.

This section includes basic information meant to help understand the principles,[17] applications, and limitations of tree-ring fingerprinting, as well as to equip readers with useful recommendations related to practical applications.

Recommended readings for more detailed information and case studies of method applications in environmental forensics include works by the following: Balouet et al. (2007a,b, 2009, 2012); Burken et al. (2011); Balouet and Oudijk (2006); Balouet (2005). In addition, useful information on tree rings and associated scientific applications can be found in the review article by Fritts and Swetnam (1989) and by consulting the following recommended web pages:

- http://phyto-forensics.com/index.html (the PhytoForensics website put together by an international team of environmental forensics professionals in 2012; note that at the time of finalizing this book, this website was still partially under construction).
- http://web.utk.edu/~grissino/index.htm (published by Dr. Grissino-Mayer from the University of Tennessee). This website has comprehensive up-to-date information in the field with many practical illustrated examples; I highly recommend checking various examples of images of tree rings for different species under different environmental conditions and various stressors.
- http://ltrr.arizona.edu/dendroecology (dendroecology page at the University of Arizona has a long tradition in tree-ring research since the establishment of the Laboratory of Tree-Ring Research in 1937 by A. E. Douglass, the founder of the modern science of dendrochronology).
- http://dendrolab.indstate.edu/nadef/. The *North American Dendroecological Fieldweek* (NADEF) page provides information on field and laboratory-based training in tree-ring techniques with different projects and locations each year.

6.4.1 Method Principles and Steps

6.4.1.1 Method Principles

In temperate climates, most trees have yearly growth rings (concentrically arranged rings as seen in the example from Figure 6.5). Typically, every year trees add a new (outer) ring to the trunks. It is well established that tree growth rings could be dated (the topic of a scientific field called dendrochronology), which is generally done for any alive tree by taking a so-called core sample and counting the visible rings from the bark toward the core of the tree. The ring closest to the bark will correspond to the year when the core sample was taken, the next ring will correspond to 1 year earlier, the next one to 2 years earlier, and so on. Note that there are some exceptions to this simple rule, as in special conditions some trees may produce more than one ring per year or no visible ring in 1 year. Therefore, to check for such anomalies and make sure the ring dating is accurate, scientists perform so-called cross-dating between trees of the same species grown within the same general area. More on cross-dating is discussed when presenting the building principles for tree-ring fingerprinting and other dendroecology/dendrochronology applications.

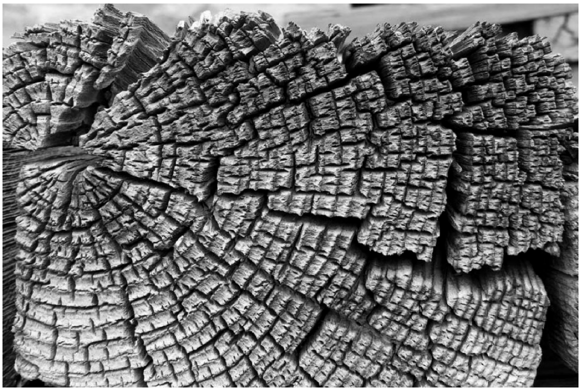

FIGURE 6.5
Tree stump with well-contoured growth rings. (Picture taken in Death Valley, CA.)

Tree-ring fingerprinting measures two parameters related to tree rings: the width of each growth ring and the chemical elemental composition ring by ring. Both of these parameters may be influenced by contaminants that are within the tree root zone. Specifically, the ring width may be reduced as a result of tree growth being affected (stunted) by the presence of contaminants, while the ring chemical elemental composition will likely be changed (have higher concentrations of elements from contaminant composition) due to the presence of contamination in the root zone (which gets up in the trees along with water and nutrients). Why these changes are expected to happen and their relevance to environmental forensics is further explained as follows:

- *Contamination Effect on Tree-Ring Widths.* If contaminants present within the tree root zone are in high enough concentration, their presence may be detrimental to the tree, resulting in stunted growth. The stunted growth may begin immediately or within few years since the contamination entered the root zone.[18] When tree growth is stunted, this would be reflected by production of narrower growth rings for the years when the tree is affected. Therefore, a sudden narrowing of ring width (as compared with the previous year) may indicate the arrival of contamination in the tree root zone. However, data should be interpreted with caution because a tree's stunted growth may be caused by many other factors, such as climate, water supply, nutrient availability, microbial plague, fires, and so on. Therefore, these factors should be taken into account when analyzing ring width patterns. One way to do this is to use "control" trees, which are trees from the same general area and of the same species as those that lie within contaminated zones but that have not been exposed to contamination. More information on the use of control trees in forensic investigations is given in the discussion of method steps.

- *Contamination Effect on Chemical Elemental Composition of Tree Rings.* When contaminants enter the tree root zone, they are absorbed by the roots (along with water and nutrients) and are transported in trees through tree growth cells, which are ring cells formed in that year (i.e., the most recent year of the tree's life). Note that only the most recently formed yearly growth ring is active for transport of water, nutrients, and any associated contaminants (present in the tree root zone). When contaminants pass through tree growth cells, they typically leave traces in the cells. Specifically, some of the composing elements of the absorbed contaminants are retained within the tree-ring cells through which they pass (i.e., corresponding to the year or years when contaminants enter the tree root zone). Thus, by measuring the chemical elemental composition of the rings, when concentration peaks of certain elements are detected, it might be deduced that contaminants containing those elements (for which peaks are observed) have been absorbed in the trees in the particular years corresponding to the growth rings in which peaks are observed.[19] Basically, all the tree rings are analyzed for chemical elemental composition, and those that show peaks (higher concentrations) of any targeted element (e.g., composing element of a contaminant that is studied) are interpreted as denoting the years when contaminants entered the tree root zone. This is the principle behind contaminant age-dating application of tree-ring fingerprinting. If the studied tree is located close to a contaminant source, the year when targeted contaminants entered the tree could be equivalent to the age of the contaminant release.[20]

Therefore, the most prominent application of the tree-ring fingerprinting technique is age-dating of contaminant releases with high precision and accuracy. However, many other forensics and environmental applications are possible using the information from tree growth rings, including tracking the source and passage of contaminants, evaluating the type of release (i.e., abrupt vs. progressive), distinguishing multiple releases, reconstructing historical contaminant plume movement, as well as mapping current contaminant plumes without the need for disturbing and more costly soil borings or monitoring wells. These applications are discussed further in the applications section.

6.4.1.2 Building Principles

The application of tree-ring studies in environmental forensics is a relatively new field. However, as described previously, it is based on well-established and largely accepted scientific techniques and principles proven in many peer-reviewed publications over the years related to the following main scientific fields:

1. **Dendrochronology** or reconstruction of past climates or environmental incidents (such as fires, pest outbreaks) and dating of archeological sites or objects based on the evidence from tree rings (usually encompassing ring width analysis). Various applications of dendrochronology are described in a well-organized manner with illustrative material in "The Ultimate Tree-Ring Web Pages" (http://web.utk.edu/~grissino/references.htm). Dendrochronology is based on the concept that most trees have growth rings that can be dated with precision. Well-established principles of dendrochronology include the following (http://web.utk.edu/~grissino/principles.htm#1):
   - *The uniformitarian principle.* First introduced by the geologist James Hutton in 1785, this principle states that: "The present is the key to the past." Basically, this principle infers that physical and biological processes that link current environmental processes with current patterns of tree growth must have been in operation in the past. Therefore, in the case of tree rings, we can now observe how different influencing factors affect the growth rings, and we can infer that similar factors must have affected the tree rings in the past when similar ring growth patterns are observed for past years (when observations no longer can be made).
   - *The principle of limiting factors.* While a variety of factors can influence tree-ring growth, this principle states that rates of plant processes are constrained by the primary environmental variables that are most limiting. In the case of environmental forensics applications, when contamination from the tree root zone has the dominant effect over tree-ring growth, it will be reflected in the tree growth ring patterns. Basically, when climatic and other factors do not limit ring width/growth in an area, but narrowing of ring width can be observed for the studied tree in contact with a contamination plume, then it can be deduced that the contamination acted as the limiting factor, and the narrowing in ring width can be attributed to the presence of contamination in that year.
   - *The principle of aggregate tree growth* states that any individual tree growth series can be "decomposed" into an aggregate of environmental factors, both human and natural, that affected the patterns of tree growth over time; thus, the pattern of tree rings that can be measured and observed through ring width analysis is the result of the totality of influencing factors. In the case of

environmental forensic applications, when more than one limiting factor exists, such as contamination and unfavorable climatic conditions within the same year, the narrowing of the ring width may not necessarily be attributed to contamination. For such a situation, additional evidence (chemical elemental analysis ring by ring or dendrochemistry) is needed to evaluate contamination effects on tree rings and age-date contamination.

- *The principle of ecological amplitude* states that tree species may grow and reproduce over a certain range of habitats, referred to as its ecological amplitude. For environmental forensics applications, it is recommended to compare trees of the same species that grow within the same general geographical area and thus are expected to have similar ring patterns. When different ring patterns are observed for some of these trees, it can be deduced that those trees with distinct patterns were affected by an additional localized factor in those years. Such a localized factor may be the presence of contamination in the tree root zone.
- *The principle of cross-dating* states that matching patterns in ring widths or other ring characteristics (such as ring density patterns) among several tree-ring series allows the identification of the exact year in which each tree ring was formed. This is an essential principle for age-dating, increasing method accuracy and reliability. In environmental forensics applications, this principle allows comparison between trees of similar species within the same geographical region, with any marked differences in tree-ring patterns potentially attributable to contamination presence in the root zone of exposed trees. This principle also allows the reliable age-dating of studied trees through comparison with control trees to make sure false rings or multiple rings (formed over 1 year), if present, are identified and would not affect the age-dating result. This ultimately increases the defensibility of forensic evidence in court. In addition, this principle allows expanding the years that can be characterized by tree-ring patterns from trees that are alive to dead trees, therefore providing the ability to evaluate older tree rings (up to thousands of years old). Basically, the year when a certain tree died can be deduced by matching its ring patterns with trees alive at the time of sampling, thus going back more years in time. This may apply to remaining tree stumps or to furniture or other objects made of wood. In fact, this is how it is possible to date archeological sites and how one can date objects or furniture made of wood. While the archeological/historical applications of dendrochronology mentioned here have less direct relevance for environmental

forensics, they are mentioned since they may help understand the method, its principles, and overall applications.

- *The principle of replication* states that the environmental signal being investigated can be maximized, and the amount of "noise" minimized, by sampling more than one stem radius per tree and more than one tree per site. This is similar to principles governing other testing techniques that usually involve taking more than one sample to increase defensibility of results. Obviously, since many environmental forensics cases end up in the trial court, ensuring the acquisition of defensible evidence is key to winning the case. For forensic applications of tree-ring fingerprinting, it is recommended (although not absolutely necessary) to sample more than one exposed tree if available and obtain more than one core sample per tree.

2. **Phytoextraction**, or remediation using plants and trees, is based on the observation that contamination from trees or plant root areas enters the trees or plants. Thus, the concept that contamination from the tree root zone is absorbed into the tree is already well established and is the basis for which phytoextraction is possible, as proven through many practical applications (see more information on the U.S. Department of Agriculture [USDA] web page at http://www.ars.usda.gov/is/ar/archive/jun00/soil0600.htm and on the U.S. EPA web page at http://www.epa.gov/superfund/accomp/news/phyto.htm). During many phytoextraction/phytoremediation studies (including field trials), it was proven that trees or plants absorb contaminants along with water and nutrients, and that at least some of the absorbed contaminants are retained within the tree or plant biomass. This observation was made possible by the highly accurate age-dating application of dendroecology/dendrochronology in environmental forensics by measuring the chemical elemental composition of tree growth rings to detect eventual peaks of certain elements that may be linked to studied contaminants. Combining the chemical elemental patterns with ring width patterns, a powerful environmental forensics application was created based on tree-ring fingerprinting.

In conclusion, tree-ring fingerprinting builds on the basic principles from dendrochronology and phytoextraction/phytoremediation discussed previously. A publication by Balouet et al. (2009) discussed the method's well-established scientific principles, its reliability, and its legal admissibility, successfully demonstrating that the method is mature enough and has been proven in many case studies to provide reliable and defensible evidence for the trial court. Tree-ring fingerprinting should be seen as an emerging application of well-established scientific methods based on sound principles.

6.4.1.3 Method Steps

The steps of tree-ring fingerprinting include the following:

1. **Screening for method feasibility and planning for adequate sampling and analysis** should be the very first step when tree-ring fingerprinting is considered. Several main limitations should be evaluated first, such as the following:
    a. Are trees present at the site to be investigated?
    b. Are the trees present old enough to cover the estimated timeframe when contamination was suspected to happen?
    c. Is the studied contamination present in the shallow subsurface (e.g., up to 30 ft bgs)?

    Obviously, this method is limited by the presence of trees at the site to be investigated that are old enough to cover the site operations (the timeframe of the site operations should be known based on the historical file review). In addition, another major limitation is the contamination depth below the ground. Obviously, deep contamination is likely much below the tree root zone and thus may not be available to be taken up by the trees. In general, the method may be applicable for contamination present from below ground to about 30 feet bgs; however, every site should be considered on a site-specific basis, and this general rule may not work for all sites. The lower the subsurface contaminant concentration is, the shallower the depth at which the method may be applied. Note that the tree roots should not necessarily be in direct contact with contaminants as contaminants may end up in trees due to so-called capillary forces from a depth below the deepest root. Also, VOC and semivolatile organic compound (SVOC) contaminants may be taken from soil vapors by trees and may travel as soil vapors from deeper groundwater if no significant geological barrier is encountered. All these factors need to be taken into account when deciding the feasibility of method application for any particular case. Plus, the use of Google maps (satellite images) may help easily identify the presence of trees in any given area or location. Moreover, the evaluation of historical aerial photographs, if available, may help date the present trees. Apart from these major limitations, other limiting factors (discussed more thoroughly in a following section) should be considered before deciding if the method should work for any particular case. These factors may include the following:

    - The distance of trees from suspected sources
    - The general health state of trees
    - The availability of control trees (from the same species as the exposed trees and within the same general neighborhood)

- The easiness of access to the trees to be sampled
- The potential presence of alternative sources for the studied contaminants in the study area
- The general type of climate in the site's region (the method may not work in most tropical climates, for example)

Once the method feasibility is established, as with most forensic methods, planning of relevant sampling is essential to ensure effective method application. Typically, a brief site visit/inspection is desirable for such planning to identify the exact trees to be sampled and any other related sampling that may be performed in the same day (e.g., soil or groundwater sampling). In addition, checking with the laboratories to ensure that adequate sampling equipment and techniques are used is highly recommended. Various types of borers may be used for core sampling, and generally those with a larger diameter may be preferred when chemical elemental analysis is to be performed.

2. **Identification of tree species to be sampled**. Once in the field, the first activity is to adequately identify the tree species for all the trees planned to be sampled. This may be performed at the planning step or on the day of sampling. In general, this step requires the consultation of special guidebooks[21] and some familiarity with trees and specific terms used in the guidebooks. For those who never performed such identification in the past, it is highly recommended to perform this step within the planning step and consult with botanists or other experienced scientists if possible. If uncertain about the tree species, it is recommended to collect a representative leaf and detailed photographic documentation of the tree itself for further checking with a specialist. If the tree has fruits, it is useful also to collect one for further checks and identification/confirmation of tree species. Note that while tree species may be identified at a later point after sampling and analysis, it is important also to sample control trees in the area. In the absence of definitive identification of tree species, detailed observations related to various distinctive morphological traits (e.g., type and arrangement of leaves, general appearance, bark aspect) of exposed trees may help identify similar trees in the neighborhood that can be sampled as control trees.
3. **Sampling of tree cores.**[22] The next step consists of sample collection. The following are recommended for correct sampling:
    a. *Sampling equipment*. The typical equipment used for collecting tree core samples is the so-called increment borer (hand operated). Increment borers are simple tools used to core trees or, in other words, to extract a tree sample from the bark and toward the core of the tree. The sample is cylindrical and of various

FIGURE 6.6
Hand-operated increment borer, including its main parts: the auger that digs into the tree and the handle. Note that the extractor tray used to retrieve the sample is not seen in this picture; that part gets inside the auger, and it is of comparable length.

diameters based on the instrument used (usually 5-mm or 10-mm borers). An increment borer is displayed in Figures 6.6 and 6.7 showing me coring a tree. The borers with bigger diameter are better for sample analysis; however, some trees with hard wood are hard to sample, and a smaller-diameter borer (i.e., 5 mm) may be needed. Electrically driven drill bits may also be used for particularly hard wood but it is quite unusual in most applications.

b. *Sample location and number.* The samples are usually collected at chest height. In general, 10–15 min per sample collection is needed per tree (but some trees may require longer times), which makes the method applicable to a large number of trees per day. In general, two cores per tree are recommended (although many times just one ends up being chemically analyzed for elemental composition). Both exposed trees (one to three or more trees within a polluted area—depending on the length of the area to be sampled and the tree's availability) and control trees (generally one control tree would suffice) of the same species (outside a polluted area) should be sampled for comparison.

c. *Sample storage.* As soon as the borer is out of the tree, the core sample should be carefully retrieved from the borer and placed in a sample holder or in a straw of fitting dimensions. The tree-coring operation followed by sample retrieval and placing in a holder[23] (a plastic ruler in this case) are shown in Figure 6.7a and 6.7b. It is important to retrieve the core sample as soon as

FIGURES 6.7
(a)–(c) Tree core sampling and sample preparation. (a) Top left image shows the operation of tree coring/sampling. (b) Lower image shows the collected core sample after it was retrieved from the borer (in the middle of the ruler). (c) Top right shows a sample prepared/processed for analysis (to the right) versus an unprepared sample (to the left); note that the sample shown prepared for analysis was obtained from another species of tree than the one shown here; that sample was also obtained using a borer with a bigger diameter than the one shown in this picture. The unprepared sample was collected with the borer shown.

possible from the borer, making sure no small parts are left in the borer since the borer needs to be reused for collecting the other planned samples. Typically, no cleaning of the borer is needed between sampling, but the borer needs to be free of any sample residue from previous sampling that could impede further tree penetration for new sample collection. Once samples are properly stored, they may be transported without the need for using ice or any other preservation techniques.

4. **Covering the created tree wounds.** After a tree is sampled, the holes left from extracting the cores should be seen as wounds and filled with special paste (commercially available for treating tree wounds). This way, insects and other potential tree infestations are prevented, and the sampled tree health will not be affected in any way. This is an important step to ensure healthy trees and should always be performed before moving to sample the next tree.
5. **Processing of collected tree core samples.** Once they reach the laboratory, the tree core samples need some processing before the analyses can proceed. This step may be performed by the receiving laboratory, but the scientist should be aware and check with the lab to ensure proper sample processing is performed. Specifically, core samples are dried at ambient conditions for 4–5 days and then prepared for analysis. Note that while drying, the samples should be kept in grooved wooden blocks or specific trays so that they can dry without twisting. After samples are dried, the preparation includes several progressive sandings of samples (with a graded series of sandpaper, from 80, 200, 400, and 600 grits) to produce flat, shiny surfaces necessary for analyses (Balouet et al., 2007b; Balouet and Oudijk, 2006). The sample is ready when the surface is sufficiently polished to reflect light, such as the right core from Figure 6.7c. The sample is then cleaned with an aerosol dust cleaner or a vacuum cleaner. Once ready for analyses, the samples may be glued to grooved wooden blocks as in the case of the sample shown in Figure 6.7c (the core to the right).
6. **Tree ring width analysis.** The prepared samples are first analyzed for ring widths. Typically, the analysis is done using magnification equipment coupled with a measuring table. Microdensitometry images of cores are obtained with a digital camera coupled with a video monitor with magnification (30–40 times). The measurement precision is approximately 1% (Balouet et al., 2007b). This analysis may be performed by any laboratory specializing in dendrochronology work (such as university laboratories). Note that I collaborated with Dr. Chris Balouet of Environment International (France) in previous projects using trees, for which Dr. Balouet performed the ring width analysis in his laboratory in France.

7. **Chemical elemental analysis ring by ring.** After being analyzed for the ring widths, samples may also be analyzed for chemical elemental composition. This may be done through energy dispersive X-ray fluorescence (EDXRF).[24] EDXRF has the advantages of low detection limits for elements with an atomic weight above 25 and of being a nondestructive technique (basically, the tree core is sent back from the laboratory after the analysis is completed and may be available for any further checks). More information on the EDXRF method and its application in environmental forensics can be found in an article by Smith et al. (2008) and a thesis by Lindberg (2004). The method is based on irradiation of the sample surface followed by spectroscopy to measure the generated photon wavelengths and peak intensities. The samples are scanned (from one edge to another, such as from core to bark), and individual spot spectra are turned into elemental counts. Note that while EDXRF is a well-established technique, its application for tree-ring analysis is less common, and it might be difficult to find the right laboratory with this particular experience. However, many university laboratories have the equipment needed and may be interested in applying the technique for tree-ring fingerprinting. For this particular analysis, I used Dendrolab at Stockholm University in Sweden, which has experience in tree-ring fingerprinting through EDXRF analysis. The EDXRF analysis technique provides the measurement of about 30 elements along the tree core. These measurements are typically not provided in concentration units, but rather in counts, which are absolute numbers of counted photons. However, concentrations are not needed since the method relies on peak identification, which could very well be done by plotting the counts against the core length. Note that these counts should be proportional with concentrations and thus, an increase in counts should likely be due to an increase in concentration for any given element. In fact, the term *concentration*, whenever used in this book when discussing chemical elemental composition of tree rings, refers to the actual counts reported by the laboratory.
8. **Facultative step to perform additional analyses** depending on the aim of the forensic project. Especially when nonconclusive data are obtained based on chemical elemental analysis, an additional analysis may help with data interpretation and resolving the forensic puzzle. Such analysis may include isotopic analysis or chemical analysis of targeted compounds (e.g., PCE and TCE if the studied plume contains these chemicals or PCBs if the contaminants of concern are PCBs). Note that checking for compounds ring by ring would typically require the combination of multiple cores to have enough material to analyze from each ring or series of rings. Generally, too many cores may be required for ring-by-ring analysis

of chemical compounds; thus, a grouping of four to five rings may be used instead, providing timeframes instead of years for age-dating, which could still be more accurate than age-dating using other techniques. Note also that both isotopic and compound analyses in tree rings use destructive techniques, such as those involving digestion followed by GC/MS (gas chromatography/mass spectrometry). It is still not clearly established if organic compounds may be found (unmetabolized) in quantifiable amounts in past growth rings (not active at the time of sampling), although the potential exists, especially for more stable compounds such as PCBs. Once compounds are detected within the tree rings, the generated evidence would be more powerful than the evidence from chemical elemental analysis alone discussed previously.

9. **Data evaluation and interpretation.** This last step is needed to reach forensic conclusions. In the case of tree-ring fingerprinting, the following information is typically obtained from the laboratory: (a) the tree ring width measurements (in an Excel spreadsheet) along with the magnified image of the analyzed tree cores, as well as (b) the elemental concentrations (for about 30 elements) versus distance from the sample end, which is toward the bark (also provided in a spreadsheet). Data evaluation is typically done by superimposing the results from EDXRF analysis (using a graphical representation of counts versus distance from the core end, based on spreadsheet data from the laboratory) on top of the magnified core image showing various rings (from bark to core). Such a representation is shown in Figure 6.8.

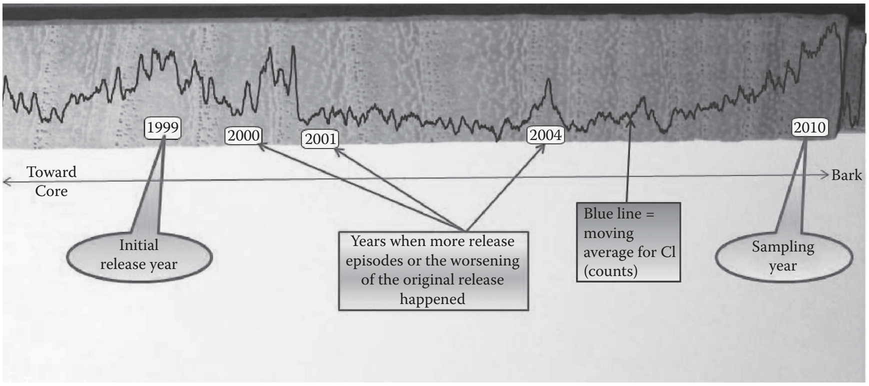

FIGURE 6.8
(See also color insert.) Example of tree-ring data evaluation in a hypothetical case study. The results of chemical elemental analysis for Cl are superimposed on the magnified core image after proper calibration; to the left is the core or so-called pith of the tree, and to the right is the tree bark.

6.4.1.4 Calibration of Chemical and Ring Data

To correctly superimpose data from the two sets of analyses (i.e., the chemical elemental data over the core image), a correlation of the chemical data to the ring years needs to be performed first. This correlation may be done using the so-called inter-ring anomalies, which are anomalies recorded by the EDXRF technique due to the changes in wood density at the borders of rings (this is why rings are visible: the cell density changes at the edges of each ring). These inter-ring anomalies are a variation of EDXRF coherent counts based on wood density and not on chemical elemental variations. These data should be obtained when conducting EDXRF analysis and should be used to calibrate the chemical elemental patterns with the correct areas of the core when superimposing the two sets of data. Note that these inter-ring anomalies have both total counts and amplitude much lower as compared to the intraring variation of individual screened elements related to pollution events. A concrete example of the calibration of chemical elemental data to ring years was provided in a book chapter by Balouet et al. (2007a).

6.4.1.5 Data Interpretation

The display of tree-ring fingerprinting results, as shown in Figure 6.8, helps identify the individual growth rings associated with any observable elemental peaks for targeted elements (linked to contaminants of concern). The example from Figure 6.8 relates to a hypothetical case study briefly discussed in the next section and provided here for demonstration purposes only. It is generally considered that sharper elemental peaks are an indication of contamination events and could be used to age-date these events. In the example from Figure 6.8, chlorine (Cl) was the targeted element because the contaminant of concern was TCE. While many small variations of Cl can be seen all along the core (which are normal and based on tree physiological changes during the years), several sharper peaks are identified and marked in Figure 6.8 with a brief interpretation related to deduced releases.

Note that when interpreting chemical elemental data, one should consider a series of processes and factors that could affect the data. Such factors include a series of processes that may result in element translocations from one ring to another (after the element entered the tree with the contamination), as well as the natural variability reported for certain elements in tree rings (usually occurring at the boundary between hard and soft woods[25]) unrelated to the presence of contaminants. These and other potentially influencing factors were discussed in detail by Balouet et al. (2007a,b). Note also that chemical elemental analysis is not considered conclusive for C, H, and O elements, which are the building blocks of trees; therefore, their variation due to potential contamination would be indiscernible as compared to their natural variability in trees. Contaminants composed exclusively of C, H, and/or O may not be investigated using tree-ring fingerprinting through chemical elemental analysis. Other elements, such as Ca, Mg, and K, may have variability within tree rings unrelated to contamination, such as variation due to the presence of injuries or microbial infections. Such occurrences may be evaluated by observations of the tree and core sample on a case-by-case basis. Moreover, soil pH variations may result in increasing bioavailability and mobility of certain elements (e.g., Fe, Zn) that may end up resulting in higher amounts being absorbed from soil in trees for the years corresponding to any significant change in pH. All these and other potentially influencing factors need to be considered on a case-by-case basis before finalizing interpretation of tree-ring data to ensure defensible evidence.

6.4.1.6 Taking Advantage of All Chemical Elemental Reported Data

Although only the elements linked to contaminants of concern can be used to provide direct evidence for age-dating or other forensic purposes, other elements (out of about 30 elements reported by the laboratory) may also show significant peaks, and they could be evaluated to better understand the "big picture" (e.g., what other events may have happened and what other contaminants may have been present at the site at different times or how these events could influence the forensic interpretations). The additional elements (if they show significant peaks) may help identify potential alternate or supplemental sources for the targeted element (other than the contaminant of concern). For example, when Na or K peaks are observed to coincide with Cl peaks, it can be deduced that salt may have been the reason for the Cl peaks (such as salt used for deicing of roads or from intrusion of ocean water into an aquifer in coastal zones) instead of TCE. In such a situation, the results of tree-ring fingerprinting may be seen as inconclusive and may not be used to age-date the TCE releases.

6.4.1.7 Using Statistical Tools

Statistical tools may also be employed to help with data evaluation. For example, each data point (e.g., the analysis result in counts) may be replaced by the average among a selected number of surrounding data points. The so-called moving averages are obtained and may be used in graphical representation of results. An alternative way of evaluating the results may include calculating average values for elemental measurements for each ring.

6.4.1.8 Cross-Dating to Confirm Ring Chronologies

Note that before the evaluation of chemical elemental data associated with the ring width information described previously, cross-dating (cross-checking) of the cores of exposed trees studied versus the cores of control trees should be performed to confirm the ring chronologies and identify any potential missing or false rings (as mentioned previously). There are situations when control trees of the same species may not be found or available for sampling. In such situations, one may use a series of available databases that provide information on tree growths for many species in many geographical regions across the globe. Two main databases available in the public domain are recommended in this respect:

1. The International Tree-Ring Databank (ITRDB) maintained by the National Oceanographic and Atmospheric Administration (NOAA) Paleoclimatology Program and World Data Center for Paleoclimatology (available at http://www.ncdc.noaa.gov/paleo/treering.html)
2. The Dendro Database maintained by the Swiss Federal Institute for Forest, Snow and Landscape Research (available at http://www.wsl.ch/dendro/dendrodb.html)

6.4.1.9 Interpretation of Ring Width Data

When chemical elemental data are not acquired, some forensic interpretations may be possible based on ring width data alone. However, ring width data should show variations or anomalies that are not due to common influencing factors, such as climate changes. Publicly available dendro databases provide information that can help evaluate contaminant effect on ring growth versus other factors, such as climatic ones. For example, a parameter called Palmer's Drought Severity Index (PDSI) is commonly used to evaluate the ring width anomalies attributable to climate variations. PDSI trends for a certain region and species may be extracted from public databases and represented along with ring width measurements for the trees analyzed (adjusted by year). When trends coincide (for certain timeframes), it may be concluded that PDSI was the limiting factor in determining observable ring width patterns. However, for the years when the trends do not correlate, it may be deduced that some factors other than climate (such as contamination) might have affected the tree. This method bypasses or could be used along with control trees for evaluating climate versus contaminant-driven ring width-induced changes. PDSI databases are available from the NOAA website (http://www.ncdc.noaa.gov/paleo/pdsiyear.html).

6.4.2 Applications, Limitations, and Recommendations

6.4.2.1 Applications

Tree-ring fingerprinting is a cutting-edge technique with powerful applications in environmental forensics, including the following main types of applications:

- **Age-dating with high accuracy (to the year)**. Basically, there is no other testing forensic technique available to date that can age-date contamination with such high accuracy. In theory, any released contaminant can be age-dated as long as it reaches the tree root zone. In practice, due to methodological and sampling limitations, contaminants that are easier to age-date using this technique include those that contain at least one composing element other than C, H, and O (the building blocks of trees). Case studies reported in the literature so far include age-dating of the following contaminants:

  - **Metals.** Most heavy metals would produce visible peaks in tree rings as shown for Pb by Balouet et al. (2007a,b); in this case, the elemental marker to be checked in trees is the metal itself.
  - **Chlorinated solvents.** Chlorinated solvents would leave peaks of Cl in the rings corresponding to the years when they entered the tree root zone, as shown for TCE and PCE (and degradation products) in several case studies in Southern California (Balouet et al., 2007b) and Germany (Balouet et al., 2012); in this case, the elemental marker was Cl.
  - **Petroleum distillates.** Petroleum products may be age-dated in trees based on additives or impurities they contain. For example, leaded gasoline was age-dated based on its Pb content, which left visible peaks in tree rings; fuel oil was age-dated based on its S content, resulting in visible peaks in the rings (Balouet and Oudijk, 2006; Balouet et al., 2007a,b; Smith et al., 2008). Note that in the case of middle distillates, it was observed that S peaks left in trees correlated with Cl peaks; it was thus concluded that peaks of both S and Cl appearing in the same year would be a strong indication for fossil fuel uptake in the trees; thus, in the case of leaded gasoline, Pb is the elemental marker, while for middle distillates, S is the main elemental marker, with Cl increasing the defensibility of results when its peaks correlate with the S peaks.
  - **Petroleum distillates**[26] **and crude oil** may be tracked in trees based on some heavy metals they contain (in traces), such as Ni and V (Balouet et al., 2007b); in this case, Ni or V serve as elemental markers.

- **Revealing the contamination history of a site where limited or no information is available,** including the type of pollution (based on type of elemental markers found to have peaks) and severity of pollution events (based on peak height and effects on the growth seen in ring width alterations). In addition, the evolution of elemental peaks (such as a sudden increase or gradual increase over multiple years) may indicate the type of release (such as sudden and accidental, as from a tank rupture or dumping events, or gradual, such as from a pipe leak); proving the type of release may be important in insurance litigation cases. Several representative case studies were presented by Balouet et al. (2007b).

- **Source identification** is also possible if trees are present between the study area and various suspected sources. In this case, one can reveal the path of contamination, and sometimes a general estimate of plume evolution in time and space may be deduced. For example, if three suspected sources exist for a TCE groundwater plume but no linkage between any of the sources and the plume itself exists through soil, soil vapor, or groundwater data, trees may reveal which of the sources contributed to the TCE groundwater plume. The condition is to have trees between each of the suspected source and the groundwater plume locations. Two or more trees between each source and groundwater plume may then be sampled and analyzed for tree-ring widths and chemical elemental analysis, looking for Cl peaks. If such peaks are found with a logical evolution away from the source, then evidence for contribution of a particular source is provided. Tree evidence may help eliminate some of the suspected sources (if no relevant Cl peaks are observed in trees between a source and the groundwater plume). Even if no source is eliminated, trees may provide definitive evidence related to each source contribution.
- **Distinguish between multiple releases at the same site.** Tree-ring fingerprinting is the only testing technique that allows accurate age-dating and identification of multiple releases of the same chemical that happened over the years at one site. Thus, if a site had several episodes of chlorinated solvent releases, the technique will reveal those based on successive targeted elemental peaks within a core (as in the example from Figure 6.8). Another example includes a site where multiple S peaks in a tree core along with one main Pb peak were attributed to several middle distillate releases and one main gasoline release that all happened at one site during the years (Balouet et al., 2007b). Such information may be crucial to resolve insurance claims when a year difference may be important since a change in insurance providers can happen from one year to another. This may also help "bring to the table" and recover damages from all the responsible parties at a site, not only the party with the most recent release that can be measured through classical monitoring techniques (e.g., monitoring for chemical concentrations).
- **Establish plume boundaries and historical groundwater velocities.** When multiple trees are sampled along a suspected plume pathway, the evolution of the contaminated plume in time and space may be reconstructed. I participated in an unpublished (confidential) case study related to a groundwater PCE plume for which about 10 trees were sampled between a suspected historical source and the plume location (at the time of sampling). Cl peaks in tree rings had an evolution revealing that the suspected source was likely to

have contributed to the plume since trees closer to the source had Cl peaks appearing in earlier years, while trees farther away from the source had Cl peaks appearing in later years. In fact, Cl peaks were observed to gradually move toward more recent years as the tree locations came closer to the current plume. With such data from multiple trees along a reconstructed groundwater plume pathway, tree-ring data may also be used to calculate velocities of plume transport between various trees, which, in turn, could be used to calibrate groundwater models and increase the defensibility of modeling evidence.

- **Forensic investigations at mitigated sites.** Since tree-ring fingerprinting is independent of the presence of contamination at the time of sampling, it is one of the very few forensic testing techniques that can be applied at mitigated sites (e.g., sites that were remediated after being bought by a new owner who seeks to recover remedial costs from previous owners that caused the contamination).

Apart from the various applications in environmental forensics investigations mentioned, information from tree growth rings (e.g., ring width or chemical composition) could be used in many environmental investigations, including the following:

- **Site characterization/site assessment.** Trees may be used to screen for the presence of contamination at the time of sampling in soil and groundwater without the need for disruptive soil borings or monitoring wells. The method is sustainable and green since no environmental disturbance and drilling or other type of equipment is needed. This application in site assessment is also known as *phytoscreening* and involves the analysis of what volatilizes from entire collected core samples (no ring-by-ring analysis is needed). Obviously, this would apply to VOC and SVOC contaminants. The idea is that only what is taken up by trees at the time of sampling would be volatilizing from the core (any contaminant traces that were absorbed in trees in the past would be fixed within the woody rings and would no longer volatilize). This application works well when multiple trees are present at a site and distributed over all the main site areas, so that the whole site is screened. Related to this particular application, the USGS published a series of reports (see, e.g., USGS, 2004); the U.S. EPA denoted the advantages of using trees for site assessment applications (see, e.g., EPA, 2005b). The method is simple and straightforward as collected core samples are put into glass vials that are immediately tightly closed and analyzed for the volatile compounds that emanate from the core (after some standard period of time). The vials may be left in an oven for increased volatilization. By analyzing the headspace, a good correlation was obtained between VOCs from core headspaces and the VOCs monitored through groundwater and soil analyses. Phytoscreening may also be performed using tree branches instead of tree cores, making the method even simpler and more time effective (Gapalakrishnan et al., 2007). Other publications on the use of trees for site screening include those by Sorek et al. (2008); Larsen et al. (2008); Limmer et al. (2011); and Burken et al. (2011). Note that the analysis method used in some of these studies is distinct from the method used by the USGS (described previously), consisting in solid-phase microextraction (SPME) instead of the GC-MS on headspace used in the USGS studies. SPME was also reported to be applied *in planta* for rapid field screening. The main advantages of using the SPME method is that it considerably decreases the detection limits, increasing phytoscreening sensitivity (Limmer et al., 2011).

- **Monitor environmental changes** (Eckstein and Krause, 1989) **and provide records of hydrologic change** (such as within a wetland; see, e.g., an interesting online article by Yanosky and Kappel, 1997).
- **Atmospheric sampling via plant tissue analysis.** Plant leaves, bark, and needles may retain contaminants present in the atmosphere. Thus, by sampling such vegetative tissues, information related to air contaminants would be obtained. Methods have been developed for a wide range of air pollutants, including particulate matter and organic and inorganic pollutants. This application is briefly reviewed in an article of Burken et al. (2011).

HYPOTHETICAL CASE STUDY 6.3

Who Bears the Liability for a TCE Plume at an Industrial Site with Multiple Insurance Carriers over the Years?

Let us consider a hypothetical case study as follows: An industrial site in an urban area was operated by one company from 1980 until the present. TCE was used and stored at the site. No recorded releases of TCE exist, and no environmental monitoring data exist until 2009, when data revealed a shallow groundwater (8–10 ft bgs) plume of TCE extending from the site downgradient. Since the company was insured by different insurance carriers over the years, a forensic investigation was needed to establish when the TCE was released. Specifically, the company was insured by three insurance carriers, the first one between 1980 and 2003, the second one between 2004 and 2005, and the third one from 2006 to the date of the investigation in 2010.

The forensic investigator started first with a historical document review, which did not reveal any releases or useful information except that the company purchased TCE from the same manufacturer during the years. Thus, a testing method was needed to solve the forensic puzzle. Two main age-dating techniques were possible for the TCE plume: atmospheric tracers and tree-ring fingerprinting. After conducting a feasibility study, the forensic investigator noticed that atmospheric tracers may not be used in this particular case. Tree-ring fingerprinting remained the only option; fortunately, a tree was identified at a neighboring property downgradient. Based on groundwater plume data, the tree was within the TCE plume area. The tree was identified as an ash tree (*Fraxinus* sp.) at least 50 years old. Two core samples were obtained from that tree and two from a control tree of the same species found several blocks upgradient of the TCE plume. Since the tree was not immediately near the source, modeling of TCE movement from the suspected release area on site (TCE storage and handling area) until the tree root zone was needed and revealed between 1 and 1.5 years needed for the released TCE to reach the location of the tree. The ring width data did not reveal any particular anomalies that could have been attributed to the TCE plume. However, the chemical elemental analysis of the core from the exposed tree revealed several Cl anomalies (peaks) that were not accompanied by other elemental anomalies. The results for the exposed tree core are shown in Figure 6.8 and reveal four more significant Cl peaks for the years 1999, 2000, 2001, and 2004. Note that only the most recent part of the core (from the late 1990s to 2010) is shown here since no significant Cl anomalies were observed for earlier years (the collected core extended to 1978 without reaching the pit of the tree, which was not needed since it covered the period of interest, 1980–2010). If we add at least 1 year for the released TCE to reach the tree, the following TCE release years are revealed: 2000, 2001, 2002, and 2005. Note that this age-dating method may not work well for the most recent 3–5 years; therefore, the possibility of a Cl release between 2005 and 2010 could not be excluded. Note also that the apparent gradual Cl peak in the last few years (as seen in Figure 6.8) should be disregarded for age-dating purposes as it is likely due to the fact that the tree was lying within the TCE plume at the time of sampling; thus, TCE was absorbed in the tree's more recent growth ring, from where it likely diffused to previous rings. This phenomenon was observed for other cases and is one reason why tree-ring fingerprinting may not work well to identify more recent releases (e.g., in the last approximately 3–5 years).

In what concerns the chemical elemental composition of control tree cores, two peaks of Cl were observed for distinct years (as compared to the exposed tree), specifically in 1988 and 1995 (the data are not shown here). Both Cl peaks were, in this case, accompanied by Na peaks, suggesting salt as the likely cause. That control tree was on the walkway, located close to a main road, so it is likely that road salt used for deicing was the source.

In conclusion, what the tree evidence revealed was that TCE releases happened during the time when the company was insured by both the first and the second insurance carriers. Therefore, both carriers would have been liable to pay part of the remediation costs. While the data could not be used for a quantitative assessment of contributions to the plume, it generally indicated that the first three releases were more significant compared to the last (fourth) one. These three releases were all within the timeframe when the company was insured by the first carrier. More information could eventually be obtained by interviewing employees as well as checking the TCE usage and purchase records as well as waste records. This information may help to further delineate contributions, if needed.

Note that this hypothetical case study is provided for demonstrative purposes only and does not go into details. Typically, a series of factors should be considered before reaching the forensic conclusions, factors that are not discussed for this hypothetical case. However, the main steps of a tree-ring fingerprinting investigation are captured and could serve as an example to help understand and apply this cutting-edge technique. Also, while the data used in Figure 6.8 were created for the purpose of this demonstrative case, the general trends shown for chemical elemental data for Cl are consistent with real case studies. Note also that the core image used in Figure 6.8 came from a real *Fraxinus* species tree collected for a real case study.

6.4.2.2 Limitations and Recommendations

The main method limitations relate to the presence of trees old enough to capture suspected past pollution events and close enough to the investigated source, along with the presence of relatively shallow contamination (in general no deeper than 30 ft below ground). In any case study, many other limitations should be considered as they could affect the feasibility of tree-ring fingerprinting or the interpretation of results. Some of these factors were discussed in a previous section when presenting the method steps. Nevertheless, a more complete list of limitations is provided here:

- **Tree availability.** Obviously, the main limitation of this technique is that it needs trees present within the contamination zone (current or historical). In many urban settings, there are no trees or no trees old enough for forensic purposes. This limitation is easy to evaluate, even without visiting the site, by using satellite images of the site.
- **Depth of contamination.** Tree ring fingerprinting will generally not work for deeper contamination that may not be close to the tree roots. In general, it is considered that the method may be applied at depths up to 30 ft bgs. Generally, VOC and SVOC compounds are more available to trees since they are also present in soil vapor after volatilization from groundwater. Obviously, the higher the concentration is, the higher the chances are that deeper VOC and SVOC contaminants enter trees that are above a groundwater plume.
- **Lack of periodic growth pattern.** This is typically not a limitation for the United States, Europe, and other regions of the globe with a temperate climate. For trees to develop annual growth rings, seasonal

climate variations are needed. In tropical climates, the method may not work. However, every case should be considered separately, and in some instances, if any climate pattern (other than the typical four seasons) is observed (e.g., a certain pattern of rainy vs. dry seasons), this may induce the formation of visible growth rings and should be considered (however, in such a situation, the rings will not necessarily be formed on an annual basis but rather following the timing between observed climate pattern changes).

- **Relocated or pruned trees.** This is an important limitation of the method that is often overlooked. It is not common for older trees to be relocated, but when this happens, the earlier tree growth rings will reflect changes from a different location and cannot be used in forensic investigation of the site where the tree is located at the time of sampling. It is therefore important to know when a tree was relocated. For example, if a tree started to grow in 1980 and was relocated in 1985, one can still use the tree-ring fingerprinting information from that tree for any period not earlier than 1985 (which should be OK if the investigated period when a suspected spill might have happened is after 1985).
- **Recent releases affecting only sapwood.** As discussed previously, tree-ring fingerprinting may not be used for recent releases (e.g., in the more recent 3–5 years) because of the contaminant diffusion process from the most recent active ring inward, which was generally shown to affect up to about five prior years. The example from Figure 6.8 showed the diffusion effect over several recent years (near the bark) that seem to have a Cl peak, which was in fact due to diffusion. In such a situation, results should be seen as inconclusive, and another forensic technique should be used.
- **Alternative sources for the elemental tracer used to track contamination in tree rings.** It is possible that the elemental marker is the result of more than one individual compound or source. Thus, when using chemical elemental analysis, one has to eliminate any significant influence from other potential sources for the observed targeted elemental peaks. For example, if both TCE and PCBs are contaminating a site (present in shallow subsurface) and two chlorine peaks are found in studied trees corresponding to the years 1985 and 1994, one may not know based on tree-ring fingerprinting alone which one is related to TCE versus PCBs versus mixed spills. In such a situation, additional evidence is needed (e.g., historical file review or historical monitoring data) to guide the forensic interpretation. Note that Cl might also come from road salt or from saltwater intrusion, but these particular situations may be easy to evaluate based on geographical location of the site, activities at neighboring sites, and chemical

elemental data from other elements (typically, as discussed in our hypothetical case example, if a Cl peak is due to salt, corresponding peaks of Na, K, or Ca are also expected to be seen for that tree). Another example of situations when alternative sources may interfere with the tree-ring fingerprinting investigation consists of the application of fertilizers at distinct points in time. Depending on the exact fertilizer composition, a series of metals and other elements (e.g., N, P) may be introduced in the tree root zone and thus create peaks in tree growth rings. As a general recommendation, historical evidence, general site conditions, and data for all the elements reported by the laboratory should be carefully considered to help evaluate and eliminate potential alternative sources for the elemental marker (targeted element) used in tree-ring fingerprinting.

- **Uptake of elements from the atmosphere.** This uptake route occurs through tree leaves. In herbaceous plants, foliar uptake was demonstrated for Fe, Mn, Zn, and Cu as well as other elements (Kabata-Pendias, 2001). This potential alternative source for elemental markers (i.e., atmosphere) should be considered especially when sources of atmospheric contaminants exist in the vicinity of the site (e.g., mining and smelting; foundries or other industrial sources with known emissions that include the targeted element). This particular alternative source would mainly influence investigations that have metals as targeted elements. Note that in the case of Hg, a nearby source may not necessarily need to be present to see a potential atmospheric Hg interference in tree rings. Thus, in general, the method may not be applicable if Hg is the only targeted element in trees. However, a case-by-case determination should always be made. Another main source of atmospheric contaminants (especially S) is acid rain, which should also be considered.
- **Presence of fake or missing rings.** As discussed concerning method steps (for interpretation of results), both fake and missing growth rings may occur in individual trees in certain years. The only way to check for such occurrences and make sure each visible ring from a core sample can be linked to an individual year is through comparison with ring patterns from control trees and from available databases for the investigated species within the investigated area (this comparison is known as cross-dating).
- **Potential element translocation** (ring to ring). In theory, once an element enters the tree, there is some potential for its translocation from one ring to other nearby rings. The exact mechanisms and causes of translocation are not well understood. However, some elements were observed to be more prone to translocation than others. For example, As, Na, and Mg were reported to have high

mobility between active tree rings, while Sr, Ca, Zn, Cu, Ni, and Cr appeared to have moderate mobility, and Ba, Al, and Cd had low mobility (Burken et al., 2011). At the same time, translocation of Pb was observed to be minor in conifers, while Cl and S were shown to have limited mobility when environmental concentrations were relatively low—observations that may encourage the use of such elements (e.g., Pb, Cl, S) as elemental markers to obtain defensible tree-ring fingerprinting evidence (Burken et al., 2011). In general, a sharp elemental peak is considered to be the result of contamination and not of potential element translocation. However, it is recommended to evaluate each case on specific bases and consider the possibility of element translocation.

- **Tree diseases and other factors affecting tree health (e.g., past fires or floods, exposed roots).** When tree health is affected, metabolic changes may occur, potentially resulting in some element translocations from one ring to another. Typically, some elements are more likely to be affected by this factor, including K, Ca, Mn, Fe, and Zn, which are important elements in tree physiology (Balouet and Oudijk, 2006). Therefore, the presence of current or past microbial infestations or fire scars could indicate potential retranslocation of some elements for the affected years. Such potential factors may be indicated by visible marks in tree tissues, and one should look for such marks.
- **Changes in soil properties that may influence contaminant transport.** An important source of various chemical elements is soil in which trees grow. This is often overlooked in the fact that it is assumed that soil composition does not significantly change in time except due to contamination events. However, even if total soil concentration of various elements does not change in time except due to contamination events, the soil bioavailable fractions of various elements (which are taken up in trees) may change in time. Various other factors than contamination may induce changes in soil conditions, resulting in changes in the bioavailable amounts of various elements present in soil. For example, changes in soil pH may free more of some chemical elements from the soil matrix, resulting in an increased uptake in trees. Depending on how substantial the change of a soil condition is, significant elemental peaks may be created in tree growth rings, artificially suggesting contamination events. This particular limitation may happen and should be carefully considered. Soil-monitoring data along with historical and climate data from the site general area may help evaluate if any significant changes in soil conditions are expected to have occurred during a studied tree lifetime.

- **Moisture stress** was shown to reduce the flow of water and elements (Smith et al., 2008). Therefore, if such a stress is strong enough, it may induce significant changes in tree rings that are independent of the presence of contamination.

As noted, some of the limitations may be overcome, but some may not. Specific recommendations have been included when discussing various limitations of the method. **General recommendations** related to this method application in environmental forensics are provided next:

- It is highly recommended to review all potential limitations as applicable to the case at hand during the first step of tree-ring fingerprinting, when method feasibility is established. This will ensure good understanding of the case study before the method is deployed and will help guide the investigation and interpretations.
- It is also highly recommended to find an appropriate analytical laboratory before planning for field activities.
- Consulting with the laboratory for sampling and handling instructions before going in the field is also necessary, ensuring that data are not compromised.
- When evaluating the data, information for all chemical elements reported by the laboratory should be considered and not only the reported data for targeted elements. Such information may reveal details that can change the interpretations or refine them, as well as help evaluate potential limitations.
- The potential for relocated trees may be revealed by consulting historical aerial photographs for the study area; although relocated trees are not common, they could compromise the entire investigation. Therefore, the potential for the presence of such trees should always be considered.
- Depending on the targeted element (to be used in tree-ring fingerprinting), alternative sources may include the soil itself if the element becomes more available for uptake into the trees due to changes in soil properties; thus various factors that can trigger such changes should be considered.
- Data from the two cores collected from one tree may differ because of the direction where the cores were taken; the collection of multiple cores does not necessarily imply that data from both cores should coincide. Rather, the more cores that are collected, the higher the chances to collect a core that is relevant (shows contamination peaks) and to catch any contradictory data that may invalidate the results. In some cases, contrasting data between cores may lead to inconclusive results.

Hints for Successful Forensic Application of Tree-Ring Fingerprinting

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- **It is recommended to use tree-ring fingerprinting along with other independent lines of evidence.** Although this technique may be used independently of any other methods, its use in conjunction with other evidence (e.g., historical, chemical, isotopic evidence) increases both the accuracy and the application range of tree-ring fingerprinting.
- **Always check all the chemical elements reported by EDXRF analysis and not only the targeted elemental markers.** This will allow
  - *distinguishing contamination from other environmental factors/contributors* and, by this, overcoming some of the method limitations due to the use of elemental markers rather than compounds. The method relies on the presence of elemental markers for compounds (e.g., chlorine for chlorinated solvents or sulfur for diesel fuel). Such elemental markers may be contributed by other sources than the targeted pollutant (e.g., chlorine may come from road salt or seawater intrusion, while sulfur may be due to acid rain). However, such limitations may be overcome by taking into account possible association of an elemental marker with other elements (provided by EDXRF analysis) as well as using historical and other types of evidence.
  - *noticing other pollutants and pollution events* as such information is useful when interpreting environmental data and contaminant fate and transport.
- **Always consider the big picture before deciding on the feasibility of tree-ring fingerprinting.** Many of the general limitations of the technique may not apply in specific situations. Thus, the technique should not be dismissed before a careful evaluation of case specifics. For example, the depth limitation may be overcome when deeper VOC contamination exists at a concentration high enough to produce significant upper soil gas and dissolved phase that reaches tree roots. Deeper contamination may also be captured in trees if it is in high enough concentration to reach tree roots through capillary forces, especially under high-moisture conditions.
- **Sampling of a control tree is useful but not absolutely necessary** as long as a database with tree data (for the species of interest) from the study area exists.
- **It is recommended to sample the side of the tree closer to the suspected contamination source** if such information is available.

This is one more reason why it is useful to complete a detailed historical review before starting any experimental testing.

- **Look for signs of fires, pests, or microbial diseases** in a tree, which may interfere with the analysis result. In general, healthy trees are the best candidates for forensic testing, but information from other trees may still be useful if carefully considered and integrated with all environmental factors.
- **Interpretations should evaluate other potentially contributing sources** of targeted elements in the tree as well as other chemicals containing those elements. This is generally valid for most forensic techniques.
- **The precision and sensitivity of the technique should be considered.** The technique is quite exact (e.g., age-dating to the year) and may go as far back in time as the tree age (for hundreds or thousands of years). The technique is also quite sensitive since, for example, in the case of chlorinated solvents, concentrations as low as 8–10 ppb in groundwater may be captured in trees if the plume is close to the tree roots (as shown by USGS reporting).
- **Interpretation of elemental peaks over a single year.** The peak of an elemental marker appearing over only 1 year (which may be linked to accidental and sudden releases) does not mean that contamination passed the tree root zone after 1 year. Rather, this is common and is due to the tree adapting to contamination by various mechanisms, which result in less contamination entering the tree and finally less contamination being absorbed and fixed in tree cells after the first year of exposure.
- **An increase in the targeted elemental concentration usually happens close to the bark of the trees, which is still within a contaminated area at the time of sampling.** This is usually an indication that the tree continues to lie in a contaminated environment or plume rather than an indication of a new release. The explanation resides in diffusion of contaminated sap[27] from the outermost rings into some of the inner rings in the close vicinity. This may generally affect the most recent 3–5 years of growth. Because of this, the method may be less precise for age-dating more recent pollution events.
- **Combined or "symbiotic" use of the method along with other forensic techniques may result in higher forensic discerning power.** Apart from using various forensic techniques independently, their interdependent (combined) use could be extremely valuable in environmental forensics. Dendroecology is especially amenable to such interdependent use since the information provided by elemental markers is less specific related to the

exact individual contaminants and potential alternative sources. If, however, isotopic analysis is done on the elemental marker in the rings with peaks, more specific forensic information may be acquired, and distinguishing between pollutants with the same elemental marker becomes feasible. Based on the same logic, tree-ring fingerprinting may be interdependently used with other forensic testing techniques. Such applications hold great potential as analytical ability improves.

Notes

1. CFCs are used primarily as refrigerants, propellants, cleaning agents, solvents, and blowing agents.
2. Note that the example is provided as a general guidance and may not be applicable for any site or conditions. It is the ultimate responsibility of the forensic practitioner to judge each site independently based on site-specific conditions and use the information from this textbook for general learning and guidance.
3. The examples provided here are for a general overview of the complexity and diversity of the sampling devices and requirements for different atmospheric tracers and should not be used without double-checking current information on the USGS website and other applicable sources.
4. The recommended copper sample tubes have the following characteristics: measuring 3/8 inch in diameter and 30 inches in length, containing about 40 cc of water, and fitted with stainless steel pinch-off clamps at each end. Note that these sample tubes are prepared and owned by Lamont-Doherty Earth Observatory, which maintains a stock of them and ships directly to the project office.
5. For example, tritium is analyzed through electrolytic enrichment and scintillation counting with a precision of about +0.6 TU. He and Ne are analyzed using a noble gas mass spectrometer with 1–2% precision margins. CFCs are analyzed by purge-and-trap gas chromatography with an electron capture detector (ECD).
6. Methods to estimate this concentration are based on measured values of ^{3}He, ^{4}He, and Ne as provided in the work of Szabo et al. (1996).
7. See, for example, the study by Burton et al. (2002) of groundwater age-dating in sedimentary rock in the Valley and Ridge Province, Pennsylvania, using CFCs and radioisotopes ^{3}H-^{3}He.
8. Duplicate samples were collected from the regional plume.
9. Note that the data from the lab consisted of CFC concentrations. The average recharge temperature was deduced as 15°C, and the results were extrapolated using the published graphs mentioned previously.
10. Note that all these are potential and not necessarily confirmed sources for atmospheric tracers mentioned in all cases. Every case needs to be considered carefully, and if present, such potential sources need to be separately evaluated.

11. As far as I am aware, such forensic applications have not yet been reported, although the potential exists. It is to be expected that such applications will develop along with advancement in testing techniques and equipment, which may allow building libraries of relevant DNA fingerprints in various media. Even without such libraries, one may attempt to use DNA fingerprints to track passage of contaminants through the environment, using comparative samples as well as laboratory experiments/proof-of-concept with source materials.
12. For environmental forensic purposes, other genes than 16S rRNA may be targeted (e.g., genes involved in the metabolism of a targeted contaminant).
13. Variable regions of a gene in various microbial species determine the polymorphism.
14. Note that, compared to the double-stranded DNA (analyzed by other methods), which displays the same 3D double-helix structure, the single strands of DNA have variable 3D structures (conformations) depending on their nucleotide sequences.
15. Please always check current costs with the laboratory to be used. These costs may change, and the amount indicated here is only for general orientation.
16. It should be specified that, although in principle this type of application may be possible, as far as I know, it has not been recorded.
17. Including both method-specific principles and basic building principles and explaining how these principles relate to environmental forensics applications of tree-ring fingerprinting.
18. The stunted growth may occur with a delay (usually between 2 and 4 years) since the pollution begins to enter the trees.
19. For example, if a chlorinated solvent (i.e., TCE) is absorbed in the trees, it is to be expected that some chlorine (Cl) will be left in the ring cells from the year when TCE was absorbed in the tree. All one needs to do to date the year when TCE entered the studied tree is to measure chlorine concentration ring by ring and age-date (through dendrochronology) the ring or rings where chlorine peaks are seen. Obviously, other potential sources of chlorine in trees should be considered before a final conclusion relative to TCE entering the tree is reached. More information and hints on things to look for and consider are provided to determine if a certain element detected in higher concentration in trees is defensibly linked to the targeted contaminant or could eventually come from other unrelated sources.
20. If the studied trees are within some distance downgradient from a contaminant source, an additional modeling step may be needed to model and calculate the time needed for contaminants to reach the tree root zone from the established source (based on release records).
21. Examples of useful guidebooks that can help with rapid identification of tree species include the *Peterson Field Guides* (for U.S. trees), available at major bookstores or online. A concrete example from these guide series is *The Concise Field Guide to 243 Common Trees of North America*, by George A. Petrides (1983), which helps identify major species quickly. Other, more detailed, guides are also available for less-common species.
22. Note that, if available, cross sections or stem disks may be used if the tree is to be destroyed or just a stump is left at the time of sampling.

23. Special sampling trays or holders may be purchased for sample storage. In some cases, using straws may be OK as long as the straw dimension would fit the sample so that no sample parts are left uncovered. Samples may also be put in wooden trays, such as the one shown in Figure 6.7c.
24. For tree core analysis, repeatability testing with EDXRF is in the percentage range (Balouet et al., 2007a).
25. *Hard wood* refers to older rings that are not active in transporting water, nutrients, and any potential contaminants, while *soft wood* refers to newer rings (three to five more recent rings in many cases), of which the most recent ring is active in transporting water nutrients and any potential contamination, and the next few rings may be affected by the transported fluids through diffusion processes from the active ring.
26. Typically, heavier distillates may be tracked in trees by checking Ni or V content in tree rings because the lighter distillates, such as gasoline, contain no compounds with Ni and V.
27. *Sap* refers to the water and nutrient liquid that circulates through active tree growth rings. When contamination enters the tree, it circulates along with the sap.

Section III

Challenges and Solutions

> The present is the key to the past.
>
> **—James Hutton**

Several case studies in which I was involved are presented (in brief) to illustrate how "real-world" environmental mysteries can be solved using multiple lines of evidence. The case studies have been chosen to cover a variety of challenges and illustrate how each type of challenge requires a subsequent tailored forensic approach. Note that while the general types of challenges presented here are commonly encountered in forensic investigations, other types of challenges (not presented in this book) exist and may require different strategies. Although this book does not include a comprehensive review of all general types of challenges confronting environmental forensic investigations, it is my hope that the challenges and solutions presented will help identify specific challenges and select the most appropriate solutions on a case-by-case basis.

It is all about solving the "mystery case" in the simplest and most straightforward way possible. Sometimes, this involves just the historical file review, while other times it may involve the use of multiple fingerprinting methods in conjunction with historical evidence. Regardless of the complexity of the case and the approach chosen, using multiple independent lines of evidence increases the defensibility of forensic evidence in the court of law. Yet, cases may settle before trial sometimes based on just one powerful line of evidence. Thus, the goal of the forensic investigation is to reach a "point of confidence." If that can be reached with one powerful line of evidence, the forensic investigation aim is accomplished.

For each case study presented here, the general historical and legal contexts are initially described. The forensic lines of evidence used in each case are further presented in brief, including a summary of the methods, results, and forensic interpretations reached. Key remarks are also included to emphasize key points and hints that could help others when dealing with similar cases. In addition, for each case, both general and more specific suggestive titles are included to illustrate the power of "storytelling." Every forensic case could be regarded as a "detective" or "mystery" story and presented in a subsequent way. When such a story is illustrated in a clear, compelling way, a successful forensic outcome is foreseen. It is extremely important to engage the audience in a well-described and scientifically sound story to obtain their understanding and approval. Often, the audience for forensic stories is juries of laypeople or prospective clients who may become easily lost in complex scientific concepts or even bored. Therefore, the cases described in this book are purposely presented more in the form of a story rather than a peer-reviewed article. By this, I hope to transmit both the "substance" and the "form" in which that scientific material should be presented for successful resolutions.

It is not within the aim of this book to delve into details for any of the case studies presented but rather to point out commonly encountered forensic issues and solutions. Therefore, the cases presented may appear too simplified. However, this book is meant to be general and simplified to be easily readable by a large audience and serve as a guide for those interested in practicing or simply understanding environmental forensics.

These case studies summarized should be regarded as "snapshots" of forensic applications to various real-world situations aimed to give examples of typical environmental disputes and forensic solutions. They are simply illustrative for real-world applications of the theoretical concepts and forensic principles discussed in the previous chapters.

Finally yet importantly, many of the case studies presented were not published. For the cases that were published previously, the specific references are included. All the cases are described here from the perspective of "challenges and solutions." Specifically, for each case presented, a strategic general type of forensic investigation is associated; the forensic approaches from each case are generalized to show how they fit into specific proposed solutions tailored for each general type of challenge.

7

Finding the "Needle in the Haystack"

7.1 Strategic Guide

This type of forensic investigation refers to practical situations when multiple sources of a targeted contaminant exist within a site area and the goal is to precisely identify contributions from only one particular source. The challenge consists of the presence of a large number of potential contributing sources and the fact that, for this type of case, the targeted contaminant is typically less amenable to common fingerprinting (e.g., chemical fingerprinting techniques). This forensic investigation type is strategically described in Table 7.1.

Case Studies 7.1 and 7.2 belong to this type of forensic investigation, illustrating how the strategic concepts briefly described in Table 7.1 have been applied in two real situations. The emphasis is on the main forensic strategies; thus, the case descriptions do not review in detail any of the described lines of evidence. Rather, snapshots of the forensic investigation are presented in a summary table synthesizing the main lines of evidence for each case.

7.2 Case Study 7.1: Forensic Evaluation of Metal Background Concentrations at a Historical Foundry Site in France

7.2.1 Case Study 7.1: Overview

7.2.1.1 Historical and Legal Context

A historical foundry (referred to here as the foundry or the site) located close to the city of Lyon in France planned remedial activities for some on-site areas affected by a series of metals due to the historical site operations. The planned remediation involved soil only since groundwater and surface water were not shown to have been impacted. Through an official document ("Arrete Prefectoral"), the overseeing regulatory agency had established specific cleanup limits for metals in soil, including the following (in mg/kg): Pb,

TABLE 7.1

Challenges and Solutions for Forensic Investigations Targeting a Particular Source in Environments with Multiple Natural and Anthropogenic Sources

Challenges	Solutions
• Multiple sources for the targeted contaminant of both natural and anthropogenic types exist within the investigated area.	• This type of complex forensic challenge can be solved using forensic testing techniques that fingerprint the contaminants within the environmental matrix in which they are found (as described in Chapter 5 of this book).
• None of the existing sources can be ruled out based on available information; basically, any of the existing sources may have contributed to the contamination observed at the time of sampling in the investigated area.	• The existence of many suspected sources within the investigated area requires the highest level of forensic characterization along with a detailed historical document review, which may help establish signatures for the investigated source.
• The targeted contaminant is not of a mixture type, thus limiting the ability of common fingerprinting techniques to differentiate between sources; examples of typical contaminants associated with this type of forensic challenge include metals and inorganics.	• Confirmation of the forensic findings through independent lines of evidence is a plus, but not absolutely necessary since the highest level of forensic scrutiny may be achieved through the recommended approaches; however, historical document review should always be performed.
→ *The goal of the forensic investigation is to evaluate contributions from only one particular source in an area with multiple contributing sources.*	• On a case-by-case basis, other forensic techniques (e.g., isotopic fingerprinting) may also work and should be evaluated.

110; Hg, 0.6; Cd, 0.9; As, 25; Cr, 52; Ni, 39; Co, 10. Some of these cleanup limits seemed inconsistent with the suspected high background concentrations of metals in soil in the area due to the presence of many natural and anthropogenic metal sources. Such sources included ancient Pb mines (including one on-site) and many industries, including several other foundries. All these sources, along with the presence of agriculture in the general area, were suspected to have contributed to higher background concentrations of metals in soil. Note that background concentrations refer to concentrations of metals in soil unrelated to the foundry operation. Such concentrations would be the result of a natural pristine background plus widespread industrial/agricultural contamination over the years that would have raised the pristine background values. Basically, any contributions except the foundry operations would result in metal background values for the purpose of the remedial activities.

Thus, a forensic investigation was proposed to estimate total background concentrations of various metals in the on-site soils to be remediated and adjust, if needed, the cleanup values of targeted metals.

7.2.1.2 Forensic Target

The forensic investigation aimed to respond to the following questions: How much did the foundry contribute to the elevated concentrations of metals found in site soils? How much is the background contribution (from various natural and other anthropogenic sources in the area)?

7.2.1.3 Environmental Forensics beyond Litigation

This case illustrates how environmental forensics may be used outside the litigation context in a typical site investigation/remediation project. In fact, distinguishing background values is part of many forensic investigations, although not a goal by itself. In this case, the multitude of sources suspected to have contributed to the metal background in soil made the client think that an environmental forensic examination was needed to solve the puzzle, and so it did.

7.2.1.4 Outcome

The background concentrations of metals obtained through the forensic study were adopted, resulting in substantial remedial cost savings equivalent to approximately $2.5 million for the foundry. The forensic study was completed within a month and had a total cost of about $25,000.

7.2.2 Case Study 7.1: Snapshots of the Forensic Investigation

Line of Evidence 1: Historical Document Review	Main Findings

Both a general and a specific document review were performed. The general review focused on reported natural background values of metals in soils worldwide, particularly focusing on lead (Pb).
The specific historical document review has been performed consulting a series of documents and reports related to the foundry historical operations, as well as other potential metal sources in the area. Some reports contained historical environmental monitoring data from the foundry and the surrounding area; one report contained a background study for metals conducted in the general foundry area (off-site locations only). Another report contained detailed information on the foundry's past activities, going back for more than a hundred years. The specific use of various site buildings, raw materials, and wastes were recorded in that report.
In addition, evidence revealing the existence of an ancient Pb mine (from Roman times) on the site itself was gathered, pointing out the probable high natural Pb background in on-site soils.
	• The general literature review revealed higher natural background values of Pb than the 110 mg/kg proposed for site cleanup; such higher Pb values in soils were reported around the world in uncontaminated and remote areas. For example, Pb values were reported as high as 150 mg/kg in U.K. uncontaminated soils (Thornton and Culbard, 1986), 160 mg/kg in Australia's rural soil (Brazi et al., 1996), and 225 mg/kg in the forest floor of the northeastern United States (Adriano, 2001). These findings reflect the natural variability of background levels of Pb in soils due to different geologic materials as well as atmospheric transport (as particulate matter) and deposition (generally by rain) of Pb from various human activities (including automobile exhaust, mining and smelting, industrial activities, burning of fossil fuels, etc.).
	• The specific historical file review revealed the most likely site "signature" or association of contaminants (metals) associated with the foundry's historical operations. The established best indicators of the foundry's historical operations include the following:
	  • Lead (Pb), zinc (Zn), and tin (Sn). Therefore, it was defensibly established that the correlation of these metals could be used as an indication for foundry contributions.
	  • The detection of precious or semiprecious metals such as silver (Ag), gold (Au), palladium (Pd), and platinum (Pt) was another potential indicator for site operations.
	• A forensic sampling and analysis plan for on-site soils was proposed in both highly impacted areas to be remediated and areas less likely to have been impacted based on historical operations; the planned forensic sampling included both shallow (0–0.3 m) and deeper (0.3–0.6 m) soils. All samples were to be analyzed for total metals; selected samples were to be analyzed for mineralogical fingerprints using the scanning electron microscopic/energy dispersive spectroscopic (SEM/EDS) technique (described in Chapter 5).

Line of Evidence 2: Chemical Fingerprinting/Statistics	Main Findings

The existing environmental monitoring data along with the newly acquired data (analyzed by CalScience Laboratory) through the proposed forensic investigation were used. A summary of relevant chemical data used in this evaluation is presented in Table 7.2. The values for the on-site metals reported in soils displayed in this table were obtained during the proposed forensic investigation; the off-site values were reported in various available environmental reports (with most investigations conducted within the 5 years previous to the forensic investigation).

Simple statistics (e.g., maximum, minimum, and average values) were used in this evaluation to compare various sets of data and calculate background concentrations of metals applicable to on-site soils. The concentration trend with depth was evaluated to select samples from depths more representative for background concentrations (i.e., little or unaffected by site operations).

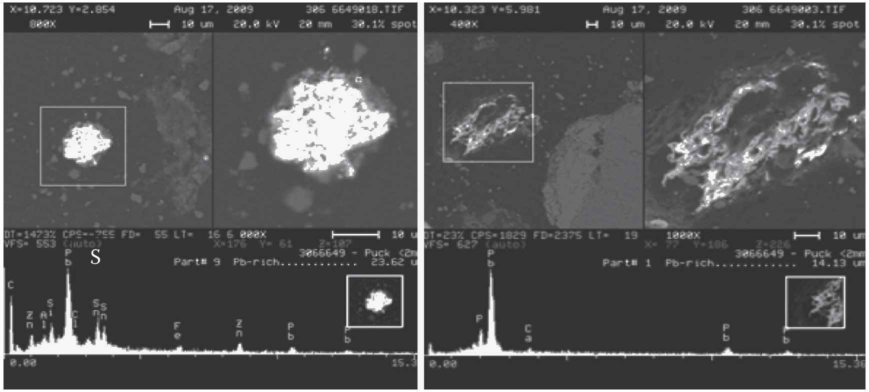
Metal correlation analysis was also used to evaluate how metal associations observed in on-site soils related to off-site soils and the established historical site signature.

TABLE 7.2

Summary of Relevant Metal Concentration Data (in mg/kg) in On-Site and Off-Site Soils

Metal	Ranges in the Background Samples Collected Off Site in 2008	Concentration Ranges in Topsoil from Site Less-Impacted Areas	Concentration Ranges in Deeper (0.3–0.6 m) Soils from Site Less-Impacted Areas	Concentration Ranges in Site Soil from Highly Impacted Areas	Previously Proposed Cleanup Limits	Newly Proposed Cleanup Limits: Background Values for the Site Soils
Lead (Pb)	15–490	540–6,900	**230–2,300**	1,300–110,000	110	***1,100***
Cadmium (Cd)	<0.5–1.8	8.1–69	**2–17**	580–5,300	0.9	***9.5***
Nickel (Ni)	19–39	18–26	**19–24**	27–8,600	39	***Same***
Mercury (Hg)	<0.1–0.6	0.92–31	**0.38–9.7**	1.9–37	0.6	***5***
Arsenic (As)	9–38	25–97	**31–73**	42–360	25	***52***
Cobalt (Co)	4–11	7–12	**8.1–10**	17–82	10	Same
Chromium (Cr)	23–52	**22–33**	**23–32**		52	Same
Tin (Sn)	Not evaluated	10–75	**9.6–51**	38–6,200	Not applicable	
Zinc (Zn)	46–150	84–280	**86–220**	2,400–29,000	Not applicable	
Silver (Ag)	Not evaluated	17–61	**15–36**	93–310	Not applicable	
Aluminum (Al)	Not evaluated	9,900–12,000	Not available	3,500–15,000	Not applicable	
Palladium (Pd)	Not evaluated	<10	Not available	<10	Not applicable	
Gold (Au)	Not evaluated	<4	Not available	<4	Not applicable	
Platinum (Pt)	Not evaluated	<10	Not available	<10–11	Not applicable	

- A general decreasing trend of metal concentrations was observed in deeper on-site soils with the exception of Cr, Co, and (to some extent) Ni. This decreasing trend denoted that the deeper collected soils were less affected by historical site operations and thus should be more representative for background values of metals. Therefore, the deeper on-site soil samples collected during the forensic sampling (fourth column from the left in Table 7.2) were used to calculate

Line of Evidence 2: Chemical Fingerprinting/Statistics	**Main Findings**
	representative background values of metals for on-site soils; these values are in bold italic in the rightmost table column and were proposed as site cleanup limits instead of the values previously proposed by the regulatory agency (sixth table column from the left). • Chemical fingerprinting denoted that the site signature established though historical review (including the association of Pb with Zn and Sn) appeared in the on-site impacted samples as compared with deeper, less-impacted samples and some off-site samples; thus, deeper on-site soils were confirmed as representative for background. • The calculated background values of metals for on-site soils were proposed as new cleanup limits for the following metals (in mg/kg): Pb (1,100); Cd (9.5), Hg (5), and As (52).
Line of Evidence 3: Mineralogical Fingerprinting	**Main Findings**
Mineralogical fingerprinting was performed on a few selected on-site soil samples to evaluate background values of Pb in on-site soil and compare the resulting value with that obtained through the chemical fingerprinting/statistics line of evidence (described previously). Two surface soil samples from both highly impacted on-site soils and less-impacted on-site soils were selected for SEM/EDS analysis (see technique details in Chapter 5). The analysis was performed by the RJ Lee Laboratory. A summary of representative results is included in Table 7.3; several representative SEM/EDS images for individual particles associated with Pb from the analyzed samples are depicted in Figures 7.1 through 7.3.	 **FIGURE 7.1** Composite SEM-EDS image of two Pb particles representative for foundry operations (left image) versus for background (right image).

The Pb particles appear brighter in the SEM images. The small squares depict the area selected for analysis (to be magnified); the spectrum shows the chemical elements associated with various Pb particles analyzed.

For each individual sample, depending on total Pb concentrations, between approximately 30 and 60 randomly selected individual particles associated with Pb were analyzed, and images similar to those from Figures 7.1 to 7.3 were obtained and reviewed. While not all the obtained images are shown here, a summary of the main associations and their prevalence in the analyzed soils is provided in Table 7.3. This is a semiquantitative analysis since only the randomly selected Pb particles were counted.

One main type of Pb particle contains Zn and Sn (see Figures 7.1 and 7.2) and likely comes from foundry operations. The other main type of detected Pb particles is representative for background Pb, including associations with P/phosphates and Ca (see Figures 7.1 and 7.2). A few minor types of Pb particles were also detected as shown in Table 7.3. In addition, Figure 7.3 shows Pb particles of unknown origin, and some particles enriched in other metals likely attributed to site operations. Different shapes and sizes were observed between the two main types of Pb particles. If we apply the average percentage of background Pb (33%) from on-site less-impacted soils to total Pb in that soil, we obtain approximately 1,100 mg/kg for background Pb on site.

TABLE 7.3

Summary of Mineralogical Fingerprinting Data

Sample	**Pb-Bearing Particles (Associations for Pb Particles)**	**Prevalence (%) (Approximated Based on SEM Counts)**
Highly impacted on-site topsoil (110,000 mg/kg total Pb)	Pb associated with tin and zinc (representative for foundry)	90
	Large particles of anglesite or susannite (natural Pb mineral)	<10
	Pb in an iron-rich phase and lead phosphate (background Pb)	<10
Less-impacted on-site topsoil (3,300 mg/kg total Pb)	Pb associated with tin and zinc (representative for foundry)	67
	Pb associated with phosphate and/or Ca (background Pb)	33
	Pb in an iron-rich phase	<1

The match with background Pb values obtained independently through chemical fingerprinting/statistics (see Table 7.2) validated the proposed new cleanup values.

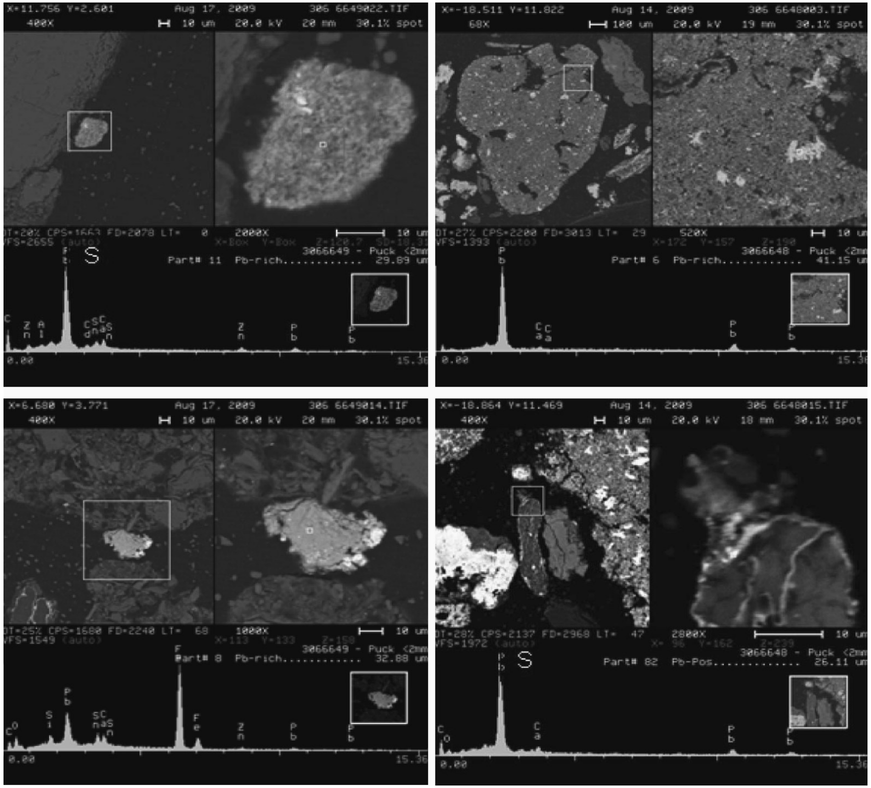


FIGURE 7.2
Composite SEM-EDS images of four Pb particles representative for foundry (left images) versus for background (right images).

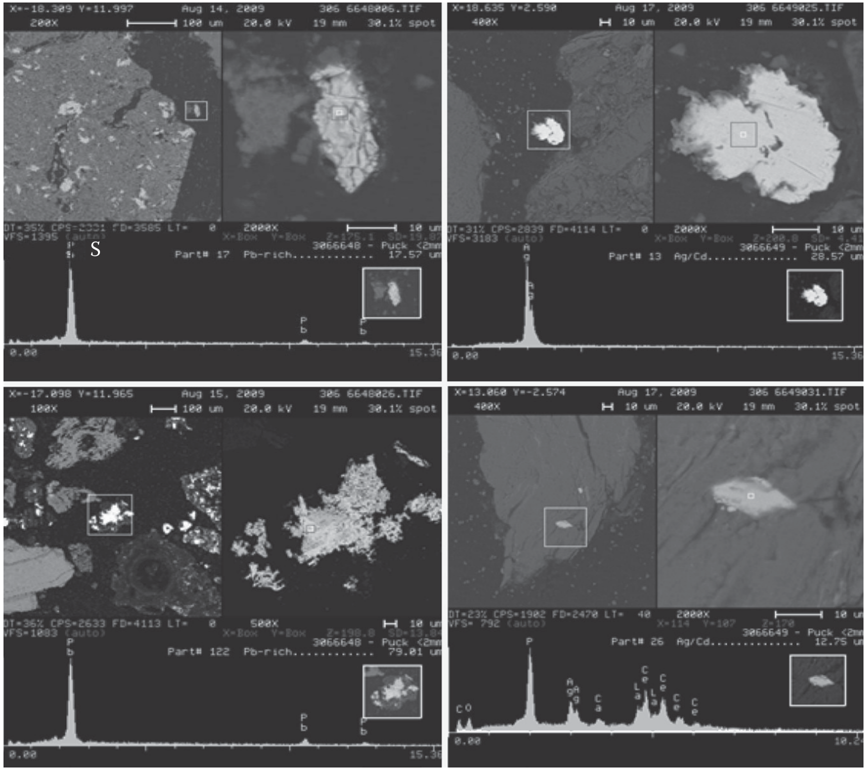


FIGURE 7.3
Composite SEM-EDS images of two Pb particles of unknown source (left) and two Ag/Cd particles representative for foundry (right).

7.3 Case Study 7.2: Forensic Evaluation of Metal Sources in Soils from Agricultural Parcels in the Vicinity of a Historical Foundry Site in France

7.3.1 Case Study 7.2: Overview

7.3.1.1 Historical and Legal Context

The same historical foundry in France as described for Case Study 7.1 was investigated. The foundry was suspected for elevated metal values found in some vegetative crops from the vicinity of the general site. Although no litigation was filed, the regulatory agency suspected the foundry's contributions. Therefore, the foundry was faced with potential liability to eventually pay for the damage and potential cleanup.

To clarify the situation and assess any potential contributions to the observed increased metals in surrounding agricultural crops from the area, the foundry decided to conduct a further forensic investigation preventively. The investigation was considered phase II of the forensic investigation already initiated at the site to evaluate background values of Pb and other metals in site soils (Case Study 7.1). The idea was to use the knowledge gained in the first forensic study (including the site-specific metal signature) to study potential site contribution to the metals in agricultural parcel soils and crops grown in those soils.

7.3.1.2 Forensic Target

The forensic investigation was initiated to identify and quantify the foundry's potential contribution to the metals in soil and vegetation of several privately owned agricultural parcels in the general vicinity of the site.

7.3.1.3 Environmental Forensics beyond Litigation

This case illustrates how environmental forensics is useful in the absence of litigation. In this particular example, the forensic investigation was conducted to prepare for potential future litigation. In too many cases, forensic investigations are triggered by initiation of litigation, when useful evidence might already be lost or altered and legal costs initiated.

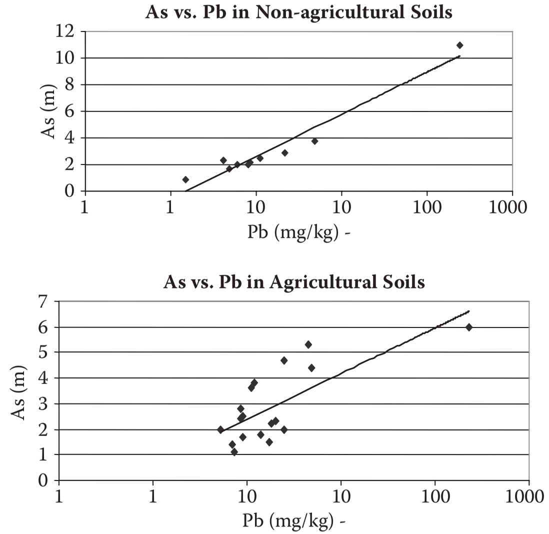
7.3.1.4 Outcome

No evidence for any recent foundry contribution to the increased concentrations of Pb and other metals from soils and vegetation of several agricultural parcels in the general vicinity of the foundry was obtained through the forensic investigation, which included several independent lines of evidence.

The forensic evidence summarized in a report provided defensible proof that the foundry was not impacting surrounding agricultural soils. The evidence protected the foundry against any alleged future claims potentially resulting in costly litigations (possibly involving millions of dollars in costs) since many agricultural parcels are present in the site general area. The overall cost of the forensic investigation was approximately $30,000, and the investigation was completed within a month and a half.

7.3.2 Case Study 7.2: Snapshots of the Forensic Investigation

Line of Evidence 1: Historical Document Review	Main Findings
In addition to the comprehensive general and specific (historical) document review described in Case Study 7.1, environmental reports related to agricultural parcels from the vicinity of the site with increased Pb and a few other metals in some vegetative crops were reviewed. In addition, specific questionnaire surveys from various sampled agricultural parcels were consulted. The surveys contained useful information related to current and historical agricultural practices, including the insecticides/pesticides and other treatments used.	• Agricultural practices could have contributed to soil contamination with a series of metals, including Cu, Hg, As, and Pb. The information was not complete in the agricultural surveys consulted; thus, further inquiries were needed for a more complete picture of historical agricultural practices for many of the parcels studied. • Apart from the foundry and the agricultural practices, many other sources of Pb and other metals exist in the study area, including: other foundries, waste from ancient lead mines, natural mineral deposits, industrial activities, lead-based paint, historical vehicle emissions, and burning of fossil fuels. • The metals present in monitored agricultural soil seem to have stable or decreasing concentration trends since the beginning of sampling campaigns (2007–2008). However, the few years of monitoring data were not enough to reliably capture any relevant changes in metal concentrations in topsoil. In addition, soil heterogeneity and agricultural activities may cause “artificial“ changes in metal concentrations. • A forensic sampling and analysis plan was developed to establish potential foundry contributions to Pb and other metals in the agricultural parcels studied; the plan included the collection of soil samples from agricultural surface soils in areas with recorded increased values of Pb and other metals. All samples were to be analyzed for total metals; selected samples were to be analyzed for mineralogical fingerprints by SEM/EDS analysis (see technique description in Chapter 5).

Line of Evidence 2: Chemical Fingerprinting	Main Findings
Old and new monitoring data (newly acquired data were analyzed by CalScience Laboratory) were used, comparing and evaluating on-site versus off-site metal concentrations in soil. Two main types of data analyses were performed: • Correlation plots were investigated between various pairs of metals (some also including metal ratios with more than two metals depicted on the graph). Selected graphs are shown in Figures 7.4 and 7.5. • Spatial distribution plots were prepared to observe metal distribution patterns away from the foundry in specific directions as well as in any direction (see selected data in Figure 7.6).	• A general correlation between various metals, including Pb and As (see Figure 7.4), was observed in the nonagricultural soils from the general study area. This is to be expected in a general mining area. Correlation of less value was observed between Pb and As as well as other metals in agricultural soils. In the correlation example of Pb and As from Figure 7.4, many agricultural soil samples displayed higher values of As. This is an indication that agricultural practices likely contributed to the currently recorded values of As in soil.  **FIGURE 7.4** Metal correlation plots for agricultural and nonagricultural soils from general site area.

Line of Evidence 2: Chemical Fingerprinting	Main Findings
Figure 7.4 includes nonagricultural and agricultural soils from the general study area (for which data were available through the historical file review); Figure 7.5 includes only the agricultural soils from the parcels investigated in the currently described forensic study (for which older data were available through historical file review; the more recently acquired data were obtained during the forensic investigation). Data displayed in Figure 7.6 include metal concentrations obtained during the forensic investigation from the agricultural parcels studied.	• Similar to the metal correlation trends observed in agricultural soils from the general study area, a general poor metal correlation was observed (including between Pb and As, as well as Pb and other metals) in the agricultural parcels soils studied (see Figure 7.5); in these soils, a generally poor correlation of Pb with Zn and Sn was observed, indicating the lack of significant contributions from the foundry; however, a relatively better correlation of Pb and Ag was also observed, indicating that potential foundry historical contributions could not be excluded since the site had recorded use of precious and semiprecious metals in the past. Overall, the metal correlation data did not reveal any significant recent foundry contributions to metals in the studied agricultural soils but could not exclude historical contributions from the foundry. • The spatial distribution of metals in the agricultural parcels studied did not reveal any significantly decreasing pattern away from the foundry (see Figure 7.6 for targeted metals). A similar nondecreasing trend was observed when data were displayed in various directions away from the foundry (data not shown). These observations suggest that there was no significant foundry impact in the studied agricultural parcels from the general vicinity area.

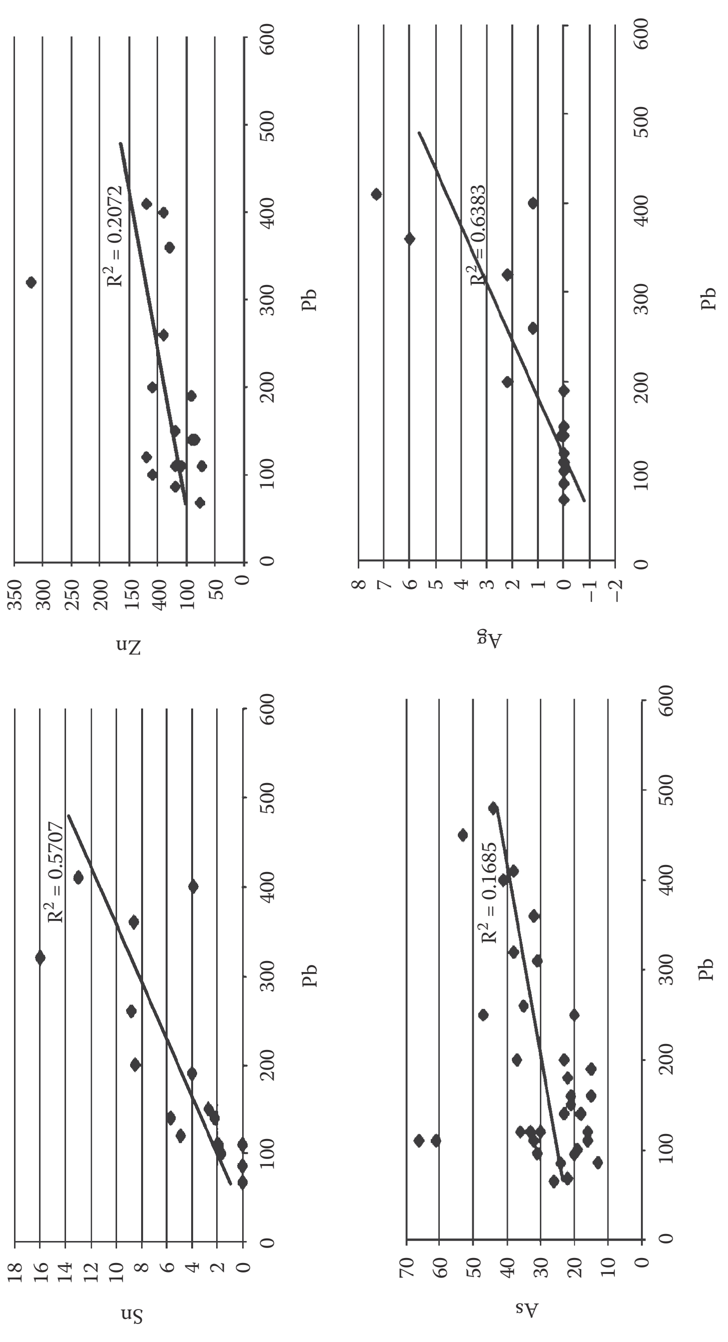


FIGURE 7.5
Metal correlation plots for soils from studied agricultural parcels (samples collected between 2008 and 2011); concentrations are in milligrams per kilogram.

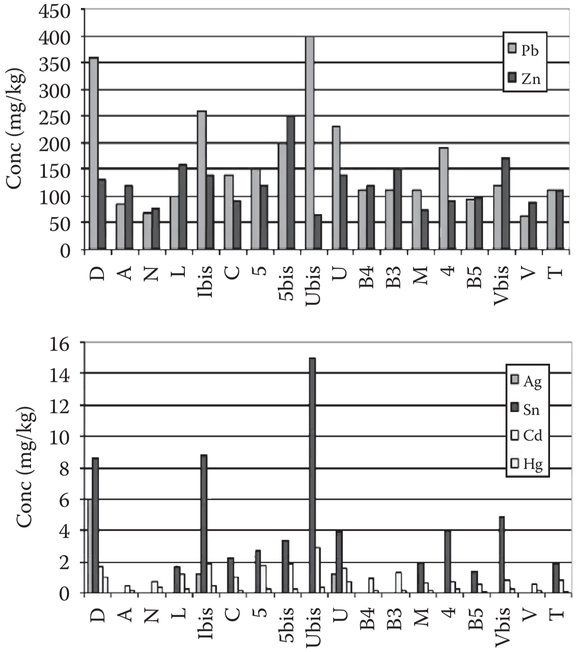
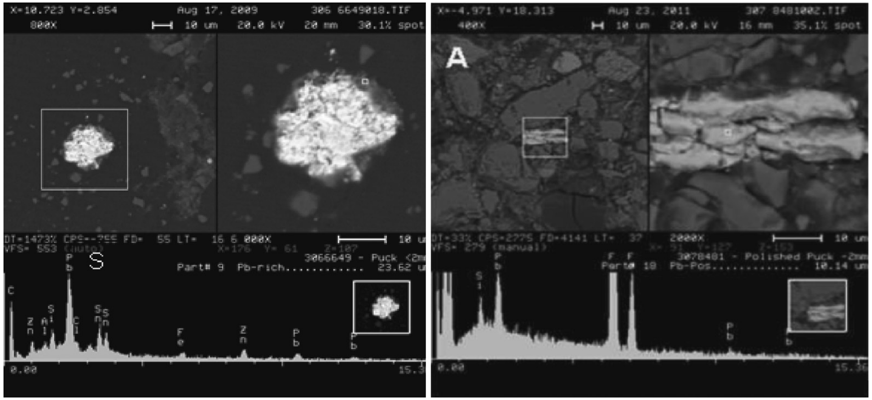


FIGURE 7.6
Metal distribution away from the foundry (in any direction). Increased distance away from the foundry is from left (the closest location) to right (the farthest away location) on the *x*-axis; locations presented on the *x*-axis include the agricultural parcels studied.

Line of Evidence 3: Mineralogical Fingerprinting	Main Findings
From the agricultural soil samples collected during the forensic investigation, four soil samples from four distinct parcels (with total Pb concentration between 200 and 450 mg/kg) were selected for SEM/EDS analysis. The samples were analyzed by the RJ Lee Laboratory. The size, shape, and chemical composition of particles associated with Pb in these samples were investigated and compared with results (mineralogical fingerprints) from the previous forensic study (Case Study 7.1) of on-site contaminated soils. Several representative SEM/EDS images for individual particles associated with Pb from the analyzed soil samples are depicted in Figures 7.7 through 7.9. The Pb particles appear brighter in the SEM images. The small squares depict the selected area for analysis (to be magnified); the spectrum shows the chemical elements associated with various analyzed Pb particles.	• The size, shape, and chemical elemental composition of Pb particles analyzed from the on-site foundry versus off-site agricultural soils were distinct, suggesting that the foundry was not a significant source of Pb in these samples; representative examples of the mineralogical fingerprints for Pb particles from agricultural soils analyzed can be seen in Figures 7.7–7.9. A direct comparison with a foundry-representative Pb particle is provided in Figure 7.7.  **FIGURE 7.7** Composite SEM-EDS image of two Pb particles: one representative for foundry operations (left image) and one representative for some of the analyzed agricultural soil Pb particles (right image).

Line of Evidence 3: Mineralogical Fingerprinting	**Main Findings**

For each individual sample, depending on total Pb concentrations, between approximately 5–30 randomly selected individual particles associated with Pb were analyzed, and images similar to those from Figures 7.7–7.9 were obtained and reviewed.	• While in the foundry contaminated on-site soils Pb was commonly associated with Sn and Zn (and sometimes with Ag), in the off-site agricultural soils analyzed, Pb particles were associated with:
	  • Mn, Ca, P, revealing a secondary precipitate derived from unstable Pb combinations or older Pb releases; the association with Ca and P is also typical for background Pb.
	  • Fe, revealing a possible industrial source.
	  • Si, suggesting glass/ceramic as a source for some of the Pb; Pb was also commonly associated with Si and Al in the agricultural soils analyzed.
	  • Paint pigments, suggesting Pb paint as a source for some of the Pb.
	  • Ash, suggesting coal as a source for that Pb.
	• Mineralogical and chemical fingerprinting revealed a series of metal sources in agricultural soils analyzed, including agriculture (mainly for As and Hg), industrial, paint, coal burning, and the glass/ceramics industry. Secondary forms of Pb could be associated with older releases of unknown sources.

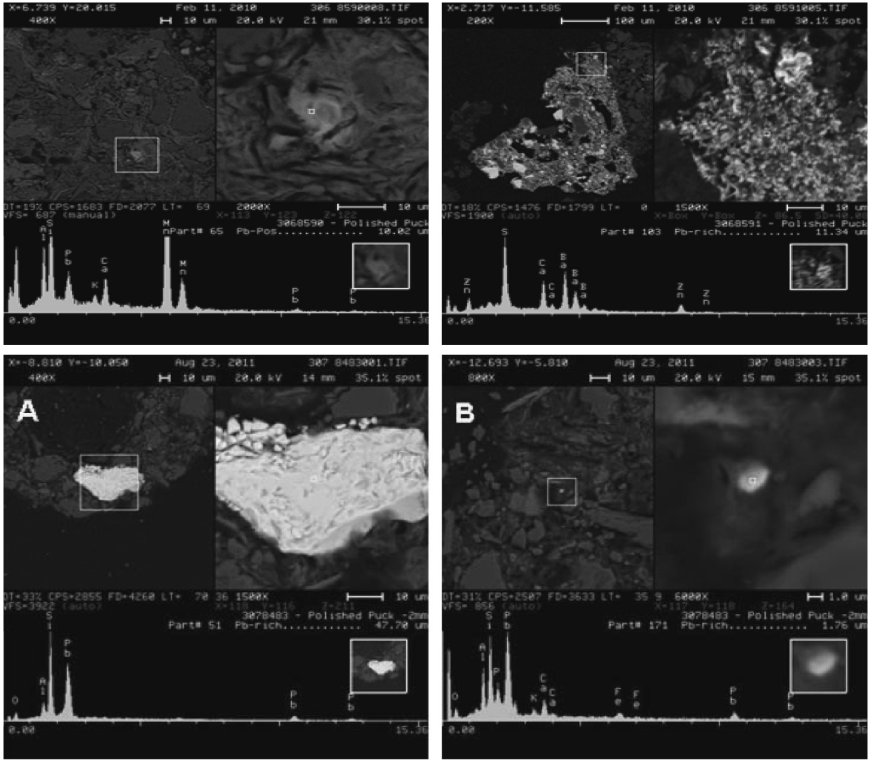


FIGURE 7.8
Examples of composite SEM-EDS images for Pb particles from off-site agricultural soils.

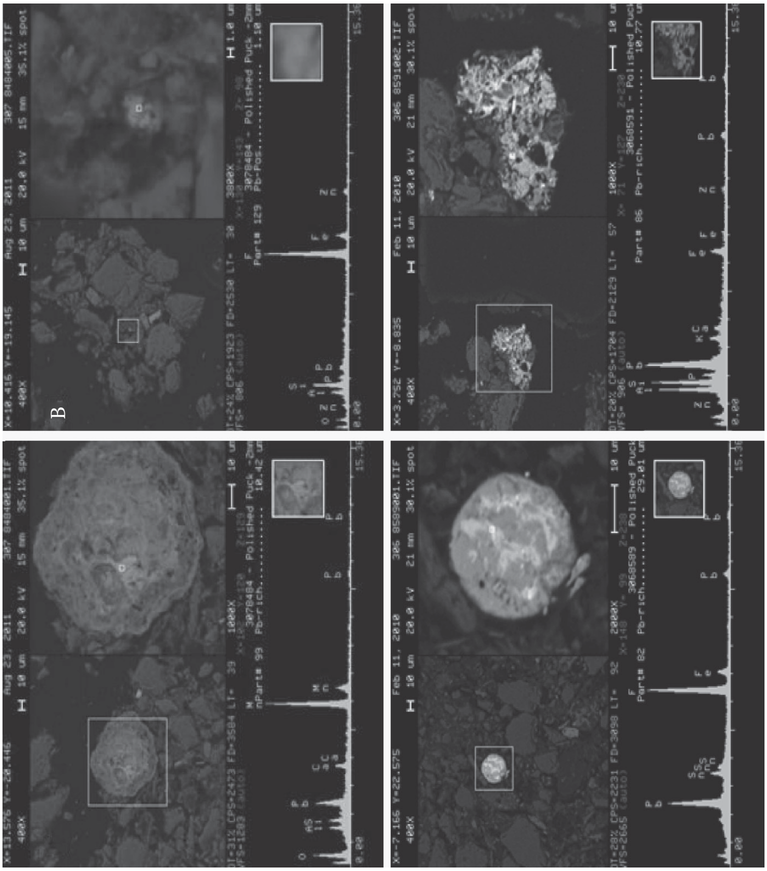


FIGURE 7.9
More examples of composite SEM-EDS images for Pb particles associated with off-site agricultural soils.

Key Remarks

- **Defining specific background values in areas with both natural and anthropogenic sources is equivalent to finding a "needle in the haystack."** This is when environmental forensics is needed more and works at its best.
- **Environmental forensic investigations proved useful in cases without an active litigation** to
  - **establish more realistic site-specific cleanup limits of metals** for contaminated soil at a historical foundry in an area with multiple natural and anthropogenic sources of Pb and other metals.
  - **gather evidence that can be used to prevent future litigation** related to potential metal contributions from a historical foundry to agricultural parcels in the general area.
- **The use of more realistic cleanup values of metals has the potential for substantial cost savings** in site cleaning and may be considered before the start of expensive remediation in similar types of areas with multiple natural and anthropogenic sources for the contaminants of concern.

8

When Site Mitigation Leaves Pollution Behind

8.1 Strategic Guide

This type of forensic investigation refers to practical situations in which contamination is discovered at redeveloped sites that have been contaminated previously (typically by industrial activities) and remediated. The challenge is to evaluate if the contamination discovered (after remediation) comes from the previous industrial site operations still found as a result of inadequate remediation. In addition, if multiple owners operated during the years and contributed to the contamination that was supposed to have been remediated, allocation between contributions is also needed. However, if the forensic investigation reveals that the discovered contamination was produced after site remediation, an evaluation of the contamination source discovered is warranted to establish who has to pay for the additional remediation needed. This forensic investigation type is strategically described in Table 8.1.

Case Study 8.1 belongs to this type of forensic investigation and illustrates how the strategic concepts briefly described in Table 8.1 have been applied in a real case. As with the other case studies presented, the emphasis is on the main forensic strategies; thus, the case descriptions do not review in detail the lines of evidence used.

TABLE 8.1

Challenges and Solutions for Forensic Investigations of Contamination Discovered at Redeveloped Sites

Challenges	Solutions
• The discovery of contamination at redeveloped sites considered to have been cleaned (remediated) in the past triggers the need to evaluate the source of the discovered contamination. • This type of challenge may involve previous industrial sites where multiple owners operated over the years, and the contamination discovered could have been attributed to any or all of the past site owners; even if only one past owner was operating in the past, there is still the need to evaluate if the contamination discovered came from operations prior to remediation versus any operations after remediation or other off-site sources. In addition, typically there is a narrow timeframe for the forensic investigation. • The targeted contaminant is not of a specific type; however, a potential challenge is the typical limited areas for new sampling considering that the site was mitigated. → *The goal of the forensic investigation is to evaluate the source and contributions (when multiple sources are revealed) for the newly discovered contamination at mitigated sites (to establish who has to pay for the discovered contamination).*	• This type of forensic challenge can typically be solved using the following forensic testing approaches: 1. Common fingerprinting techniques (e.g., chemical fingerprinting or other techniques described in Chapter 4) if the discovered contaminants are mixtures and samples are available for collection over an area representative for the site's past sources. The main goal is to compare the discovered contamination in samples from various site areas with samples from suspected sources, such as samples representative from past site operations; if such past source representative samples are not available, the samples may be compared with each other to reveal either common or distinct sources (see Case Study 8.1). 2. Forensic techniques that fingerprint traces left by contamination (e.g., those described in Chapter 6) if only limited sampling is available; this strategy may work well for simpler contaminants (not mixtures). The main goal in this case is to age-date the contamination from the site to evaluate if any releases might have happened postremediation; however, this may not work for very recent releases. • Confirmation of the forensic findings through independent lines of evidence is recommended.

8.2 Case Study 8.1: Source Identification of Petroleum Hydrocarbons Discovered after Soil Remediation at a Redeveloped Site in France

8.2.1 Case Study 8.1: Overview

8.2.1.1 Historical and Legal Context

In the city of Lyon, France, no more expansion/development outside the already-developed land can be done, so more and more of the formerly industrial land is reclaimed for other types of use. In this context, a developer started the construction of a big underground parking structure (more than 800 parking spaces) on what was claimed as rehabilitated terrain (redeveloped industrial site) in the city.

The discovery of petroleum hydrocarbons (ranging between 11,000 and 46,000 mg/kg) in site soils during the construction work triggered temporary cessation of all building activities, followed by the initiation of a forensic investigation to evaluate the contamination source for remediation and cost recovery of the unexpected remedial work. In addition, an oil pipeline was discovered during the construction work. The pipeline still had some old product in it that was characterized as a heavy petroleum distillate.

Note that about half of the site (northern side) was used previously by a major oil company as a service station; the other half (southern side) was used by a chemical plant. In theory, the hydrocarbon contamination could have been associated with either of these past occupancies, as well as with potential off-site sources.

8.2.1.2 Forensic Target

The forensic investigation was initiated to reveal the sources of the petroleum hydrocarbons discovered. The idea was that immediate remediation work would have been performed by the current developer to continue with the construction work, and at a later date, the remedial costs would be claimed from the responsible parties, with the claim supported by defensible evidence.

8.2.1.3 Environmental Forensics beyond Litigation

This is another case that illustrates the utility of environmental forensics in the absence of litigation. In this particular example, the forensic investigation ensured that proper remediation was achieved; the evidence gathered was to be used to recover the remedial costs from any responsible parties identified. In addition, should a forensic study not have been completed immediately after the contamination discovery, useful evidence would have been lost after the second remediation, and cost recovery would have become problematic even if litigation action would have been initiated at some point by the developer.

8.2.1.4 Outcome

The forensic investigation revealed a major common source for all sampled hydrocarbon contamination, which was likely the major oil company that previously operated on part of the site. The forensic evidence gathered was summarized in a report that was shown to the responsible party identified (major oil company), with that party offering to cover the remediation costs to the developer to avoid litigation involving a possible lengthy and expensive trial. The overall cost of the forensic investigation was approximately $7,000, and the study was completed within a month.

8.2.2 Case Study 8.1: Snapshots of the Forensic Investigation

Line of Evidence 1: Historical Document Review	**Main Findings**
As with any forensic investigation, historical document review was conducted as the first step. In this case, due to the narrow timeframe available for the forensic study (including any sampling and analysis), a general review was not performed, and the specific review was a focused one that included a few relevant available documents. Relevant historical documents were gathered to reveal past occupancy and operations at the former industrial site. Emphasis was on the past use as a service station, as that happened on the side of the property where the petroleum contamination was found. However, general documents related to the other past use of part of the property as a chemical plant were also targeted for review.	• The documents consulted confirmed the major oil company as the past operator of a historical service station, including storage and handling of petroleum products on about half of the redeveloped site where the petroleum contamination was actually discovered. The location of various site features that could have been sources of petroleum contamination, such as pipelines and storage tanks, was also established. Evidence was obtained pointing out that the pipeline discovered with heavy product was associated with the site's previous use as service station. • Based on the document review and the information related to where contamination and old pipeline were discovered, a forensic sampling and analysis plan was developed to establish the extent and chemical "signature" of the petroleum contaminants in various areas. Soil samples were to be collected on a grid pattern (on a 10-m grill), along with any potential free product encountered during the proposed sampling. All samples were to be analyzed for an extended hydrocarbon range (C5–C40); selected samples (representative for the location of potential previous sources) were also to be analyzed for various hydrocarbon classes.
Line of Evidence 2: Chemical Fingerprinting	**Main Findings**
All samples collected were analyzed for TPH (total petroleum hydrocarbons); four samples (one from near the broken pipeline discovered) were selected for detailed chemical fingerprinting of various hydrocarbon classes as shown in Table 8.2. The chemical fingerprinting analyses were performed by Zymax Forensics Laboratory.	• Selected chemical fingerprinting results for the four samples analyzed are included in Figures 8.1 through 8.4. • Diagnostic ratios (including pristane/phytane, C2-dibenzothiophenes/C2-phenanthrene, C3-dibenzothiophenes/C3-phenanthrene, n(8α drimane)/r(8α homodrimane), and nonylcyclohexane/heptylcyclohexane), were calculated as shown in Figure 8.1. Similarities between these ratios for all four samples along with sample locations and concentration distributions revealed a main common source for all the petroleum contamination discovered.

TABLE 8.2

Specific Chromatograms Generated for Fingerprinting Analysis

Ion (*m/z*)	**Compound Class**
TIC	All compounds
85	n-Alkanes
113	Iso-alkanes and isoprenoids (acyclic)
83	Alkylcyclohexanes
134	C_4-benzenes
123	Bicyclanes (bicyclic sesquiterpanes)
191	Terpanes
217	Steranes
253	Monoaromatic steranes
231	Triaromatic steranes

Chemical fingerprinting data consisted of various chromatograms (for analysis at each *m/z* value) along with individual hydrocarbon compounds reported in relative concentrations based on a semiquantitative analysis (extracted ion counts). The forensic analysis consisted of the evaluation of chromatograms and histogram patterns for each class of hydrocarbons analyzed along with the calculation of a series of diagnostic ratios providing information on the source as well as the weathering and maturation stage of the petroleum contamination in each sample. Many of the diagnostic ratios using isoprenoids (e.g., pristine, phytane), PAHs, hopanes, and steranes published in the literature and included in Chapter 4 of this book were used.

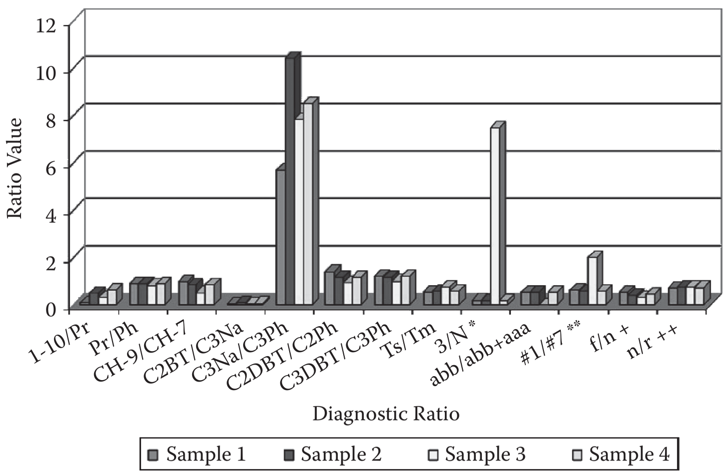


FIGURE 8.1
Selected diagnostic ratios for selected four soil samples.

- Overall, the investigation pointed out the presence, in all samples, of a main petroleum product consisting of a weathered (20 years or more) middle distillate that originated from a common source. This product was mixed with a heavy distillate in many samples (see discussion for next figures). The location, distribution, and weathering characteristics were all consistent with the historical service station operated by the major oil company as a major source.

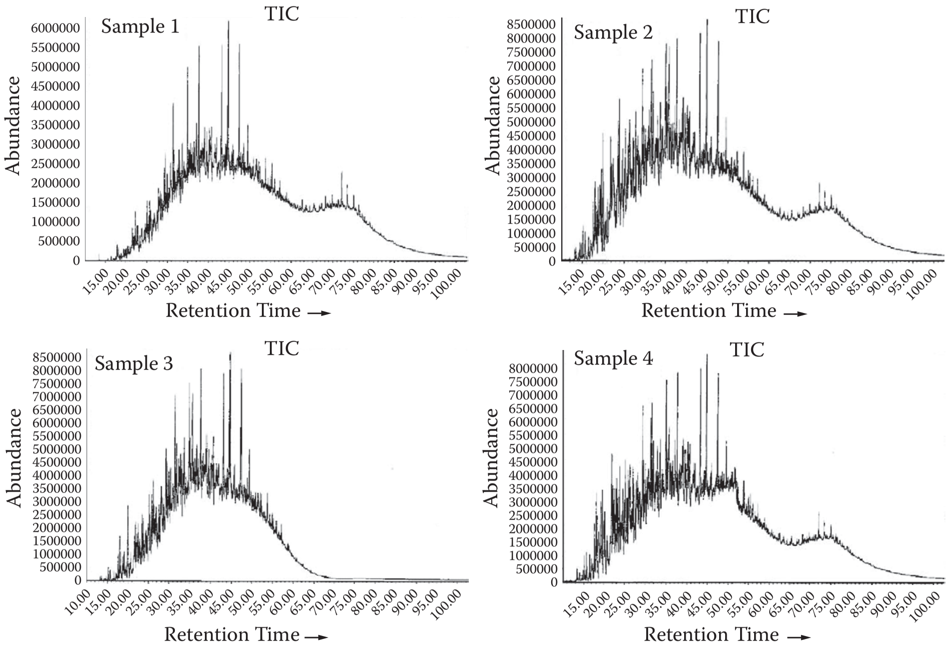


FIGURE 8.2
Total ion chromatograms (TICs) for the four selected samples. The chromatographic profiles shown are consistent with the presence of a weathered middle distillate in all samples along with a heavy distillate in all samples except sample 3. Note the preeminent unidentified complex mixture (UCM) hump in all samples, which indicates that biodegradation occurred, being also consistent with the lack of n-alkanes in all samples except sample 2, with some small amounts of n-alkanes still present. Small differences between weathering stages of these samples (with sample 1 the most weathered) may be due to slight differences of environmental conditions between sample locations (spread across the site), while the data are consistent with a common source for the middle distillate in all samples. The heavy distillate profile (see second chromatographic hump area) is also consistent with a common source in all samples where it is detected, consistent and likely related to the discovered broken pipeline.

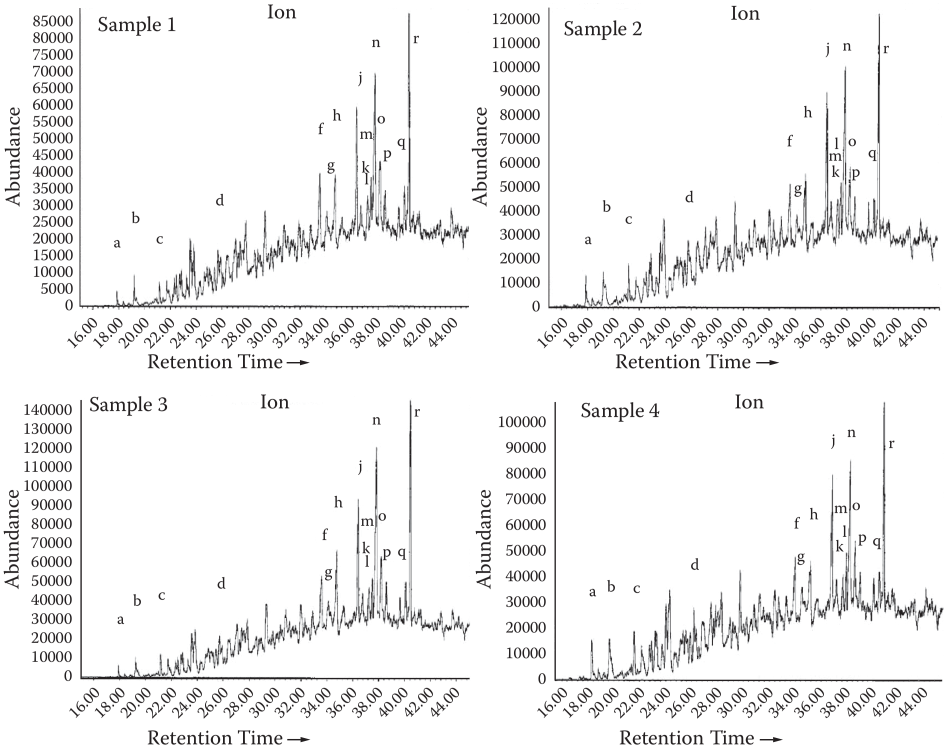


FIGURE 8.3
Chromatograms for bicyclanes/bicyclic sesquiterpanes (m/z 123). This hydrocarbon class is in the range of middle distillates; thus, the striking similarity between the chromatographic profiles of all four samples confirms a common source for the middle distillate in all samples. This is consistent with the chromatographic information from TIC and other hydrocarbon classes.

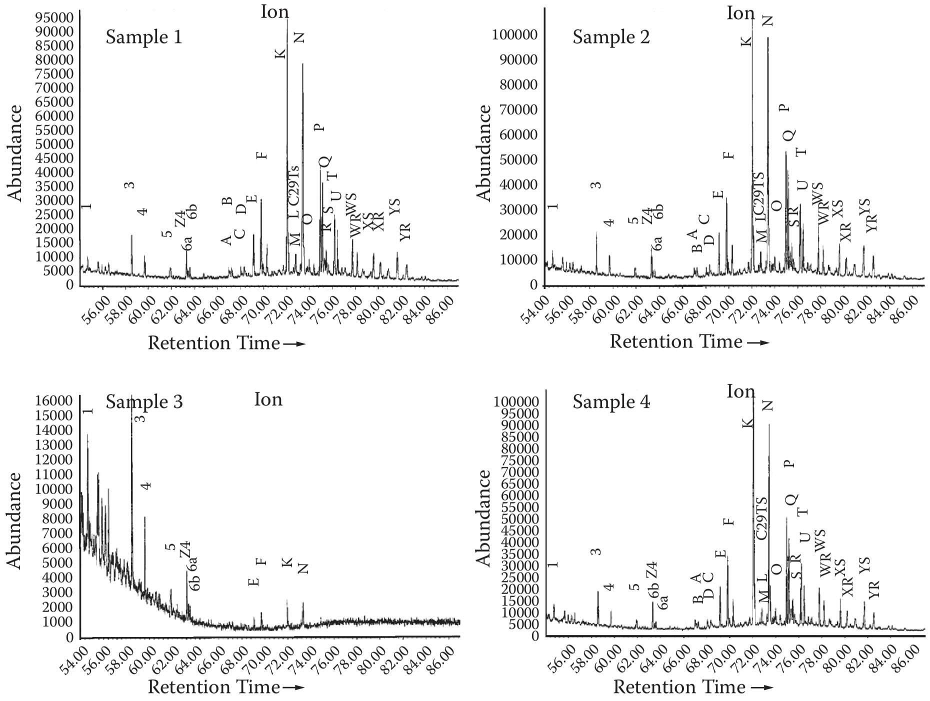


FIGURE 8.4
Chromatograms for terpanes/hopanes (*m*/*z* 191). This hydrocarbon class is mostly in the range of heavy distillates; thus, the similarity between the chromatographic profiles of samples 1, 2, and 4 confirm a common source for the heavy distillate (i.e., hydraulic or lubricating oil) in these three samples, which is consistent with the results from TICs discussed previously. The distinct chromatographic profile observed for sample 3 is due to the lack of heavy distillate in this sample for which the observed chromatographic peaks may be due to the presence of a petroleum residue. These observations are also consistent with those from TIC discussed previously.

Key Remark

- **It is never too soon to start a forensic investigation.** Apart from the potential for substantial cost savings and cost recovery from responsible parties, the forensic investigation ensures the removal of identified contaminant sources and the long-term remediation success. Should a forensic investigation have been conducted before the first remediation, no additional hydrocarbon contamination would have remained to be discovered later.

9

Neighboring Industrial Sites with Complex Releases of Similar Contaminants

9.1 Strategic Guide

This type of forensic investigation refers to practical situations in which multiple contaminants of the same type were released over the years at neighboring industrial sites with similar historical operations. The challenge is to evaluate if the contamination released at each of the sites affected the environment of the other site. This is particularly challenging when most of the contaminants released are similar between sites, and the sites have recorded historical releases and similar operations. This forensic investigation type is strategically described in Table 9.1.

Case Study 9.1 illustrates how the strategic concepts briefly described in Table 9.1 have been applied in practice. As with the other case studies presented, the emphasis is on the main forensic strategies, without reviewing in detail any of the lines of evidence described.

9.2 Case Study 9.1: Forensic Investigation at Two Neighboring Industrial Sites with Similar Past Operations in Southern California

9.2.1 Case Study 9.1: Overview

9.2.1.1 Historical and Legal Context

Complex soil, soil gas, and groundwater contamination with chlorinated solvents and petroleum hydrocarbons, as well as a series of organic solvents (e.g., methyl ethyl ketone [MEK], methyl isobutylketone [MIBK], acetone) have been discovered at two neighboring industrial properties in Southern California. These properties had similar historical businesses, consisting of chemical storage, handling, and repackaging. The properties are separated

TABLE 9.1

Challenges and Solutions for Forensic Investigations at Neighboring Industrial Sites with Similar Releases and Operations

Challenges	Solutions

• Contamination exists in the subsurface at neighboring industrial sites as a result of recorded releases of multiple similar contaminants that occurred during the years at both sites.
• Both sites had similar historical operations, handling and releasing similar multiple contaminants during the years; therefore, in theory, contamination released at any of the site could have reached and affected the subsurface environment of the other site, contributing to the contamination observed at the time of the forensic investigation.
• The targeted contamination for this type of challenge includes many individual contaminants of various common types, such as chlorinated solvents, petroleum products, organic solvents, or inorganic compounds; in addition, evidence for both nonaqueous phase liquid (NAPL) and dense nonaqueous phase liquid (DNAPL) releases may exist at these types of sites.
→ *The goal of this type of forensic investigation is to evaluate contributions from any one of the neighboring sites to the contamination present in the subsurface environment of the other site (to establish if any of the sites would have to pay for any of remedial costs at the other site).*
	• This type of complex forensic challenge can only be solved using multiple lines of evidence, including two or more of the following main forensic testing techniques (from those described in Chapters 4 and 5):
	  • chemical and geochemical fingerprinting followed by data visualization techniques;
	  • signature chemicals;
	  • isotopic fingerprinting;
	  • contaminant modeling;
	  • multivariate statistics.
	• Obviously, the proper use of the lines of evidence suggested would involve detailed historical document review for each site.
	• The main goal would be to use samples representative for each specific site's recorded release area to evaluate the fate and transport of released contaminants and obtain useful forensic signatures.
	• Confirmation of the forensic findings through at least two independent lines of evidence is recommended.

by railroad tracks and a drainage ditch/creek (Figure 9.1). For storytelling purposes, we refer to the property to the north of the ditch as Site A and to the property south of the ditch as Site B. Various site features are shown in the Figure 9.1, some of them representing source areas.

The sites are located in a heavily industrialized area of Southern California. Both sites had underground and aboveground storage tanks (USTs and ASTs) for storage of bulk chemicals and waste. Both sites also stored chemicals in 55-gallon drums. In addition, Site A used to store chemicals in a few railroad cars permanently parked on some railroad tracks located at the western-northwestern border of the property (Figure 9.1). A large variety of chemicals was stored and handled at these sites, including methylene chloride (MC), tetrachloroethylene (PCE), trichloroethylene (TCE), 1,1,1-trichloroethane (1,1,1-TCA), acetone, methyl ethyl ketone (MEK), methyl isobutylketone (MIBK), toluene, xylenes, isobutyl acetate, butyl cellosolve, propanol, kerosene, as well as fuels such as diesel and

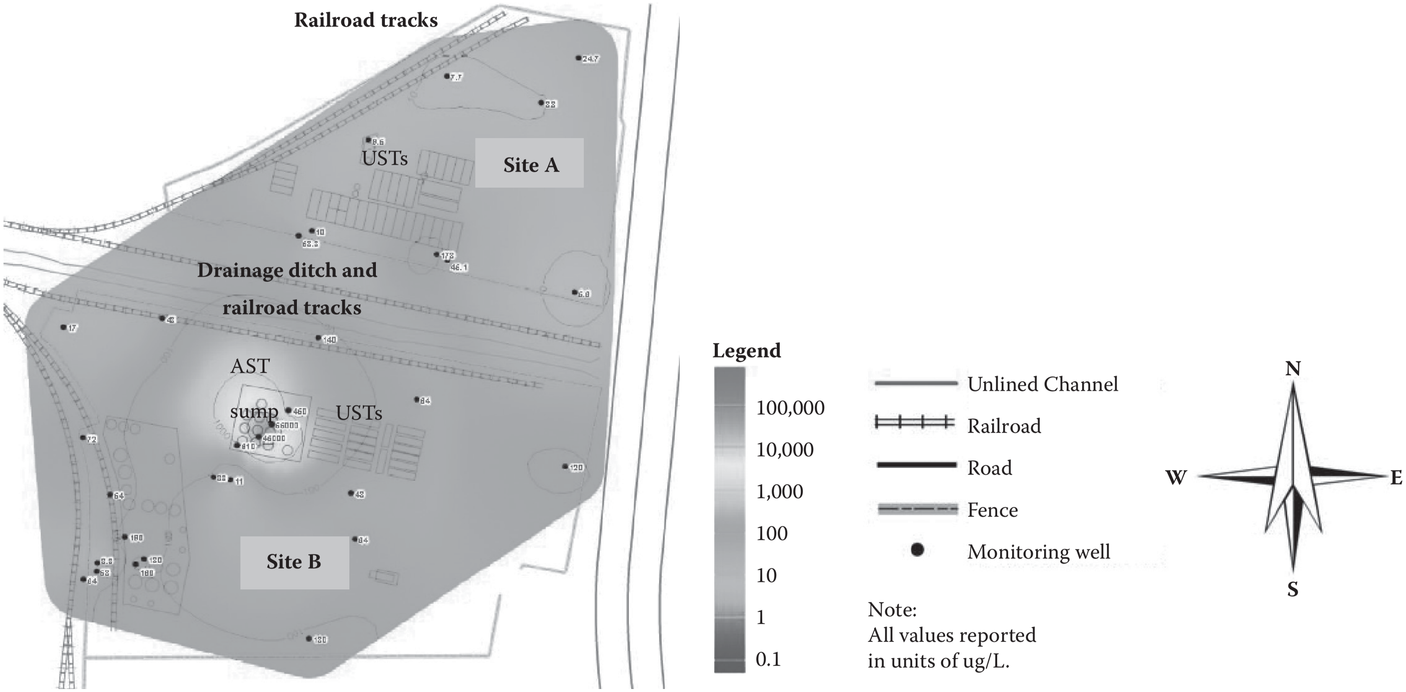


FIGURE 9.1
(See also color insert.) Location and main features of Sites A and B, along with TCE concentration in deeper regional groundwater.

gasoline. Both sites started to operate in 1976. Site B ceased operations in 1986; Site A continued operations until 2000. Site A was about half the size of Site B. In general, Site A handled and sold fewer chemicals per year compared to Site B but operated for a longer time. Site B had historically discharged to the drainage ditch located between the sites and had a National Pollutant Discharge Elimination System (NPDES) permit. Site A did not discharge to the ditch. The Site B surface slope was toward Site A, while Site A sloped toward the north and east (away from Site B).

Both sites had recorded historical releases of contaminants and both sites were found to be contaminated with chemicals historically handled at the sites. In addition, both sites overlaid a regional groundwater plume with several volatile organic carbons (VOCs) (i.e., chlorinated solvents) that originated at an upgradient Superfund site.

Several groundwater aquifers have been delineated below the sites; the major ones are as follows:

- a shallow aquifer (generally found between approximately 25 and 30 ft bgs) with generally fluctuating water and flow direction;
- a deeper regional aquifer (generally found deeper than 45 ft bgs) with consistent flow reported toward the south-southwest, thus from Site A toward Site B.

A lawsuit has been brought by Site A (the plaintiff) alleging that Site B (the defendant) had contributed to the contamination found at Site A through historical operations and releases affecting the vadose zone and the shallow aquifer. Those involved with Site B, in turn, alleged that not only it did not contribute to any contamination at Site A but also it was and may still be impacted by Site A releases via transport with deeper regional groundwater.

9.2.1.2 Forensic Target

The forensic investigation was triggered by the litigation brought by those involved with Site A. The aim was to respond to the following main questions:

- Had Site B contributed to any of the contamination found at Site A? If yes, what is the Site B contribution?
- Did Site A have an impact on the deeper regional groundwater?

9.2.1.3 Environmental Forensics at Its Best

This case study provides an example of the typical use of environmental forensics in the context of complex litigation support. Overall, this forensic investigation lasted for more than 5 years and pursued multiple lines of evidence, starting with a detailed document review and ending with application of complex fingerprinting, subsurface modeling, as well as data visualization and animation.

9.2.1.4 Outcome

This multiyear forensic investigation (conducted in the 2000s) revealed multiple lines of evidence in support of the claim that historical operations at Site B contributed indeed to the contamination found in the subsurface at Site A (the client). Based on these lines of evidence (see the next section), the case settled before trial. In addition, the forensic investigation provided solid evidence related to the lack of significant contributions from Site A releases to the regional groundwater plume, building a defensible case in favor of removing Site A from the list of potentially responsible parties (PRPs) for the regional groundwater plume (over a mile in length). The forensic investigation resulted in the production of expert and rebuttal reports and had substantial contributions to the Remedial Investigation/Feasibility Study (RI/FS) for Site A. The substantial forensic costs (over the entire multiyear project duration) were paid by the insurance carrier of Site A.

9.2.2 Case Study 9.1: Snapshots of the Forensic Investigation

Line of Evidence 1: **Historical Document Review**	**Main Findings**

A thorough document review was performed. This is generally typical for complex litigation support cases. The review consisted of both a general and a specific review. The general review focused on chemical storage and repackaging business characteristics and practices recorded in the 1970s and 1980s.
The specific review included the detailed consultation of thousands of documents. The following main types of documents were acquired and consulted: aerial photographs (including historical photographs), comprehensive company records, regulatory agency files (including permits and violations), correspondence, past trial transcripts, and over 200 deposition testimonies from past employees at both sites.
	• The shallow aquifer was strongly influenced by precipitation and water infiltration (e.g., from spills or dumping) regimes and had various recorded flow directions (both toward the north-northeast and the south-southwest). The deeper aquifer had consistently reported flow direction toward the south-southwest.
	• Releases from Sites A and B were distinct from various points of view, including the following:
	  • *amounts released* (higher for Site B);
	  • *proportion of handled and released contaminants* (Site A had prevalent peroleum products and nonchlorinated solvent releases versus chlorinated solvent releases; Site B had prevalent chlorinated solvents and freon releases);
	  • *type of releases* (Site A had several accidental releases, a broken pipeline that discharged for multiple years, as well as small spills and leaks during the years; site B had several major dumping events, apart from small spills and leaks and accidental releases).
	• Site B had documented chemical dumping on site, including as part of operating procedures, such as
	  • occasional dumping of the line flushes (what remains in hoses after chemical transfer and cleaning with solvent) into the unlined AST dike (on bare soil) during the 1970s and early 1980s;
	  • dumping at the railroad tracks (between the two sites) during the first 8 months of operation (1976–1977).

Line of Evidence 1: Historical Document Review	**Main Findings**
In addition, available environmental monitoring data were carefully reviewed. Both sites were investigated, and a wealth of monitoring data was available, mostly from the 1990s and 2000s (including boring logs and chemical analysis of affected media). However, only limited monitoring data existed (and only for Site B) from the period when both sites were operating (1976–1986), with basically no relevant data related to groundwater presence and flow direction at that time.	• Site A had a main documented release due to broken underground piping leading into the waste underground storage tank; another main release area at Site A proved to be the railroad spur area (northwest of the site) where mostly shallow soil was affected. • Site B had constant discharges into the drainage ditch and several related violations. • Site A did not have recorded dumping of chemicals on site and did not have discharges into the drainage ditch; Site A was carefully collecting and reselling the line flush and other waste. • Site B had generally poor housekeeping, while Site A had generally good housekeeping practices. • Site B had a "zero-spill" tolerance policy, especially in later years. Yet, various testimonies questioned the application of the policy during daily activities. • Site B used mostly reconditioned drums; Site A used mostly new drums. • Site A had a corrosion protection system for its USTs that were checked periodically; it is not clear if protection existed for Site B's USTS. • Methylene chloride was the prevailing chlorinated solvent used at Site A; other chlorinated solvents prevailed at Site B (e.g., TCE, PCE, 1,1,1-TCA). • Site B had an entire operation and a dedicated area (toward the northeastern border with Site A) for handling freons; Site A had only one recorded drum of a freon 113 product during the years. • Site A had regular testing of chemical storage devices (e.g., stick testing) to check for integrity and spills. • Several lithological layers were characterized, and some were continuous below sites. **These findings constituted the basis for the selection and interpretation of other lines of evidence.**

Line of Evidence 2:
Lithological/Hydrogeological Modeling—Main Findings

The wealth of existing monitoring data enabled reconstruction of subsurface lithological layers below both sites. The resulting lithological layers are depicted for Site A in Figure 9.2; for both sites, the lithological layers can be seen in a north-south cross section depicted in Figures 9.3a and 9.3b.

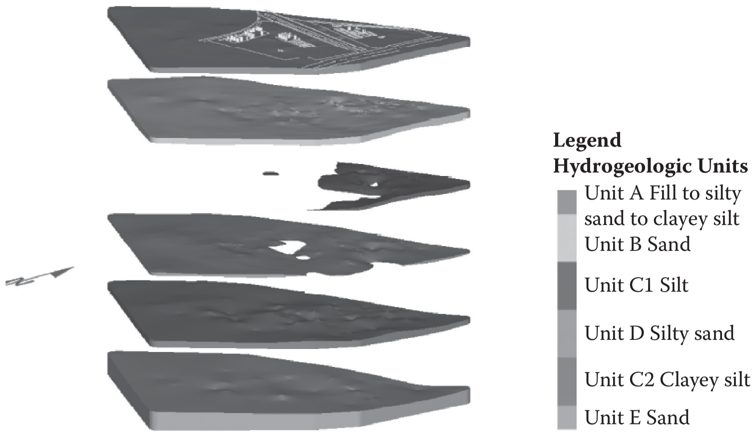
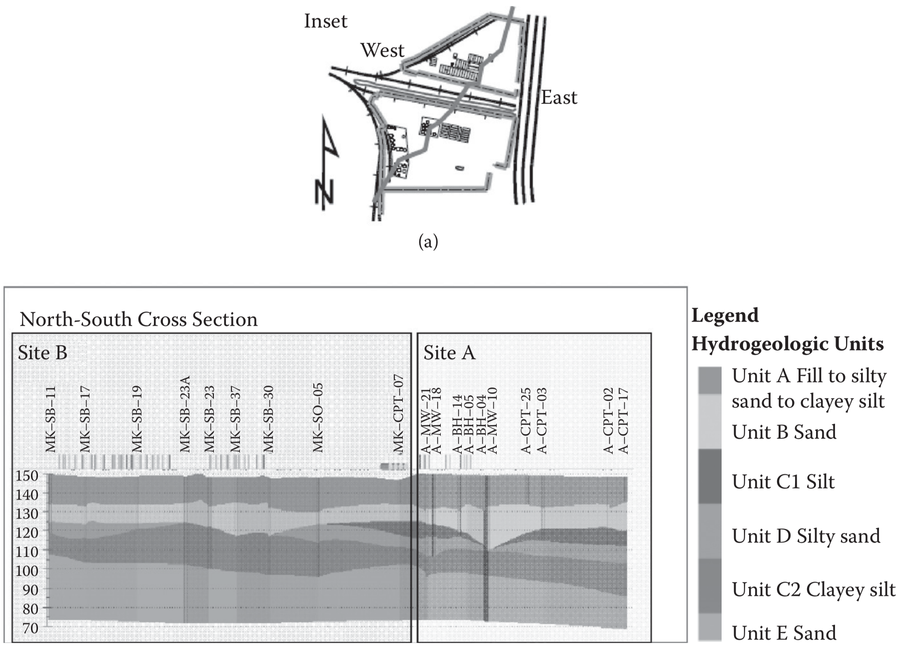


FIGURE 9.2
(See also color insert.) Reconstructed lithological layers (below Site A).

Based on the detailed review of relevant hydrogeologic/lithologic data (e.g., from boring logs and environmental reports), a subsurface model was proposed to reveal contaminant conduits on top of lithological layers with lower permeability. Contaminant transport conduits were observed between the two sites (continuous lithological layers/hydrogeologic units). Specifically, unit C2 (a clayey silt) was interpreted as aquitard (not allowing water percolation); thus, any water or liquid reaching the top of it (i.e., within unit D) would flow based on the slope of unit C2 (apart from hydraulic pressure). As seen in Figure 9.3b, the slope is from the middle of Site B (right in the location of the AST dike source area) toward Site A. **Therefore, the surface spills recorded at Site B's AST dike during the years would have percolated through soil and then moved laterally toward Site A on top of layer C2.**



(a)

(b)

FIGURE 9.3
(See also color insert.) (a) North-south cross section location along the two sites (A and B)—note that Site A is toward north of Site B. (b) North-south cross section along the two sites (A and B)—note that north is to the right.

Line of Evidence 3:
Signature Chemicals—Main Findings

As mentioned, the historical document review revealed that in spite of the general similarity in operation and chemicals handled at the two sites, a major difference was observed related to the use of different types of freons. Site A documented the presence of only one drum of freon product, while Site B had an entire operation and dedicated area to handle freons (chlorofluorocarbons, CFCs). This particular evidence had remained "hidden" until later in the case because freons were not considered of concern and not looked for at Site A.

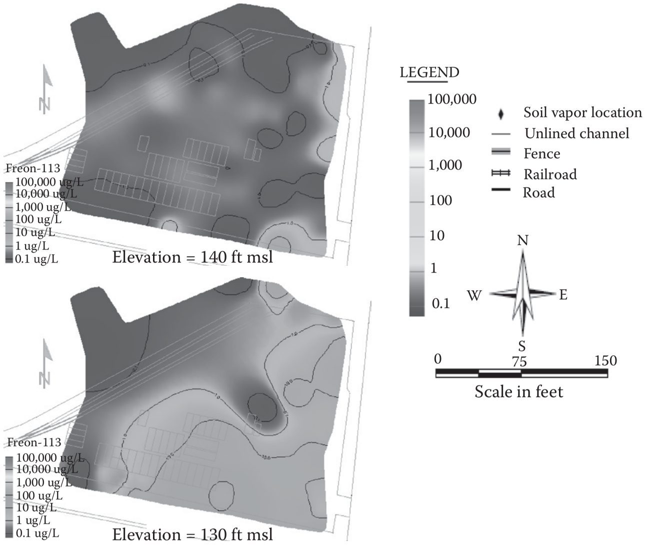


FIGURE 9.4
(See also color insert.) Freon 113 detection (isoconcentration plumes) at Site A in soil vapor at 10 ft (top) and 20 ft (bottom) below ground.

While digging deeper into the historical evidence, freon use history was revealed, and freons were qualified as "signature" chemicals for Site B. Basically, freons were not used at Site A (with a minor noted exception of one drum), but massively used, spilled, and detected at Site B. Once this was established, all that remained was to evaluate the potential presence of freons in the subsurface at Site A. Fortunately, although regular subsurface monitoring did not report these contaminants (i.e., freon 113), several soil vapor surveys (from the late 1990s) did report freons, including freon 113. The detections of freon 113 in soil vapor at 10 and 20 ft bgs (upper and lower images) are depicted in Figure 9.4. The mere presence of freon 113 in the subsurface environment at Site A along with its detection pattern with higher concentrations at 20 ft (closer to a shallow groundwater table) and toward the south-southeast (where the Site B freon area was) clearly denoted that Site B contamination must have reached and affected Site A.

Should the freon source have been from Site A, both its vertical and horizontal distribution pattern would have been different (with a higher concentration closer to the surface and in established source areas for Site A). In addition, it was demonstrated that freon 113 could not have intruded from the regional plume due to the presence of the aquitard layer and other geologic/hydrogeologic evidence (not presented here).

In conclusion, the presence of freon 113 and its detection pattern in the subsurface at Site A was the "physical proof" that Site B had indeed historically affected Site A.

Line of Evidence 4:
Chemical Fingerprinting/Data Visualization—Main Findings

The lateral and vertical contaminant distribution patterns in the subsurface can tell the contamination "story" (e.g., where they come from and how). Much evidence was evaluated and considered in this case (data were analyzed at various labs). Findings are summarized here using two relevant examples depicted in Figures 9.5 and 9.6. Additional related examples and a detailed discussion are provided in Chapter 5 (Section 5.4.3) illustrating the use of data visualization.

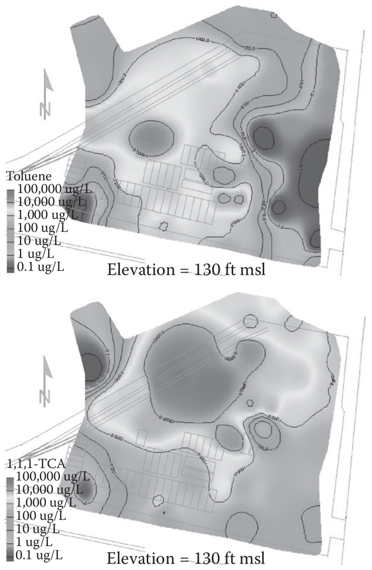


FIGURE 9.5
(See also color insert.) Soil vapor concentrations at 20 ft bgs for toluene (top) and 1,1,1-TCA (bottom) at Site A.

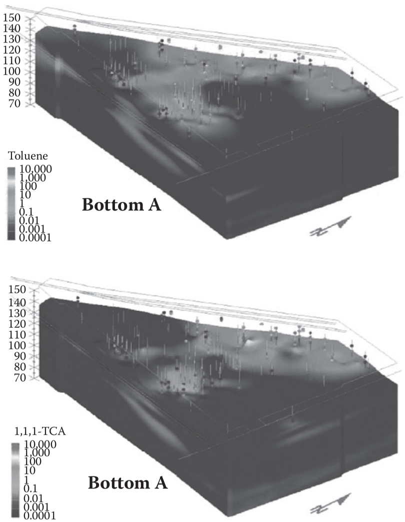


FIGURE 9.6
(See also color insert.) Soil concentration profiles (bottom of unit A) for toluene (top) and 1,1,1-TCA (bottom) at Site A (note that in both Figures 9.5 and 9.6, the red color is used to show the highest recorded concentrations, and blue color indicates nondetects).

By comparing contaminant concentration distribution patterns in different media and at various depths (Figures 9.5 and 9.6), it becomes apparent that, overall, there was only a slight fit between concentrations in soil vapor (at 20 ft bgs) and shallow soil (10–15 ft bgs representing the bottom of unit A). It is also evident that while there was a general fit between 1,1,1-TCA and toluene shallow soil concentration profiles, there was little fit between the concentrations of these two contaminants in deeper soil vapor. These observations along with the fact that shallow soil contamination was of a lower magnitude than deeper soil vapor contamination indicate that the contamination detected in soil vapor was representative for shallow groundwater, which likely contained commingled contamination. Basically, the surface spills at this site cannot explain the complex subsurface contaminant profiles. Overall, this confirms the existence of commingled contamination from on-site and likely off-site sources in the shallow aquifer.

When this type of evidence was correlated with the other lines of evidence, some historical intrusion of contaminants from Site B (to the south) appeared probable.

Line of Evidence 5:
Geochemical Fingerprinting—Main Findings

As described in Chapter 5, when combining lithological/hydrogeological with chemical evidence, in-depth information is obtained related to contaminants within the environmental matrix. Figure 9.7 depicts the concentration of 1,1,1-TCA from several boring logs shown overlaid over the encountered lithologic layers. This type of data representation helps interpret the observed contaminant concentrations. Specifically, a sudden increase of concentrations at deeper depths within the same layer cannot be explained as the result of contamination coming solely from surface sources. This logic also applies when deeper contamination increases compared to that from a shallower layer with the same or higher ability to adsorb contamination. In the absence of subsurface-specific sources, lateral transport with groundwater from potential off-site sources may be suspected. Part of the example provided in Figure 9.7 and a detailed discussion are provided in Chapter 5 (Section 5.2.2) illustrating the use of geochemical fingerprinting.

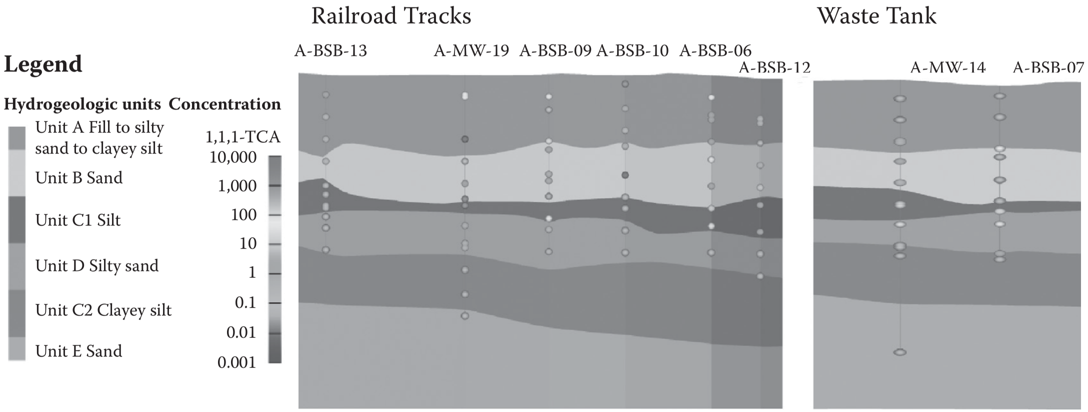


FIGURE 9.7
(See also color insert.) Vertical profile of 1,1,1-TCA in soil at two historically recorded source areas at Site A (see color-coded concentration scale and hydrogeologic units in legend to the left).

The results displayed in Figure 9.7 denote that not all the subsurface contamination reported at Site A is attributable to surface or close-to-surface historically recorded on-site sources.

NOTE: The forensic investigation snapshots provided address only the first part of the investigation, aiming to establish if Site B contributed to the contamination found in the subsurface at Site A. In addition, environmental modeling was used to allocate Site B contributions, which is not presented in the synthetic guiding-type material of this book. Note also that the second main part of the forensic investigation focused on the evaluation of the potential contributions of Site A to the deeper regional groundwater plume. Multiple lines of evidence were also used for this part of the investigation. While snapshots related to this part of the investigation are not presented here, an example of evidence investigated is provided in Figure 9.8.

As shown in Figure 9.8, there was no correlation between the temporal concentration trends of contaminants shown in the shallow groundwater well from Site A versus any of the downgradient deeper wells at Site B. The selected monitoring well from Site A (MW1) was one of the wells suspected

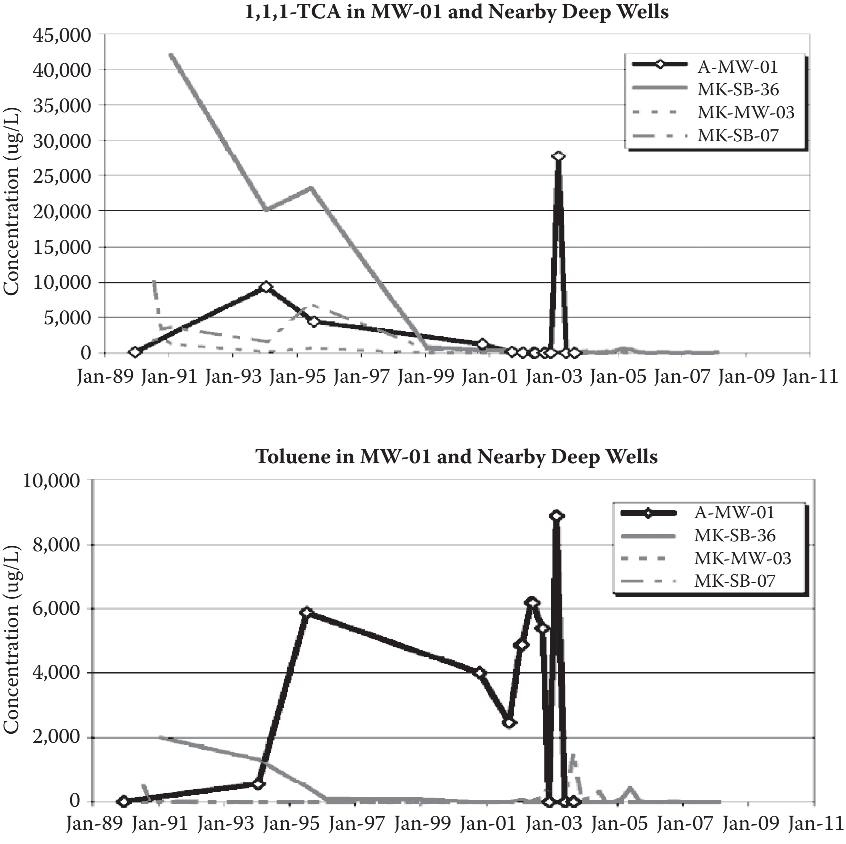


FIGURE 9.8
Temporal concentration patterns for 1,1,1-TCA and toluene in a shallow groundwater well at Site A (MW01; see darker line) and in downgradient deeper groundwater wells at Site B.

to have been cross screened in shallow and deeper aquifers, thus potentially providing a conduit for shallow contamination to reach below toward the regional aquifer. This type of evaluation has been performed for other shallow wells, also using hydrologic data. The resulting evidence was similar with what is shown in Figure 9.8, with no correlations observed between shallow and deeper downgradient wells. Other lines of evidence, including fate and transport evaluation as well as chemical and geochemical fingerprinting, confirmed the finding that no significant contamination from Site A had reached and affected the deeper regional groundwater.

Key Remarks

- **Multiple lines of evidence are necessary at complex contaminated sites.** Case Study 9.1 denoted this. Specifically, several independent and interdependent lines of evidence were used to forensically investigate the complex mixed contamination below the neighboring sites with similar historical operations and to decipher contributions and impacts from the sites.
- **At least one of the investigated lines of evidence should provide straightforward evidence** confirming the findings from environmental modeling and complex statistical and fingerprinting evaluations. For Case Study 9.1, signature chemicals and evaluation of temporal contamination patterns provided such straightforward evidence that increased the defensibility of other lines of evidence.

10

Environmental "Poisoning" Story

10.1 Strategic Guide

This type of forensic investigation refers to practical situations in which some sort of environmental "poisoning" is claimed. Typically, this type of investigation involves neighboring residential properties, with contamination being discovered at one of the properties as a result of alleged releases from a neighboring property. For this type of case, intentional releases of contaminants from the neighboring properties are usually claimed to have damaged the environment and health of residents at the other property. Basically, a lawsuit is filed (one neighbor suing the other one) for compensation of such damages. The challenge is to evaluate the exact allegations when most of the released contamination might have changed at the time of sampling or not be available for sampling. Instead, the forensic investigator may be asked to rely on previous testing done by the plaintiff that typically does not fit the requirements of forensic investigation. This investigation type is strategically described in Table 10.1.

The case study that follows (Case Study 10.1) illustrates how the strategic concepts briefly described in Table 10.1 have been applied in practice. Here again, the emphasis is on the main forensic strategy, not revealing in detail any of the described lines of evidence.

10.2 Case Study 10.1: Was a Resident "Poisoning" the Property of a Neighbor?

10.2.1 Case Study 10.1: Overview

10.2.1.1 Historical and Legal Context

The owner of a Southern California residence sued his neighbor, claiming that the neighbor "poisoned" his property. Specifically, intentional contamination of vegetation and pool water from the plaintiff's property by

TABLE 10.1

Challenges and Solutions for Forensic Investigations at Residential Properties Evaluating the Claim that One Neighbor Intentionally Poisoned the Other Neighbor's Property (with Contamination)

Challenges	Solutions

• One neighbor (the plaintiff) is suing another neighbor (the defendant), claiming intentional poisoning of his property. Specifically, some sort of environmental contamination is alleged to have been intentionally released by the defendant, causing property damage and potential health issues to the plaintiff.
• At the time when a forensic investigator is brought in (after the initiation of the lawsuit), the critical evidence might have been lost (e.g., the plaintiff's property might have been cleaned), and the forensic investigator might need to rely (in part or exclusively) on testing done by the plaintiff to initiate the lawsuit.
• The contamination for this type of challenge includes various contaminants, which may involve chemicals associated with herbicides/pesticides, household chemicals, fuels, or fertilizers.
→ *The goal of the forensic investigation is to evaluate the validity of the environmental "poisoning" claims using existing evidence and any testing that may reveal the presence and fate and transport of alleged released contamination (to provide evidence in the lawsuit).*
	• Simpler is better. This type of forensic challenge should be solved using simple, straightforward evidence acquired through the following main techniques:
	  • Interviews with both the plaintiff and the defendant to understand the claims and the defense; interviews with other people as relevant to the case;
	  • Review of existing evidence, including any relevant documents and available testing; make sure also to understand the properties and fate and transport of any alleged contaminants;
	  • Site visit and potentially additional forensic testing (methods from Chapter 4).
	• The main goal is first to understand the allegations and the existing evidence thoroughly; based on these, an adequate forensic strategy is created related to things to check during a site visit and potential forensic testing; the main strategy is to look for things that do not fit or contradict the allegations (see Case Study 10.1 as an example).
	• Confirmation of the forensic findings through independent lines of evidence may not be necessary; typically, if one line of evidence clearly contradicts the allegations, that may be enough to decide about the validity of the allegations.

the neighbor (the defendant) was alleged, and a lawsuit was brought forth. Alleged contaminants included nitrate and malathion (a pesticide). The plaintiff was claiming adverse health effects due to the regular usage of a contaminated pool, as well as nuisance claims due to a tree's death and fall on his property, located just between the allegedly polluted pool and the fence separating the two properties.

10.2.1.2 Forensic Target

In this context, a forensic study was initiated by the defendant to investigate the claims brought by the plaintiff against him and determine the source of elevated nitrate, malathion, and other compounds allegedly detected by the plaintiff in the pool water, soil, and vegetation from the plaintiff's residence.

10.2.1.3 Environmental Forensics in the Context of Minor Litigation

This case illustrates the use of forensic investigations in relatively minor environmental litigation cases involving residential properties. Although these cases are usually less complex from the point of view of the amounts and types of released contaminants, the main challenge relates to gathering relevant forensic evidence that may no longer be possible when the forensic expert begins involvement in the case. This was the situation in this case, as I was faced with no pool water sampling option since the pool had been drained for some time by the plaintiff. Fortunately, soil sampling was still available, as soil had not been disturbed and had been alleged as one of the main contaminant conduits.

10.2.1.4 Outcome

The case settled before deposition and trial in favor of the defendant (the client). The settlement happened soon after the results of the forensic investigation were revealed to the plaintiff's representatives. The forensic study was once more successful not only in solving the "mystery" but also in saving money and time associated with the lawsuit. Note that a written forensic report was not needed. The forensic investigation cost was approximately \$5,000, and the study was completed within 2 weeks.

10.2.2 Case Study 10.1: Snapshots of the Forensic Investigation

Line of Evidence 1: Historical Document Review	Main Findings
As with any forensic case, historical document review was performed as the first step of the investigation. In this case, this consisted of: • Historical document review, including existing environmental testing done by the plaintiff (including pool water, vegetation, and soil), as well as statements of the plaintiff, defendant, and family members; • Site reconnaissance visit and interviews with residents (plaintiff and defendant).	• The defendant had built a new concrete fence between his property and the plaintiff's property (Figures 10.1a and 10.1b). The fence was close to a big tree on the plaintiff's property and extended along the plaintiff's pool—at a short distance from the plaintiff's pool boundary (there was no more than 1 m of land between the fence and the plaintiff's pool border). • Soon after the new fence was built, the big tree by the plaintiff's pool (between the pool and the fence) suddenly fell into the pool. The plaintiff associated a strange smell with the fallen tree. Since the tree was always healthy, the plaintiff believed that the incident was due to the fence construction by the defendant. Specifically, it was thought that the defendant might have intentionally poisoned the tree because it was hindering the construction work, and some of the tree roots extended below the defendant's property. • Having that suspicion in mind, the plaintiff decided to take samples from the dead tree and from soil around the tree as well as from the pool water. He sent the samples to a laboratory, which analyzed them for various organic and inorganic compounds. • The results showed the pesticide malathion was detected in many samples. Also, higher amounts of nitrate than expected were detected (e.g., levels of 400 mg/L of nitrate were found in the pool water; while usually nitrate in pool water is reported up to 10–220 mg/L). Some polycyclic aromatic hydrocarbons (PAHs) and semivolatile organic compounds (SVOCs) were also identified in some samples. • Because of these results, the plaintiff decided to initiate the lawsuit, drain the pool, and discontinue its use until the situation was resolved. In addition, various health symptoms were claimed by the plaintiff, including skin rashes, headaches, and general poor health. These health issues were associated with the alleged property contamination by the neighbor, especially via exposure to pool water while regularly swimming. • The plaintiff's main allegation was that "poisoning" of his property and pool water happened as a result of the defendant injecting toxic chemicals in the subsurface soil close to the fence between the properties. The plaintiff alleged that the defendant injected the chemicals at several points along the property border below the separating fence, and that somehow the chemicals must have gotten into the pool water, infiltrating through the pool walls from the surrounding soil. The tree would also have been exposed to the injected chemicals as they came in contact with the roots.

(a)

(b)

FIGURE 10.1
(a) and (b) Concrete wall between the two properties. (a) The concrete wall viewed from plaintiff's property; the pool wall is noticeable at the bottom of the image, while the narrow soil area between the pool and the wall is observable; note that the tree that fell was located close to the standing tree from this image. (b) The concrete wall viewed from the defendant's property.

Apart from guiding the forensic testing (identifying locations to be tested and chemicals to look for), the review of relevant documents, along with the site visit and interviews conducted on-site, allowed establishing alternative explanations for the contamination detected through the plaintiff's testing. Specifically, the following alternative explanations became evident:

- Alternative sources of nitrate in the pool, such as human sweat and air transport and deposition due to some recent fires in the area, were identified. Even the tree leaves, which seemed to remain uncollected on top of pool water, could have provided a source for nitrate formation in water. In fact, anything coming in contact with the pool water that would bear nitrogen would add nitrogen in the pool, which would end up forming nitrate. In time, because the pool water was not replaced for long periods of time, nitrate would be expected to accumulate/concentrate since it is not lost by volatilization or precipitation. That could potentially explain the high concentration reported in the pool water.
- Related to the other reported contaminants, a nearby fireplace on the plaintiff's property could have accounted for PAHs and some other contaminants. This is also true for the wildfires reported in the area previous to the whole incident.
- As for the dead tree, it was likely that the impact on its roots due to the wall construction would have mechanically affected the tree roots or a major part of them resulted in the tree death and caused it to fall over the pool.

Line of Evidence 2: Chemical Fingerprinting	Main Findings
Forensic sampling and chemical fingerprinting analysis (of the alleged toxic chemicals, along with general tap water chemistry and pH) were conducted. Samples were taken from soil (both shallow and deeper), vegetation, and tap water from the two properties and from the general area/neighborhood (as control samples). Since the pool had been drained, tap water was collected instead. The chemical testing was done by CalScience Laboratory. Note that the very detailed allegations by the plaintiff guided the soil testing to focus on the locations adjacent to the concrete wall (between the wall and the pool) indicated to have been affected by contaminant injection.  **FIGURE 10.2** One of the collected soil samples adjacent to the concrete wall between properties. This sample was located on the plaintiff's property between the pool and the concrete wall; notice the dry vegetation from that location.	• Chemical fingerprinting involved the investigation of the alleged contaminants in soil at various depths and locations on the border between the plaintiff's and defendant's properties, including the alleged points of injection for the toxic chemicals (see example in Figure 10.2). The exact sampling points were selected based on an interview with the plaintiff conducted on site the day of sampling. The idea was to evaluate the allegation that contaminants were introduced directly in deeper soil via injection. If that were accurate, higher contaminant concentrations were to be expected in deeper soil. In addition, similar chemicals were tested in collected control soil and vegetation for comparison. • The results contradicted the allegations of contaminant injection in deeper soil. In fact, the data suggested that most probably the source of alleged chemicals was coming from the soil surface (0–6 inches deep), possibly from the plaintiff's property itself. This was really simple to prove since the highest concentrations of both malathion and nitrates were found in several areas on the plaintiff's property in surface soil. If the plaintiff's allegations were founded, deeper contamination (below 6 inches depth) should have been higher in concentration, with the hottest spots closer to the defendant property. • There were no higher-than-background values of any contaminant in the tap water and vegetation samples. This also suggested that the contamination found on the plaintiff's property soil was relatively recent (did not affect the vegetation) and probably could not have accounted for the alleged pool contamination that happened approximately a half year prior to the start of the forensic investigation. The chemical fingerprinting therefore confirmed the findings from the document review phase, which suggested a series of alternative sources as more likely explanations for the contaminants recorded on the plaintiff's property. In addition, **the testing results directly contradicted the plaintiff's allegations of how the contaminants were introduced in the environment of the plaintiff's property. Such straightforward evidence resulted in the immediate settlement of the case.**

Key Remarks

- **The key to successful forensic studies relies on looking for straightforward evidence** in support of reasonable scenarios.
- **Alternative explanations/sources should always be considered to strengthen a forensic case;** in this case, alternative, more reasonable, explanations were provided for aspects brought up by the plaintiff's allegations.
- **This case study showed how important it is to put things into context and design and interpret fingerprinting results after site history is known and a site reconnaissance has been performed** by the expert. Interviews with the residents and other knowledgeable persons are also a plus.

11

Residential Pool Disputes

11.1 Strategic Guide

This type of forensic investigation refers to practical situations involving neighboring residential properties with recreational pools, with damages to one residence claimed as a result of water release from a neighboring pool. However, typically, multiple sources for the released water (i.e., multiple pools) are present in the immediate neighborhood, although the allegation usually involves one particular source. A lawsuit may or may not be filed at the time when the forensic investigator is brought to the scene. The challenge is to be able to track the source of released water when dealing with multiple similar sources and restricted sampling opportunities. This forensic investigation type is strategically described in Table 11.1.

Case Study 11.1 illustrates how the strategic concepts briefly described in Table 11.1 are applied in practice. As in other chapters, the emphasis is on the main forensic strategies without providing details for any of the described lines of evidence.

11.2 Case Study 11.1: Tracking a Culprit Pool for Water Infiltration at a Residence Surrounded by Pools

11.2.1 Case Study 11.1: Overview

11.2.1.1 Historical and Legal Context

Regular flooding at a residential property in Southern California has been reported by the owner as a probable result of pool water infiltration from an allegedly leaking pool of a backyard neighbor. Note that the complaining resident also had a pool in his own backyard. At that point, a prelitigation investigation was initiated by the backyard neighbor whose pool was blamed. The neighbor was interested to know if his pool was at fault and to settle and prevent a costly and almost inevitable lawsuit.

TABLE 11.1

Challenges and Solutions for Forensic Investigations Involving Residential Pool Disputes

Challenges	Solutions

• In a residential area where multiple neighboring properties have recreational pools, water damage to one property (house) may trigger the allegation from the property owner that the damage is caused by leaking of a neighboring pool;
• Although more than one pool may exist in the neighborhood and any of the existing pools could potentially be the source of the released water, the allegations typically involve only one specific pool that is a more obvious source in the eye of the property owner (e.g., is located closer to the damaged property); in addition, the damaged property itself may contain a pool, which is rarely seen as a potential source by the worried property owner.
• The contamination for this type of challenge consists in the pool water itself; although pool water typically contains a series of chemicals, most disputes involving this type of release relate to water infiltration damage rather than damage from any chemicals from water.
→ *The goal of the forensic investigation is to track the source of the damaging water considering all the potential sources in the area (to provide evidence that can be used to remediate the problem and settle any dispute).*
	• This type of forensic challenge should be solved using the signature chemicals technique (described in Chapter 4), specifically:
	  • The forensic investigator should inquire about each pool chemical used for all the immediate neighboring pools.
	  • If a unique chemical is found to be used by only one pool, it should be tested for in water samples taken from the damaged property.
	  • If no unique chemicals are found to be associated with any of the pools, the investigator may collect samples from each neighboring pool and test them for pool chemicals (typically used in residential pools) as it is possible that people may not know or recall all the chemicals used in their pools; in addition, water samples representative for the damaging water should be collected and analyzed for the same chemicals.
	• The main goal is to track any potential source (pool) in the damaging water using signature chemicals; if a signature chemical is identified for one pool and it is also identified in the damaging water, this would conclude the case with the culprit pool identified without the need for further testing (or signature chemicals identified for every other pools).
	• If no signature chemicals are found, tracking compounds for each neighboring pool may be used to evaluate leaking and confirm transport toward the damaged property structure.
	• Confirmation of the forensic findings through independent lines of evidence may not be necessary since the signature chemicals technique provides straightforward evidence to uniquely identify a source.

11.2.1.2 Forensic Target

While the main focus of the initiated forensic investigation was to evaluate the particular neighbor's pool alleged to be leaking, a general evaluation of the area, including other potential sources of water leaks, was also targeted.

11.2.1.3 Environmental Forensics as a Prelitigation Step

This case illustrates the use of forensic investigations in support of a prelitigation study meant to help solve the dispute before a costly lawsuit was filed. A prelitigation step is always desirable in anticipation of a lawsuit. As a result, the lawsuit may never happen, and even if it still happens, the parties have fewer surprises related to what the evidence actually shows.

11.2.1.4 Outcome

Using an identified signature chemical, the forensic study found convincing proof that the alleged neighboring pool was not the source of damaging flooding water that appeared at the residence in question. That concluded the dispute between the two neighbors, avoiding an unnecessary lawsuit. Although the exact source of damaging water was not identified, the existence of several potential sources was pointed out, and it was up to the owner of the damaged property to conduct his own forensic study to specifically identify which of the potential sources was the culprit. A written forensic report was not needed. Overall, costs for this environmental forensic investigation were about $1,700, and the study was completed within a single day.

11.2.2 Case Study 11.1: Snapshots of the Forensic Investigation

Line of Evidence 1: Site Visit and Interviews	Main Findings
This particular case is an example for relatively few forensic cases that can be solved without the typical historical document review step. Two main reasons justify the lack of a typical document review: (1) the absence of relevant documents for review since no legal case was filed and no testing was done and (2) the fact that relevant interviews could be done to understand the context and the exact issues. Therefore, without any particular preparation, a site reconnaissance visit was performed. To maximize visit efficiency and minimize costs, apart from conducting relevant interviews with the involved neighbors, water sampling was performed during the visit, and some initial testing was done on site using field analysis kits. In addition, the identification of and visit to other potential sources (e.g., neighborhood pools) were also planned and performed the same day.	• Based on the interviews with the involved residents and the site visit, the exact story was established. It was found that, in the past half year, water appeared to be regularly flooding the soil close to the damaged residential home, and water damage signs were visible in the wood floor of the house. Since the water damage signs appeared close to the area of the yard that was observed to be flooded regularly, it was deduced that water was infiltrating under the house foundation, and the damage could be serious. Therefore, the resident thought that leaking of a certain neighbor's pool that was closer to his residence might be the cause and started the dispute. Some flooding water could be observed during the site visit. However, the location was in front of the house, while the allegedly leaking pool was near the backyard border of the house (Figure 11.1). That was a first indication that the supposed allegations may not hold. • The resident of the damaged property did not know what chemicals are used regularly in his pool. • A visit to the backyard neighbor resulted in the observation that the pool in question seemed in good shape (Figure 11.1). In addition, it was established that one of the chemicals regularly used to treat that pool water was cyanuric acid. The resident confirmed its regular use, and a bag full of this product was observed on the property. • A third residence bordering the side of the damaged residence was observed to have a backyard pool, and a visit was permitted to observe that pool also; it was not known what chemicals were used to treat that pool.

FIGURE 11.1
The allegedly leaking pool from the neighbor's backyard (the damaged home can be seen across the fence toward the left of the image); toward the right, the third residence with a pool identified as another potential source for flooding is visible. Note that the plaintiff's pool and the third identified pool were right behind the fence.

Line of Evidence 2: Signature Chemicals	**Main Findings**
Based on the interviews and site reconnaissance, it was decided to test both the flooding water (Figure 11.2) and the pool water from the allegedly leaking pool (Figure 11.1) for cyanuric acid. This compound was selected as a potential signature chemical for the allegedly leaking pool since its regular use in that pool was established with certitude. In addition, screening of this compound in water was possible immediately since this was a common pool chemical for which a testing kit was available during the site visit. If the results of screening were inconclusive, water samples were to be sent to a laboratory for common pool additives testing. It should be specified that cyanuric acid is a chemical that protects chlorine from being destroyed by the sun in outside exposed pools. Thus, this chemical is added regularly with the chlorine tablets as a "conditioner" or stabilizer.	• The results of the water testing on site using a mobile kit can be seen in Figure 11.3. The results clearly showed the presence (positive identification) of cyanuric acid in the allegedly leaking pool water only. While the test was semiquantitative, it was considered relatively accurate for establishing the presence or absence of a chemical. Therefore, follow-up with laboratory testing was not needed.

FIGURE 11.2
Sampled flooding water.

FIGURE 11.3
Results of the test kit analysis for cyanuric acid performed on site. Lighter color in test tubes 6 and 8 (from left to right) indicates the presence of cyanuric acid; the two test tubes contained water from the allegedly leaking pool; the other test tubes contained flooding water and tap water from each of the two residences in duplicate.

While no testing or sampling were performed on the damaged residence pool water or on the third neighboring pool identified as a potential source of the flooding water, recommendations were made to the resident of the affected home for further testing. The forensic investigation stopped before such testing since it was paid for by the resident of the property with the allegedly leaking pool. Therefore, the final scope was to establish if that pool was indeed the source of the flooding water. The forensic investigation took only 1 day and clearly established that the allegedly leaking pool was not the source of damage. This resolved the dispute and prevented a potentially costly lawsuit from being filled.

Key Remarks

- **Every forensic case is distinct; thus, a forensic investigator should always adjust the forensic approach to case specifics and the client's needs.** In this case, since the client was a potential "defendant," the forensic investigation was targeted to check the potential contribution from client's source rather than to "absolutely" solve the puzzle and establish the identity of the "culprit."
- **More is not always better.** A forensic investigator should know when to stop. Complex cases (such as Case Study 9.1) need detailed investigations and multiple lines of evidence, while other cases such as this one may simply involve taking a few representative samples and analyzing those with test kits. The results are defensible and straightforward once they are tailored to the case.
- **Environmental forensics brings long-term cost-benefits that fully justify the initial costs.** This is true in all cases, regardless if big corporations or just citizens are involved. This case illustrates how a straightforward forensic investigation performed at the right time could save money and hassle associated with a lawsuit. If the owner of the blamed pool had not acted and initiated a forensic investigation before the foreseen lawsuit, he would have ended up spending more money, plus had to deal with all the worries of the lawsuit proceedings. This is because he would still need to pay for a forensic investigation to build a defense plus all the fees and worries associated with the lawsuit. On the other hand, by deciding to act before the lawsuit was filed, he would only gain since, even if the evidence indicated his pool was the potential flooding source, he could come to an agreement with the neighbor and still prevent a potentially "lost case" lawsuit.

12

When All Is Uncertain or Unknown

12.1 Strategic Guide

This type of forensic investigation refers to practical situations in which contaminants are accidentally discovered at sites where no historical documents, monitoring data, or other useful information exists to establish the cause of contamination and identify the sources. These types of cases may involve any contaminants in any type of setting. In spite of the large variety of conditions that may apply for this type of case, the main challenge remains the same: where to start and how to balance timing and costs of the investigation with the need for focused relevant results. This forensic investigation type is strategically described in Table 12.1.

Although Case Study 12.1 does not directly illustrate how the strategic concepts briefly described in Table 12.1 have been applied in practice, the case demonstrates the potential of tree-ring fingerprinting to establish past releases at sites with no contamination history where the technique was deployed to obtain control (background-type) data. As with other presented cases, the discussion does not go into details but rather provides snapshots of relevant information.

12.2 Case Study 12.1: How Tree-Ring Fingerprinting Unravels the Unknown

12.2.1 Case Study 12.1: Overview

12.2.1.1 Historical and Legal Context

The application of tree-ring fingerprinting for age-dating and characterization of chlorinated solvent releases to soil and shallow groundwater was tested at a site in Southern California. The site was chosen since it was affected by a well-characterized tetrachloroethylene/trichloroethylene (PCE/TCE) plume from a neighboring industrial facility. I conducted a vapor intrusion

TABLE 12.1

Challenges and Solutions for Forensic Investigations at Sites with No Available Information

Challenges	Solutions
• When contamination is discovered by accident at sites with limited or no historical or other useful information available, the need arises to establish the cause of contamination to eliminate it and prevent any future additional contamination. • With no information available, building an appropriate forensic strategy may be difficult, while the time and budgetary constraints may not allow deploying a comprehensive testing program. • The contamination for this type of challenge could be anything (e.g., any chemical), starting with the discovered chemicals and extending to many more yet to be discovered within the site boundaries. → *The goal of the forensic investigation is to identify key contaminants and past events/sources on which to focus the environmental testing (to evaluate the type and location of contaminants, as well as any sources to be remediated). Once sources are identified, the data may be used for cost-recovery, too.*	• This type of forensic challenge may be solved using the tree-ring fingerprinting technique (described in Chapter 6) to establish past release events based on associated contaminant markers in trees; the resulting information may be used in conjunction with historical aerial photographs, which can help establish past types of operations and uses. • If the tree-ring fingerprinting technique is not feasible, the use of past aerial photographs along with information from the contamination discovery event may help establish the type of operations and potential released contaminants and sources. • Potential off-site releases should also be considered for tree-ring fingerprinting, aerial photography, and historical investigation. • Confirmation of the findings through independent lines of evidence may not be feasible. *This is an example of how the forensic investigation may be used as an integral step of site investigation and remediation.*

study and noticed an abundance of trees in the yard and vicinity. This observation, along with the presence of a shallow groundwater table and the well-documented release timing of chlorinated solvents (mid-1980s), recommended the site as an excellent candidate to check tree-ring fingerprinting applicability for age-dating of chlorinated solvent plumes. Thus, this case involved no legal actions or disputes of any kind. It was simply meant to test tree-ring fingerprinting applicability at chlorinated solvent sites.

During the investigation, the collection of a control tree core sample from an upgradient location (a few blocks away from the site, the control tree being located on the walkway) was performed as routine sampling related to this forensic technique. When the control tree core was analyzed, evidence that the control tree was also contaminated during several distinct years was surprisingly obtained. Specifically, parallel peaks of phosphorous (P) and sulfur (S) were observed over two main timeframes. In addition, several peaks of chlorine (Cl) were also observed, appearing in distinct years disparate from those of the P and S peaks. Therefore, the forensic investigation had, in this case, accidentally revealed past subsurface contamination events in the area of the control tree with no release history and away from any industrial site.

Note that this case study was conducted in collaboration with Dr. Chris Balouet of Environmental International (Paris, France) and has been published in the *Environmental Forensics Journal* in an article related to dendroecology application in environmental forensics (see Case Studies 2 and 3 from Balouet et al., 2007b, where illustrative material and additional discussions can be reviewed).

12.2.1.2 Forensic Target

While the main forensic target was to evaluate the accuracy of age-dating chlorinated solvent plumes using tree-ring fingerprinting technique, the forensic testing had accidentally revealed a series of contamination events in an area considered to be cleaned and with no recorded sources. Therefore, unintentionally, this study showed the efficiency of using trees to provide detailed information of past contamination events in the absence of any other information to document or even to suggest potential for contamination.

12.2.1.3 Environmental Forensics in a Practical Demonstration

This case illustrates the utility of forensic investigations in the absence of litigation or disputes of any kind and outside the framework of site remediation. The forensic study was conducted for purely demonstrative purposes.

12.2.1.4 Outcome

This practical demonstration revealed the utility of the tree-ring fingerprinting technique to accurately age-date chlorinated solvent releases. In addition, the utility of the technique to provide detailed information on past contamination events at sites with no information or suspicion of contamination of any kind was also demonstrated. Not only did tree-ring fingerprinting provide useful information on past releases of any kind (going as far back in time as the tree age allows), but also it is a nondisturbing "green" investigative technique. Typically, few cores are enough to describe past contamination events at a site, which makes the technique also cost-efficient. The sampling was performed in 1 day, and all the testing (including sample preparation) was performed within a month.

12.2.2 Case Study 12.1: Snapshots of the Forensic Investigation

Practical Demonstration of Tree-Ring Fingerprinting: Gathering Forensic Evidence	Main Findings
I teamed with Dr. Chris Balouet of Environmental International (Paris, France) and collected several core samples from both exposed trees (within the plume; see Figure 12.1) and a control tree. Most of the trees (including the control tree) were Chihuahua ashes as identified using field guides. Samples were collected (one or two cores per tree), transported using special wooden trays, and prepared for analysis (see method described in Chapter 6). The prepared samples were analyzed for ring width (using a microscope connected to a computer) at Dr. Balouet's lab in France; also, selected samples were sent for chemical elemental analysis by energy dispersive X-ray fluorescence (EDXRF) at Dendrolab at Stockholm University, Sweden (see method in Balouet et al., 2007b).	• The accuracy of tree-ring fingerprinting to age-date shallow plumes of chlorinated solvents was demonstrated. A timeframe for PCE/TCE contamination was established, including successive releases, which correlated well with the documented timeframes (Balouet et al., 2007b). Specifically, chemical elemental analysis of exposed tree cores revealed several peaks of chlorine, with the first peak corresponding to the tree growth ring developed in 1986. This was an excellent fit with the recorded chlorinated solvent releases in the mid-1980s considering also the timeframe needed for the releases to have reached the downgradient tree. Other chlorine peaks in 1988 and in the mid-1990s were observed, suggesting additional releases. • The opportunity to apply the tree-ring fingerprinting technique at sites with no information or suspicion of past or present contamination was also demonstrated. This happened by "accident" as the control tree core denoted signs of past contamination (Balouet et al., 2007b). Thus, an interesting observation was that several chlorine peaks appeared in the control tree core. However, these peaks corresponded to distinct years other than those from the analyzed exposed tree. In addition, parallel peaks of sulfur (S) and phosphorous (P) perfectly matching each other appeared also in the control tree. Several possible explanations/scenarios for such unexpected anomalies in the control tree include the possibility of a distinct contamination event in the area of the control tree (possibly construction work since a new apartment complex was observed nearby). The various Cl anomalies could have been due to migration of the main PCE/TCE plume in what was considered the upgradient direction, or they could have been related to distinct chlorinated solvents or other Cl compounds reaching the area of the control tree. Note that the P and S anomalies may also be due to fertilizer application. This matter was not investigated further since it was not the aim of the study. However, this observation confirmed the applicability of the method to characterize environments for which no information exists at the time of sampling.

Sampling trees is simple and can be done using increment borers as shown in this picture; 10-15 minutes per tree are usually needed to collect core samples. The environmental data is of similar sensitivity as that collected through soil boring.

FIGURE 12.1
Tree boring in the site yard.

Key Remarks

- **This case study demonstrated the effectiveness of tree-ring fingerprinting to**
  - **accurately age-date shallow chlorinated solvent plumes** (based on data from the exposed trees).
  - **reconstruct contamination history and possible contamination scenarios at sites where nothing is known or suspected** (based on data from the control tree).
- **One should always build the forensic story after checking all evidence and never assume that the lack of information and data means no contamination.** In addition, everything interrelates, so one should use any information from a case to better understand contaminant fate and transport.
- **Forensic techniques such as tree-ring fingerprinting unravel the unknown and can help to better understand hydrogeology and contaminant fate and transport.** In addition, tree-ring information may identify past contamination events that would otherwise remain hidden, possibly forever.

13

Forensic Investigation Leading to Scientific Discoveries

13.1 Strategic Guide: When Forensics Investigations Open New Opportunities

This type of forensic investigation refers to practical situations in which forensic studies may lead to the discovery of a new scientific concept or a new natural or anthropogenic source for a targeted contaminant. Typically, a source investigation is conducted for a targeted contaminant with multiple sources in the investigated area. The challenge is to "think outside the box" or keep an open mind when interpreting the results so that additional previously unconsidered sources are not excluded rather than "force" the results interpretation based on expected preestablished patterns and hypotheses. This forensic investigation type is strategically described in Table 13.1.

Case Study 13.1 illustrates how the strategic concepts briefly described in Table 13.1 have been applied in practice. As with the other case studies presented, the discussion does not provide details but rather snapshots of relevant information.

13.2 Case Study 13.1: Discovery of a New Form of Naturally Occurring Perchlorate in Southern California

13.2.1 Case Study 13.1: Overview

13.2.1.1 Historical and Legal Context

During routine monitoring, the reporting of perchlorate contamination in several groundwater wells at a shotgun site (private sport club) in Southern California (north of San Diego) was highly unusual and unexpected since perchlorate is generally not associated with firing range activities. Hence, this puzzling situation triggered an environmental forensic investigation.

TABLE 13.1

Challenges and Solutions for Forensic Investigations that Lead to Scientific Discoveries

Challenges	Solutions
• Forensic investigations typically involve in-depth analyses—beyond what is routinely done during environmental site investigations. Such in-depth analyses, while challenging, could sometimes lead to scientific discoveries. • Typically, forensic investigations focusing on source identification/allocation involve the presence of multiple potential sources of contamination, some of which may not be previously established. The results may reveal a source that was not previously suspected or even known as a potential source for the targeted contaminant; in addition, the results may point out new mechanisms for contaminant fate and transport not previously described in the literature. • The contamination for this type of challenge could be anything (e.g., any chemical). → *The goal of the forensic investigation is to keep an open mind and look for additional explanations when the well-established ones do not satisfy the rigors of scientific scrutiny.*	• This type of forensic challenge requires an open mind, which means evaluating and interpreting the results of testing without preconceived notions. We have to admit the boundaries of our personal and collective knowledge and be open to new explanations. What is suspected is not always what actually happens. • The forensic scientist needs to find the most logical and scientifically sound explanation for the actual results; if such an explanation does not fit any preestablished scenarios (e.g., suspected sources or mechanisms), new scenarios might be considered to fit with the results. The conclusions should fit with the results and not the other way around. • Natural sources may exist for most, if not all, of the contaminants under specific conditions. One should always keep an open mind for the potential natural formation of targeted contaminants under specific site conditions, especially when no other sources or logical explanations exist. • Confirmation of the findings through independent lines of evidence is recommended.

The forensic approach was a step-by-step process following the evidence revealed at each step. In other words, the results from one line of evidence prompted the initiation of the next line of evidence and so on.

This case study has been published in the *Environmental Forensics Journal* (Duncan et al., 2005), which provides more details and illustrative material.

13.2.1.2 Forensic Target

The forensic investigation was initiated to characterize the occurrence and establish the source of the perchlorate detected at the firing range.

13.2.1.3 Environmental Forensics Leading to Scientific Discoveries

Regardless of the specific application context (e.g., litigation, prelitigation, site investigation, and remediation), this case study illustrates how environmental forensics investigations may lead to scientific discoveries. While any study could, in theory, lead to a discovery, forensic studies are more prone to this since a more in-depth characterization is targeted, and sophisticated advanced investigative techniques are being used.

13.2.1.4 Outcome

This forensic investigation identified the source of perchlorate as a natural formation not previously reported in the literature. Specifically, a mineralogical formation rich in carbonates was pointed out as a natural source of perchlorate in Southern California. Apart from solving the forensic puzzle, this investigation resulted in enriching the state of knowledge related to perchlorate natural formation in semiarid environments.

13.2.2 Case Study 13.1: Snapshots of the Forensic Investigation

Line of Evidence 1: Historical Document Review	Main Findings
The historical document review included both general and specific reviews. The general review focused on understanding any potential perchlorate use at firing ranges. Perchlorate is not a common contaminant of shotgun and small arms firing ranges. However, its detection in proximity of a range and in an area with no other anthropogenic sources suggested the firing range as the only anthropogenic source in the study area. Consequently, a documentary study was initiated to investigate the potential link of perchlorate with firing range activities, especially related to propellant use and chemistry. The specific review focused on the historical information assessment, which included aerial photography and firing range usage centering on propellant use. This information was necessary to plan and interpret the additional experimental forensic testing to be done.	• The general review revealed that, although not common, perchlorate might be occasionally used at firing ranges. Specifically, perchlorate could be mixed with black powder in shotgun shells loaded by individuals to achieve more powerful shots (typically a 50/50 mixture of fine aluminum and potassium perchlorate would be used). In other words, while perchlorate shotguns are not commercially available, individuals could prepare such loads from commercially available products (including perchlorate salts) using information available on the Internet. It was therefore established that such practices do exist, but there was no specific information to denote that such practices were used at that particular firing range. In the absence of relevant information one way or another, the perchlorate contamination due to firing range activities could not be completely ruled out. • The specific review helped to better understand the location and settings specific to this case study and to plan for adequate forensic testing as the next step of the investigation. Note that specific information related to any recorded use of perchlorate at this firing range could still not be revealed. In the absence of such specific information, it was assumed that if perchlorate were to be used at this firing range, its environmental detections may correlate with the propellant use (established though document review).

Line of Evidence 2: Chemical Fingerprinting/ Statistical Evaluation	Main Findings

Chemical fingerprinting was initiated as the next step of the forensic investigation. It consisted of sampling both soil and groundwater from the affected area for perchlorate and other common ions, such as nitrate, sulfate, chloride, orthophosphate, calcium, magnesium, potassium, iron, and sodium.
In addition, sampling included collection of whitish formations observed above two of the wells, with detection of perchlorate in water and of soil beneath these formations. The formations looked distinct from soil (being whitish in color). Intrusive trenching (<5 feet) was also performed to evaluate this unusual soil formation. Moreover, the presence of similar material formations was investigated outside the range in the general area to evaluate if it is a common occurrence or was particularly linked to the firing range.
Note that a method with a low detection limit (i.e., 2 μg/kg) was needed to capture the small amounts of perchlorate present in soil and the formation material. A U.S. Department of Agriculture (USDA) method was used (see details in the article by Duncan et al., 2005).
	• The pattern of detected perchlorate in soil and groundwater was analyzed with the gathered historical evidence related to site usage (i.e., propellant use). It was observed that the perchlorate detections were not consistent with the propellant use as a source. In addition, no apparent correlations between perchlorate and the commonly analyzed ions were identified when using the linear regression statistical technique. Note that the lack of correlation between perchlorate and the commonly analyzed ions was reported in other areas of the world where no apparent human sources of perchlorate exist (such as the Atacama Desert and West Texas).
	• The intrusive trenching of soil in areas with perchlorate detections in groundwater revealed the presence of a white, crushed material. This material was probably placed in the early 1970s during an expansion of the shooting range trap house. When chemically analyzed, the white material revealed the presence of perchlorate (in concentrations of up to 123 μg/kg). This material was referred to as Rancho Bernardo formation.
	• Further observations in the general study area revealed the same type of whitish material in a nearby road cut (Otay Mesa formation). Six samples from the road cut material were chemically analyzed for perchlorate, which was also present in these samples (in concentrations up to 40.2 μg/kg). Other common ions (as described previously) were also analyzed in these samples, and no statistical correlations with the detected perchlorate were identified.
	• Soil underlying the white crushed material contained perchlorate in concentrations as high as 10.6 μg/kg.
	• Overall, the observations and results from the chemical fingerprinting suggested the following:
	  • The white material was likely the source of perchlorate detected in groundwater wells.
	  • **The white material was likely of natural origin** since it was present in other locations (outside the range site) with no specific link to the firing range or other human activity, as well as based on its location and general chemistry.
	Based on these findings, mineralogical fingerprinting of the white material was identified as the next step of the forensic investigation.

Line of Evidence 3: Mineralogical Fingerprinting	Main Findings
Mineralogical fingerprinting included performing a variety of microscopic testing associated with chemical analysis on the white material samples from Rancho Bernardo and Otay Mesa formations identified. Note that the type of fingerprinting used here is different from the combined use of SEM-EDS described in Chapter 5 and used in the case studies presented in Chapter 7 (case studies 7.1 and 7.2). In this case, the focus was to identify the mineral composition of the selected samples rather than particular associations with the contaminant of concern (i.e., perchlorate). Specifically, the following microscopic techniques were used (in conjunction with chemical analysis, as applicable): X-ray diffraction (XRD), polarized light microscopy (PLM) and scanning electron microscopy (SEM). The testing was performed at RJ Lee laboratory.	• *X-ray diffraction* revealed the mineralogical composition of samples, which was similar between samples and included smectite [$Ca_{0.2}\ Mg_3Si_4O_{10}(OH_2) * 4H_2O$], calcite ($CaCO_3$), and quartz ($SiO_2$) with plagioclase [$(Na, Ca)AlSi_3O_8$], orthoclase feldspar ($KAlSi_3O_8$), and muscovite [$KAl_2(Si_3Al)O_{10}\ (OH)$] (to a lesser extent). Also, a gypsum binder was identified. This composition is consistent with the reported composition of the natural Mission Valley Formation in the general area of San Diego. • *Polarized light microscopy* (PLM) investigated the mineral crystals and morphology on the sample further analyzed by SEM (see the next item). PLM denoted the presence of quartz crystals along with feldspar minerals. The presence of muscovite was evident. • *Scanning electron microscopy* (SEM) pointed out calcium and silica as major elements in the sample (corresponding to the mineralogical composition consisting mainly of calcium and quartz). Sulfur was also present, probably due to inorganic biological processes. Note again that this was a different use of SEM than the one described for case studies 7.1 and 7.2, which involved elemental associations with metals (Pb). In this case, SEM was used to identify elemental associations present within the sample to identify minerals and confirm the sample's suspected natural mineral origin (already suggested by previous chemical and microscopic testing). Thus, although the targeted contaminant was perchlorate, SEM was not targeting particles specifically associated with perchlorate in these samples. • Results from all three microscopic evaluations correlated well and were consistent revealing composition of the Mission Valley Formation. • No evidence for the presence of sylvinite, hanksite, or other natural sources of perchlorate reported in the literature (by the time of this investigation/publication in the mid-2000s) was found, attesting that the discovered perchlorate was a new natural source. **In conclusion, mineralogical fingerprinting identified and confirmed that the white material** (containing perchlorate) **was a carbonate-rich layer of marine origin** (note that mollusks were found within the layer) **as part of the Mission Valley Formation.** Note that the Mission Valley Formation is described as a sandstone formation composed mostly of quartz and potassium feldspar.

Therefore, this forensic investigation that started focusing on perchlorate detections at a private firing range in Southern California ended up pointing out a new natural source of perchlorate in the area. The findings correlated well with the observation of natural perchlorate in other semiarid areas of the United States, such as Texas and New Mexico, suggesting that large portions of the southern United States or similar areas may contain more perchlorate natural sources than it was previously thought. In fact, natural perchlorate was also recently discovered in northern areas, such as in Antarctic dry valleys (Kounaves et al., 2010), which denotes that natural formation of perchlorate happens in a large variety or areas and geographic locations.

Key Remarks

- **Environmental forensics may lead to basic scientific discoveries.** Thus, one should always emphasize investigative aspects and not eliminate new unreported possibilities based on any preestablished patterns or hypotheses.
- **The obvious source is not always the real source.** After all, detective stories emphasize this on a constant basis—since the obvious choice of the criminal is usually far from correct.
- **Natural perchlorate likely exists in many other areas of the world with a dry climate.** Forensic investigations of perchlorate in such areas should especially consider its potential natural occurrence.

14

When Nothing Else Works

14.1 Strategic Guide

This type of forensic investigation refers to practical situations in which the forensic investigation is conducted at sites where the potential exists for multiple releases to have occurred in time. These types of sites were in operation over many decades, with the same type of business conducted and the same type of contaminants handled during the years. The challenge is to point out releases that occurred in the past for which no documentation and no monitoring data exist. A typical example involves age-dating of older releases at sites with similar recent releases that may interfere and obstruct any potentially still existing older evidence. This forensic investigation type is strategically described in Table 14.1.

Case Study 14.1 illustrates how the strategic concepts briefly described in Table 14.1 have been applied in practice at a historical gas station site. As with the other case studies, the discussions do not provide details but rather snapshots of relevant information, pointing out the main forensic findings.

14.2 Case Study 14.1: Age-Dating of Petroleum Releases at a Historical Gas Station in the Northeastern United States

14.2.1 Case Study 14.1: Overview

14.2.1.1 Historical and Legal Context

A gasoline station located in the northeastern United States had a long history of petroleum product storage and handling. The gas station was in continuous operation from the early 1930s until the late 1990s, after which it started to operate occasionally as a junkyard and auto repair shop. Note that the gas station was surrounded by residential neighborhoods. The site was suspected to be impacting the neighboring residential community with

TABLE 14.1

Challenges and Solutions for Forensic Investigations Evaluating Older Releases at Historical Sites with Recent Releases of the Same Type of Contaminants

Challenges	Solutions
• Many contaminated sites have a long operation history with multiple decades of continuous operation in the same type of business. At this type of site, the same main contaminants have been handled and potentially released over the years, although different parties might have operated the site during various periods of time. In most cases, scarce or no historical and other types of relevant evidence exists related to potentially older releases. • When recent releases occur at such sites, environmental investigations are triggered. However, the routine environmental investigations (which are typically performed) reveal the type and nature of subsurface contamination but cannot differentiate between the recent and any potentially older releases of the same contaminants that might have occurred and commingled with the newer releases. However, with multiple years of past operations, older releases may still affect the environment at the time of remediation, which, if proved, trigger the responsibility to contribute to the remediation costs. • The contamination for this type of challenge could be anything (any chemical) that was used at the investigated site during the years. → *The goal of the forensic investigation is to identify and provide evidence for any potentially older releases (to reveal all the parties that may contribute to remediation costs).*	• This type of forensic challenge requires the application of fingerprinting techniques targeting traces left by contaminants in the environment, such as those described in Chapter 6 of this book. • Typically, the application of tree-ring fingerprinting should be attempted, if feasible. Currently, this is the only testing technique that allows the defensible identification of multiple releases of the same contaminants at the same site over the years. • Under specific conditions, other fingerprinting techniques may also be helpful, although the evidence provided would not be as exact as that from tree-ring fingerprinting. Such techniques may include those described in Chapter 5 of this book, focusing on interpreting the results within the environmental matrix; therefore, any inconsistencies observed with the scenario of the recent release as the only contributor to contamination could be used to suggest the likelihood of older releases. • Confirmation of the findings through independent lines of evidence is not absolutely necessary as long as conflicting data do not question the results and conclusions of the forensic investigation.

methyl tert-butyl ether (MTBE), a main fuel oxygenate used in the United States after the phaseout of leaded gasoline in the late 1970s to early 1980s. Specifically, the discovery of petroleum-associated contamination (by MTBE) in the neighborhood community during some construction work in the early 2000s triggered a series of environmental investigations. During these investigations, it was found that the gas station soil and shallow groundwater were impacted by MTBE and a series of petroleum hydrocarbons, including BTEX (benzene, toluene, ethylbenzene, and xylenes) and other hydrocarbons in the range of gasoline and fuel oil. Several on-site source areas were also evident based on environmental testing and location of historical potential sources. The discovery of contamination confirmed the site as the source of MTBE in the neighborhood residential community and triggered remedial activities, including soil excavation and the installation of a vapor extraction system.

The regulatory agency required the site owner at the time of the contamination discovery (generally referred to from now on as the "more recent owner") to pay for costly remediation (estimated at approximately $4 million). The more recent owner bought the site in 1982 from an oil company, which operated at the site for almost 50 uninterrupted years (between the early 1930s and 1982). No environmental investigations or reported spills or accidents were recorded during those 50 years. Thus, in spite of the fact that the oil company operated at the site for much longer than the more recent owner, it was not identified as a potentially responsible party (PRP) for the subsurface contamination. Consequently, the more recent owner was to pay for all remedial and associated investigative costs.

At that point, everything seemed rightly solved except for one "unfitting detail": the discovery of a leaking fuel oil tank during the site excavation activities. This was an unfitting detail since the more recent owner was never aware of the presence of such a buried storage tank (UST—underground storage tank) on site and had never bought, handled, or stored fuel oil product during his operation of the site. This was, therefore, the small unfitting detail that triggered forensic investigations and provided valuable clues. Thus, the more recent owner decided to conduct an environmental forensic study to track the source of that fuel oil tank and age-date the fuel oil releases. The logic was that if the fuel oil tank started to leak before his ownership (pre-1982), that would indicate that the major oil company had contributed to the contamination to be remediated at the site and therefore would be responsible for some of the remedial costs. Obviously, considering the total cost of the remediation estimated at around $4 million, potentially substantial cost savings were envisioned through cost sharing, which fully justified the initial costs related to the forensic investigation.

Note that apart from the leaking fuel oil tank, the remaining of another highly damaged buried tank was discovered during excavation. No documentation was found for this tank either, and no petroleum product was observed around it. It was, however, suspected that the tank used to carry leaded gasoline due to its proximity to the pump island. If evidence related to leaded gasoline release was to be found, that would have been another indication of releases within the timeframe of oil company operations.

14.2.1.2 Forensic Target

The main target of the forensic investigation was to age-date the middle distillate/fuel oil releases. Particularly, it was of interest to establish if the leaking of the fuel oil tank started before 1982. A minor target was to evaluate potential leaded gasoline releases (pre-1982).

14.2.1.3 Environmental Forensics Providing Evidence for Cosharing of Remedial Costs

This case study illustrates another important use of environmental forensics outside the litigation context. Specifically, environmental forensic studies may provide evidence related to past releases at a site with more recent releases of similar contaminants. Such evidence may enable the more recent site owner/operator to recover part of the remedial costs from previous owners or operators. Once provided to the regulatory agency, such evidence would be the basis for including past owners or operators on the PRP list that would trigger cost sharing for remediation activities. In such a situation, litigation may not be needed, but even if the case ends up in litigation, the acquired forensic evidence would likely trigger successful resolution for the more recent owner.

14.2.1.4 Outcome

The environmental forensic investigation conducted at the historical gas station provided evidence that at least one fuel oil release did happen at the site prior to 1982. Age-dating was performed using tree-ring fingerprinting. Historical document review and chemical fingerprinting were also conducted, enabling a better understanding of site conditions and contaminant fate and transport, as well as helping with interpretation of tree-ring fingerprinting results. The acquired evidence made it possible for the more recent owner to attempt the recovery of part of the remediation costs from the oil company previously operating at the site. The overall forensic investigation cost (including written reporting) was approximately $30,000, and the study was completed within a month and a half.

14.2.2 Case Study 14.1: Snapshots of the Forensic Investigation

Line of Evidence 1: Historical Document Review	**Main Findings**
A historical document review was initiated first. This review focused on the following: • the historical site file, including documents related to site transactions and UST information (e.g., capacity, installation and removal dates, reported contents); • aerial photographs; • a series of environmental reports related to regular groundwater monitoring (in the past approximately 5 years from the time of the forensic study in 2007) and site excavation activities (including both soil and groundwater data); • a large number of photographs (more than 300) taken during site excavation activities (in 2003), some revealing the discovery of buried tanks, as well as trenches of stained soil or soil with obvious petroleum product within the excavation trenches.	• The general site settings included the following main features: a building in the middle of the site (located more toward the southern border); the former pump island (no longer existent at the time of the forensic investigation) just east of the building; and the UST area northwest of the former pump island. • Two main source areas were revealed: the former pump island and the location of the USTs. As noted previously, these locations were adjacent to each other toward the middle and the eastern side of the site. • A third source area was identified related to the discovery of a leaking fuel oil tank (a 500-gallon UST) buried toward the southwestern area of the site (close to the building toward the west) (see the tank in the excavation trench in Figure 14.1); some fuel oil product found around the excavated tank matched the chemical fingerprint of the fuel oil that was still in the tank, therefore confirming that the tank had been leaking. • The highly damaged remains of what appeared to have been a leaded gasoline tank was discovered within the former pump island general area toward the southwestern side of the pump island in between the pump island and the building (see excavated remains in Figure 14.1). • No evidence of any recorded spills/accidents was found. • No mention was found related to the installation or usage of the two damaged USTs discovered during excavations (depicted in Figure 14.1). Therefore, those USTs were considered "phantom" tanks. • The off-site contamination with MTBE was toward the west of the site, while some contamination with petroleum hydrocarbons (in the gasoline and fuel oil range) was revealed off site toward the east (on a more limited area). • The shallow groundwater flow direction varied during the years, mostly reported toward the west. • Several trees were observed bordering the site toward the south, the north, and the east (the tree from the east was just across the street from the site); the trees seemed old enough to cover periods from before 1982, and since the groundwater table was shallow (around 8–10 feet bgs), this site was a good candidate for tree-ring fingerprinting age-dating. • While the historical document review did not provide clues related to age-dating of the fuel oil release or the occurrence of any leaded gasoline release at the site, it enabled the building of a forensic strategy and subsequent sampling and analysis plan for both the chemical and the tree-ring fingerprinting testing planned next.

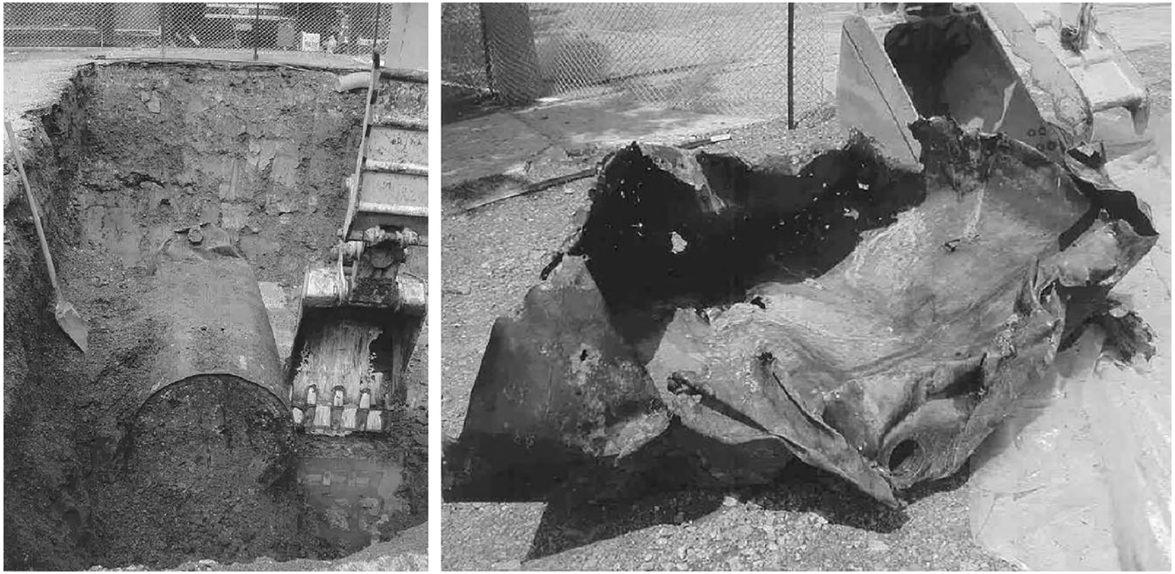


FIGURE 14.1
"Phantom" tanks discovered during site excavations: the leaking fuel oil tank (left) and the remainder of what potentially appeared to be a leaded gasoline tank (right).

Line of Evidence 2: Chemical Fingerprinting	**Main Findings**
Chemical fingerprinting involved the collection of soil samples at various depths (e.g., every 2 ft between the surface and the groundwater table at about 8-10 ft bgs) from the main established source areas on site. Of particular interest was the area between the former pump island and the building, especially immediately adjacent to the building, where it was believed that older releases might still be preserved (if leaked free product migrated below the building, which was on the site for a long time). All collected samples were analyzed for TPH (total petroleum hydrocarbons), BTEX, and alkyl lead compounds, with selected samples analyzed for more in-depth chemical fingerprints, including polycyclic aromatic hydrocarbons (PAHs) and the whole hydrocarbon range (e.g., C5–C40). The in-depth chemical fingerprinting analyses were performed by Zymax Forensics laboratory in California; the other analyses were performed by Life Science Laboratories (LSL) in Syracuse, New York. Note that LSL developed and calibrated a special method for alkyl lead compound analysis (in soils) to achieve very low detection limits.	• The acquired data confirmed the main established source areas on site. In addition, the data clearly showed that both gasoline and fuel oil hydrocarbons were present in site soils that needed remediation. • A map showing areas on site mostly affected by gasoline, by fuel oil, and by the mixture of the two types of petroleum products was produced to help understand the fate and transport of released contaminants. It was established that gasoline compounds were found mostly to the north-northeast (adjacent to UST storage area) and toward the southeast (adjacent to the former pump island); fuel oil compounds were found mostly toward the west-northwest over a large area of the site, while the mixture of gasoline and fuel oil products was found over the middle and most of the eastern part of the site. The data representation on the map denoted likely fuel oil migration toward the north and east of the site. • While the impact of fuel oil releases had been delineated in several areas on site, the age of these observed fuel oil releases could not be established based on chemical fingerprinting data. • An alkyl lead compound, tetraethyl lead (TEL), was detected in very low amounts in one soil sample adjacent to the building (close to the area where the remainder of what was believed to have been a leaded gasoline tank was found); the sample was collected at about 6 ft bgs, suggesting that leaking of leaded gasoline might have historically occurred. Note that TEL was one of the most common organic lead additives used in leaded gasoline for a very long time, until about 1979. Therefore, TEL may serve as a signature chemical for leaded gasoline releases. Although TEL detection would indicate that at least one leaded gasoline release occurred before 1982, the fact that it was only detected in one sample weakened the evidence, making it unusable for forensic purposes (unless confirmed by other lines of evidence, such as tree-ring fingerprinting, which did not happen, as discussed next in the description of tree-ring fingerprinting findings). • The in-depth fingerprinting denoted the presence of gasoline-range hydrocarbons in the selected soil samples (taken between the former pump island and the building) with the exception of one soil sample collected adjacent to the building, where a mixture of gasoline and heavy distillate was evident in the chromatographic profile of the sample, as shown in Figure 14.2. The data did not allow establishing the exact age of the gasoline, but in the absence of other evidence, the gasoline seemed consistent with more recent spills (in the 1980s or 1990s), which caused the MTBE contamination. The heavy distillate likely came from the recent occasional operation of the site as a junkyard and auto repair shop. Note that the in-depth fingerprinting did not reveal any significant fuel oil or middle distillate in the selected soil samples.

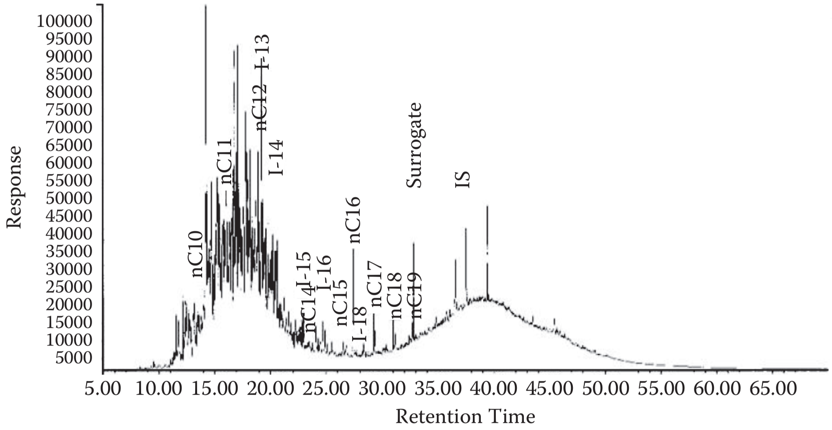


FIGURE 14.2
Chromatographic profile of a soil sample showing a mixture of gasoline and a heavy distillate. The two observable humps correspond to the unidentified complex mixture (UCM), with the first being in the carbon range of a gasoline product and the second of a heavy distillate, such as motor oil or lubricating oil; the presence of well-defined UCMs denotes that both products have been biodegraded.

Line of Evidence 3: **Tree-Ring Fingerprinting**	**Main Findings**
Tree-ring fingerprinting was performed the same day with soil sampling for chemical fingerprinting. Two core samples were collected (using a 5-mm Pressler borer) from each of the three trees bordering the site (south, tree E1; north, tree E2; and east—across the street, tree E3) selected for tree-ring fingerprinting. In addition, two core samples were collected from a control tree a few blocks away toward the south. The sample collection preparation and analysis were done according to the method described in Chapter 6. The tree-ring width analysis was performed by Dr. Chris Balouet of Environmental International in his laboratory in Paris, France, while the energy dispersive X-ray fluorescence (EDXRF) analysis was performed by Dendrolab at Stockholm University, Sweden (see also details of the method in the work of Balouet et al., 2007b). All samples were analyzed for ring widths; while selected core samples from each tree (one sample per tree) were analyzed for chemical elements through the EDXRF analysis. While 28 chemical elements were reported for each core by the lab, the evaluation focused on sulfur (S) (as a marker for fuel oil) and Pb (as a marker for leaded gasoline). Chlorine (Cl) was also carefully checked as any anomaly coinciding with a sulfur anomaly would strengthen the argument that observed sulfur anomalies were related to fossil fuel (i.e., fuel oil in this case) and no other type of sulfur compounds. This is based on empirical observations made and published for other cases (see, e.g., Balouet et al., 2007b).	The trees were identified in the field as follows using guidebooks: • tree E1 as a maple; located on site on the southern border toward the eastern half of the site; • tree E2 as a black locust; located on the walkway close to the site's northern border (also in the western half of the site); • tree E3 as a white ash (*Fraxinus americana*); located across the street, east from the site on a walkway; this was the oldest of the three trees (see details in Figure 14.3). • The core samples from trees E1 and E2 did not extend before the year 1982 (these cores dated since around the mid-1980s); thus, the information from these two trees could not be used to reveal any potential pre-1982 releases; in addition, no Pb anomaly was observed in these trees, while the S and Cl anomalies from tree E2 (Figure 14.4) were likely due to the excavation performed on site in 2003 rather than a new release; see also comments provided for Figure 14.4 displaying the magnified core image and EDXRF results for Pb, S, and Cl in tree E2. • The core samples collected from tree E3 did extend much before 1982, dating to the early 1940s. Therefore, these cores could capture older releases. The EDXRF data for this tree did indeed reveal some anomalies for S and Cl (fuel oil markers), while no significant Pb anomaly was observed in this tree core either. Selected results from tree E3 are depicted in Figure 14.5, including magnified core image as well as EDXRF data for Pb, S, and Cl. A series of pre-1982 anomalies is evident for S (over most of the 1950s and in 1967 and 1973) and for Cl (in 1962 and 1973). **These data indicated that at least one release of fuel oil happened pre-1982, namely, in 1973,** for which both S and Cl anomalies were observed.

FIGURE 14.3
Details of tree E3.

In conclusion, multiple lines of evidence were investigated, including historical document review, chemical fingerprinting, and tree-ring fingerprinting. Tree-ring fingerprinting was the only method providing evidence able to reveal the age of fuel oil releases on site, with at least one release defensibly revealed pre-1982. Note that while the first two lines of evidence did not reveal the age of fuel oil releases on-site, the information gained helped interpret tree-ring fingerprinting data. In addition, the information gained through both historical review and chemical fingerprinting confirmed the scenario of a pre-1982 fuel oil release migrating toward the east and thus affecting tree E3, as the tree-ring fingerprinting data showed. That release was likely still reflected in the on-site petroleum compounds detected within the fuel oil range in need of remediation, since no evidence for any more recent (post-1982) fuel oil release was observed during the forensic investigation.

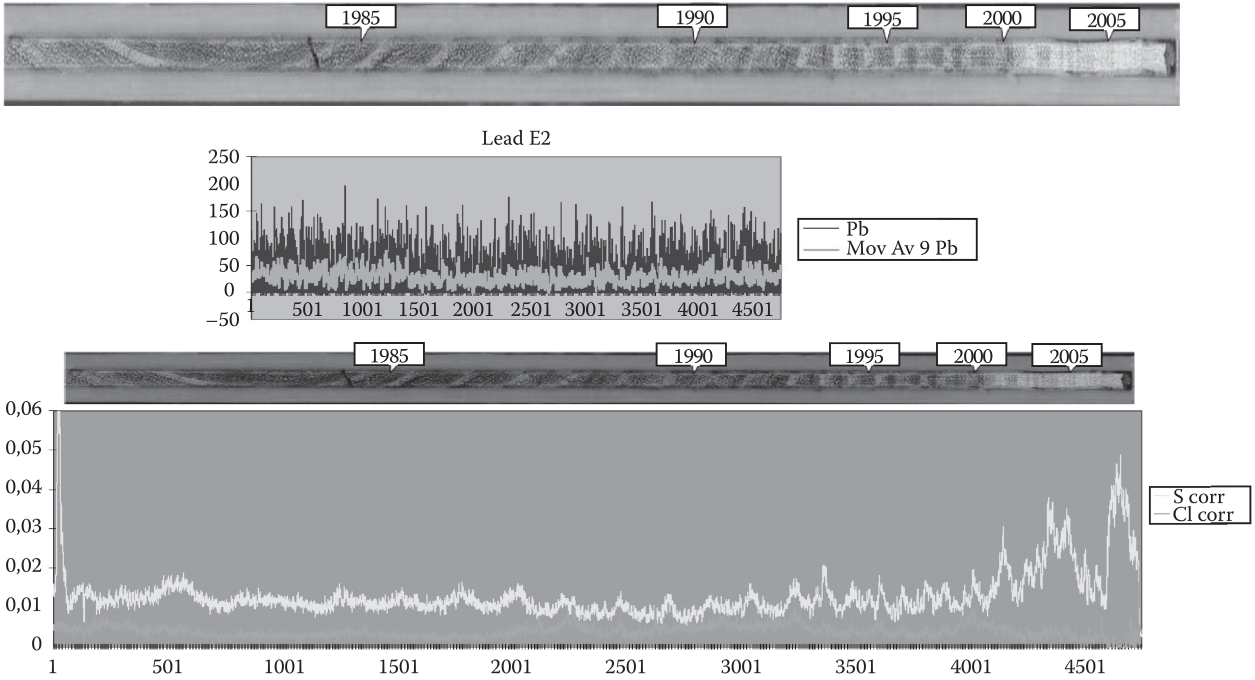


FIGURE 14.4

(See also color insert.) Selected tree-ring fingerprinting results for tree E2: magnified core image with some years indicated for orientation (top), Pb profile across the core (middle), and S and Cl profiles across the core (bottom). The magnified core image is provided again with S and Cl profiles for easier identification of years corresponding to each anomaly (while there are no Pb anomalies, S had an anomaly in years 2002–2003 when a slight Cl anomaly was also observed; these anomalies may be due to the excavation work done in that period at the site, which could have mobilized older fuel oil releases from site soil). EDXRF profile data are in counts; "Mov Av" stands for moving average, which refers to corrected data, with each data point corrected over the two earlier and two later points as explained by Balouet et al. (2007b).

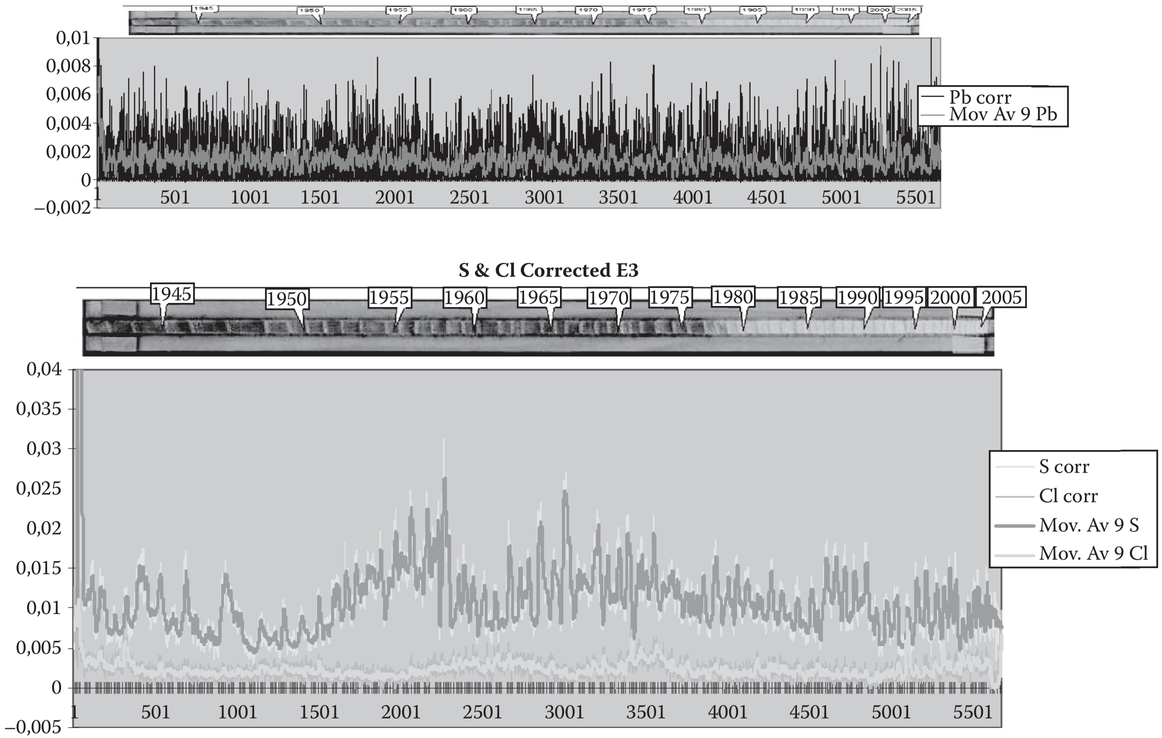


FIGURE 14.5
(See also color insert.) Selected tree-ring fingerprinting results for tree E3: Pb profile across the core (top) and S and Cl profiles across the core (bottom) with the magnified core image provided at the top of each profile (some years are indicated for orientation). While there are no Pb anomalies, there are several S and Cl anomalies as discussed before for the pre-1982 period of interest in this case. EDXRF profile data are in counts; "Mov Av" stands for moving average, which refers to corrected data, with each data point corrected over the two earlier and two later points as explained by Balouet et al. (2007b).

Key Remarks

- **Tree-ring fingerprinting reveals the long-forgotten past.** If old-enough trees are available, environmental impacts can be accurately pointed out when no other forensic technique works.
- "Signature chemicals" are important forensic tracers regardless of their actual concentrations. Their mere presence may be forensically relevant. However, when signature chemicals are only observed in one sample and the data are not confirmed through other lines of evidence, it is advisable not to use the signature chemical evidence to build forensic conclusions or opinions.
- When the focus is on detecting contaminants coming from old releases, it is recommended to ask the laboratory for special analysis methods that look for very low amounts of those contaminants.
- **This case study is an example of how a forensic "mystery" may be solved by experimental evidence many years after the spill occurrence,** while historical records are lacking.

Conclusions

This book was written with the intent to:

- Raise awareness and interest in the emerging field of environmental forensics.
- Provide an easy-to-follow guide for understanding and learning environmental forensics, addressing both students and a large variety of interested professionals.
- Equip the reader with appropriate strategies for a variety of environmental challenges.
- Demonstrate the myriad environmental forensic techniques and applications, starting with the court of law and ending with site remediation/rehabilitation for a green sustainable future.
- Provide useful basic information, selected references, and hints for designing and conducting successful environmental forensic investigations and retrieving defensible evidence.

Major hints to remember for the environmental forensic scientist include the following:

- **Treat each case as unique.** Every case is distinct, and the forensic investigation should be tailored to case specifics and client needs. While general forensic concepts and investigation steps may be used in various cases, a standardized approach should not be attempted.
- **Envision a "mystery story."** As in detective novels, environmental forensics cases have their unique stories. Once a story is envisioned, the forensic strategy will be better designed and clues more obvious. To solve a case, a detective should not only understand but also "feel" the case and have an enthusiastic approach. This cannot be achieved by treating the forensic investigation as just another case. One should consider the long-running TV series *CSI* (Crime Scene Investigation), which has amazed and continues to amaze a worldwide audience. The key lies in storytelling. Cases are not just other jobs but rather amazing detective stories with unpredictable endings.
- **Collect all the available facts first.** Never rush to conclusions or plan experimental approaches before consulting all available data and historical information. If you come to California during some of the very few rainy days, you should not rush to conclude that the

weather in California is bad. Making judgments and interpretations based on some facts only may lead you astray.

- **Link the available data to understand the "big picture" and identify data gaps.** Understanding the context (both general and specific) of a case is crucial. This is why, especially for complex cases, it is highly recommended to conduct both general and specific historical document reviews. While most investigators would do some specific review related to the case at hand, fewer would spend time and effort conducting a general review that included other similar reported cases, historical practices generally associated with a certain type of business, and typical environmental issues and contaminants associated with that type of business. Such information may not be readily available, and the client may not be interested in paying for this. However, it is important to educate clients and peers alike concerning the importance of general information gathering to put things into an appropriate context.
- **Start with the most simple and straightforward applicable forensic method.** Not all forensic techniques are sophisticated. Cases may be won or lost based on one simple document or some straightforward testing contradicting the other side's hypothesis (e.g., as shown in Case Study 10.1). When building a strategy, always start with the simplest methods and ways of investigation and advance from there as needed.
- **Look for the "unfitting detail" within the big picture.** It is in the detail that the force of forensic investigation lies. Yet, it is within the big picture that the detail should be interpreted. See, for example, Case Study 14.1, in which a small unfitting detail triggered the forensic investigation, which revealed releases not considered before that were affecting the site at the time of remediation.
- **"Fish" for the "unknown" and be ready to adjust your hypothesis and approach based on any new relevant finding.** Never start an investigation with preconceived notions and ideas. Try to keep an open mind and develop opinions only after documents are consulted and any experimental evidence is available for review. In addition, always consider new explanations if they may fit the existing evidence better. This may even lead to scientific discoveries, as shown in Case Study 13.1.
- **Stop when the confidence level is achieved**. This is true no matter how tempting it would be to continue collecting more data and information in the absence of budgetary or time constraints.
- **Use two or more independent lines of evidence** unless the case can be straightforwardly solved and if limited options are available for deployment of forensic techniques.

- **When feasible, use lines of evidence in a combined interdependent way**. You may increase the power of each single forensic technique and overcome its limitations by combining two or more techniques to build one line of evidence. For example, the associated use of isotopic analysis on elemental markers identified in tree-growth rings could more accurately identify sources for the marker element, apart from the exact age-dating of its release.
- **When presenting the forensic findings, always tell a "story."** Whether you are in front of a jury in a court of law, in front of the client, or just in front of peers at a conference, you should always present the case as a story to get and keep the audience interest alive. This should not be difficult if you have envisioned the story of the case from the beginning (as suggested previously).
- **Communicate with the client and others involved in the investigation** constantly. Communication, transparency, and teamwork are keys for building successful forensic cases that stand the scrutiny of tough trials and cross-examinations.

Key Concepts Reflected in This Book

- Environmental forensics is an emerging scientific field using multidisciplinary, cutting-edge approaches along with simple common ones to solve environmental puzzles.
- An environmental forensic scientist is a "detective of the environment," undertaking great challenges and facing even greater responsibilities. **It is the combined knowledge, persistence, and ingenuity that define a successful forensic investigator.**
- Environmental forensic investigations provide long-term cost savings and a comprehensive understanding of processes happening within impacted environments. Ultimately, all these will enable us to design a greener and more sustainable future for our planet.

Epilogue: What Does the Future Hold?

Some time ago, I was approached by a peer from a company providing remedial products. He was interested in learning more about the environmental forensic field to better understand and evaluate the success factors at sites where his company's products were deployed. Basically, when a remedial product seems not to work as expected, one can only wonder if that is because the product is not appropriate for the application, it is not appropriately used, or perhaps there might be other explanations, such as an additional or ongoing source or an unexpected change in contaminant fate and transport. Since environmental forensic science is known to check small details and provide in-depth environmental information, it might just provide the right answers. I was glad to notice that when confronted with difficult situations, people turn to forensics—and this is just the beginning.

Sure enough, I have seen more and more environmental applications and interest in environmental forensic science in recent years. This is reflected in the increasing variety of articles published in *Environmental Forensics Journal* along with the increasing number of countries of origin for the authors of those articles. The increased interest in the environmental forensic field is also reflected in the inquiries I keep getting from students all over the world on how to pursue a forensic career. Moreover, a large variety of professionals, including regulators, are more and more interested to learn and understand the unique tools and opportunities that this emerging science provides. Some of these tools are already well recognized and included in regulatory guidance materials, such as isotopic testing as a means to evaluate the occurrence of monitored natural attenuation (MNA).

Yet, the general belief was and may still be that environmental forensics is equivalent to litigation or some sort of legal dispute. This is clearly a misconception. Examples of the use of environmental forensics outside the court of law and unrelated to disputes of any kind have been provided in some of the case studies presented in this book. In addition, a recent publication to which I have contributed presents a complex case study in Romania along with a detailed discussion related to the relevance of environmental forensics in usual site investigations and remediation (Bica et al., 2009).

To summarize, the following are the main applications and advantages of conducting environmental forensic investigations outside the legal context as reflected in this book:

- **Effective Site Remediation.** Environmental forensics may ensure tailored remedial design and help achieve site closure in a timely and cost-effective manner. Forensic techniques could be integrated into site investigations and, this way, help refine the site conceptual model and ensure that all sources are properly addressed.
- **Establish Site-Specific Cleanup Limits.** Environmental forensic techniques provide unique tools that can be used to define and obtain regulatory acceptance of site-specific cleanup limits; such limits should take into account off-site contributions, as well as potential natural/background-type contributions. In many cases, the use of site-specific clean-up limits results in substantial cost savings related to remediation work as proven by Case Study 7.1.
- **Prevent or Be Prepared for Potential Future Litigation.** Environmental forensics studies help design a sampling and analysis program that ensures the acquisition of evidence both defensible (in court) and relevant from a liability point of view. Even if not needed at the time of the sampling, such evidence would exist forever and may be used by any future bearer of liability to prove innocence. Otherwise, if a lawsuit is brought at some future time, evidence may be hard, if not impossible, to retrieve.
- **Site Investigation.** Environmental forensics studies maximize the chance to identify potentially responsible parties for cost sharing of remediation costs, especially in the case of commonly found contaminants with many potential sources (such as chlorinated solvents). This is like “fishing for potential contributors” when the chances to find and catch some are high. However, timing might be crucial. After all, if not fishing at the right time, one may not catch any fish. By incorporating forensic techniques into original site environmental investigation design, the chances for “fish catching” are maximized.
- **Acceptance of Unintrusive Green Remedial Alternatives.** Environmental forensics provide adequate tools to evaluate unintrusive remedial alternatives such as MNA. For example, specific forensic evidence such as isotopic and chiral fingerprints provides convincing information to help decide if biodegradation processes are actually occurring in subsurface environments. Such evidence is generally accepted by regulators and may help plan future costs and evaluate the time needed for site closure.

Environmental forensics is undoubtedly gaining interest not only within the consulting and legal communities but also among academia, industry, and regulators. What was previously considered exclusively linked to the court of law and legal dispute has expanded much beyond the legal arena. This is because the forensic techniques provide detailed, accurate, and innovative information that can be used in basic science, site rehabilitation, and ultimately to ensure a greener sustainable future for our planet.

Future trends, as foreseen and encouraged, include the following:

- Common use of forensic techniques in routine site investigation/remediation and property transactions
- Combined interdependent use of various forensic techniques to obtain "ideal evidence"
- Increased use of mobile analytical devices for site screening, sampling design, and on-site analyses, as well as real-time monitoring
- Introduction of environmental forensics classes in universities around the world
- The ultimate use of forensic techniques toward a greener, more sustainable future

The rapid advancement of instrumental techniques and scientific progress will open infinite possibilities and forensic tools. In this context, **it will be the enthusiasm, persistence, and innovation of the forensic scientist that will make a difference.**

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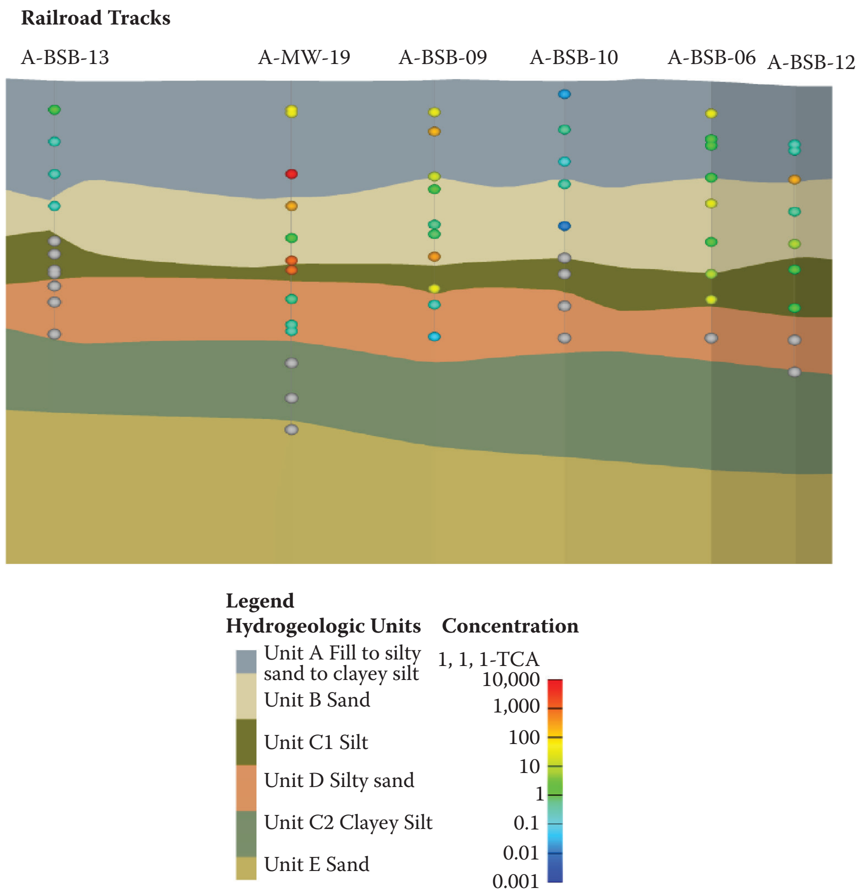
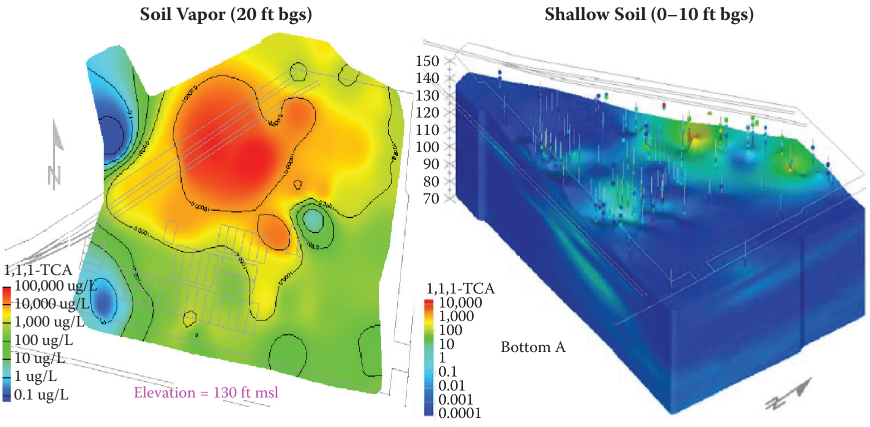
SI and U.S. Units of Measure Conversion Chart

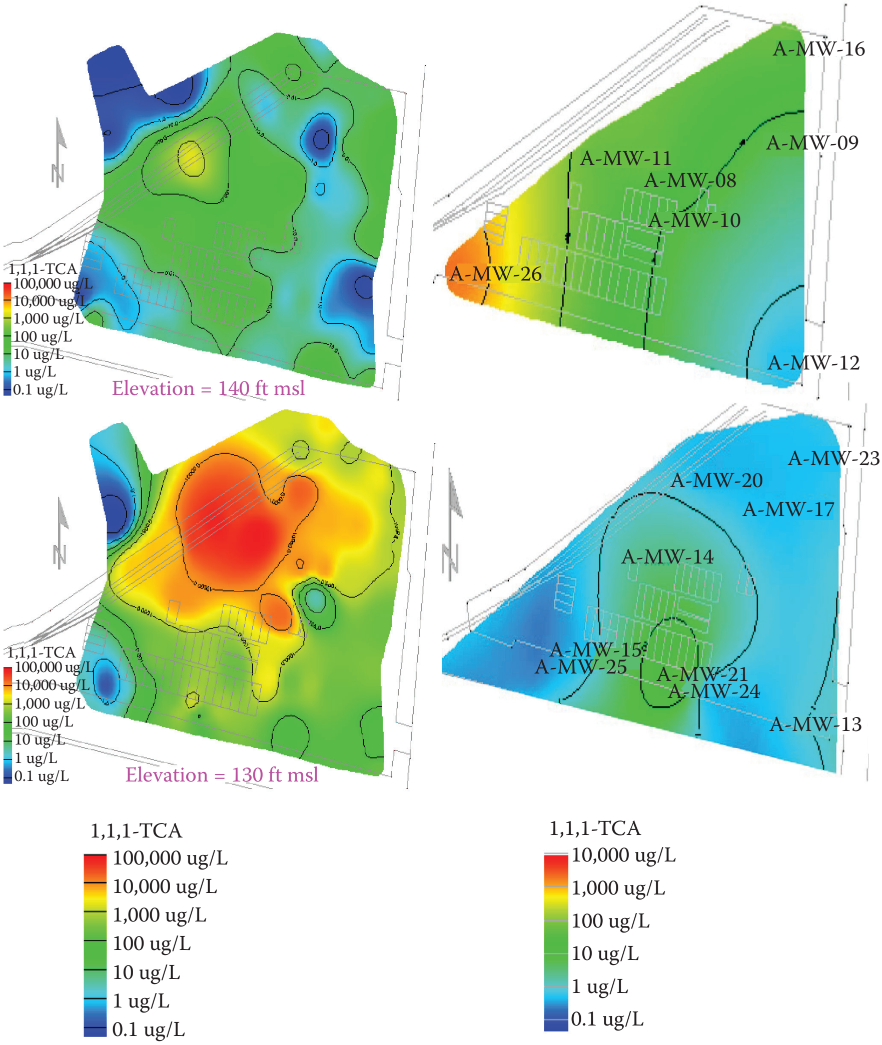
Measured Parameter	SI Unit	U.S. Unit
Length	1 meter (m) = 0.001 kilometers (km)	3.2808 feet (ft) = 1.0936 yards (yd)
	1 centimeter (cm) = 0.001 meters (m) = 10 millimeters (mm)	0.0328 feet (ft) = 0.39 inches (in.)
	1 kilometers (km) = 1,000 meters (m)	0.621 miles (mi)
	1,000 millimeters (mm) = 100 centimeters (cm)	39.37 inches (in.) = 0.00062 miles (mi.)
Weight	1 metric tonne (t) = 1,000 kilograms (kg)	2,204.6 pounds (lb) = 35,274 ounces (oz)
	1 metric tonne (t)	1.102 ton (t)
	1 gram (g) = 0.001 kilogram (kg)	0.0353 ounces (oz)
Volume	1 liter (L) = 1 cubic decimeter (dm^3) = 1,000 milliliters (mL)	33.814 ounces (oz) = 2.113 pints = 4.226 cups = 0.264 gallons (gal)
	1 cubic meter (m^3) = 1,000 cubic decimeters (dm^3)	1.308 cubic yard (yd^3)
Area	1 square centimeter (cm^2) = 100 square millimeters (mm^2)	0.1550 square inches (in^2)
	1 square meter (m^2) = 10,000 square centimeter (cm^2)	1.196 square yard (yd^2)
	1 hectare (ha) = 10,000 square meters (m^2)	2.471 acres
	1 square kilometer (km^2) = 100 hectare (ha)	0.386 square mile (mi^2)
Temperature	1°C (Celsius)	33.8°F (Fahrenheit)
Pressure	1 bar = 1.0197 kilograms/centimeter (kg/cm)	14.500 pounds per square inch (psi)



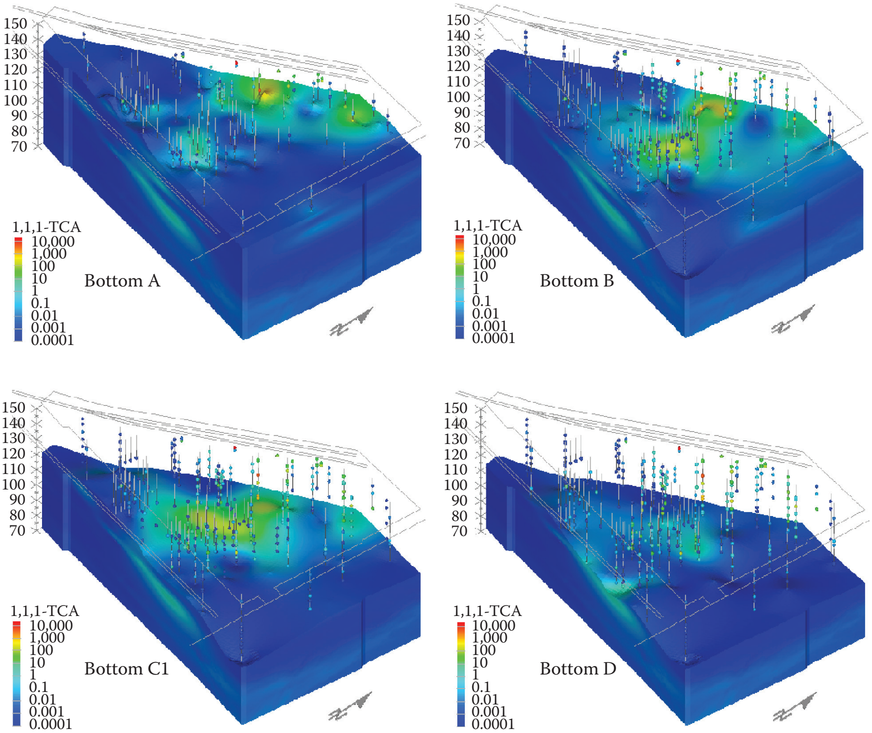
COLOR FIGURE 5.1
Geochemical fingerprints within a vertical section depicting the area of recorded historical releases at a site in Southern California.



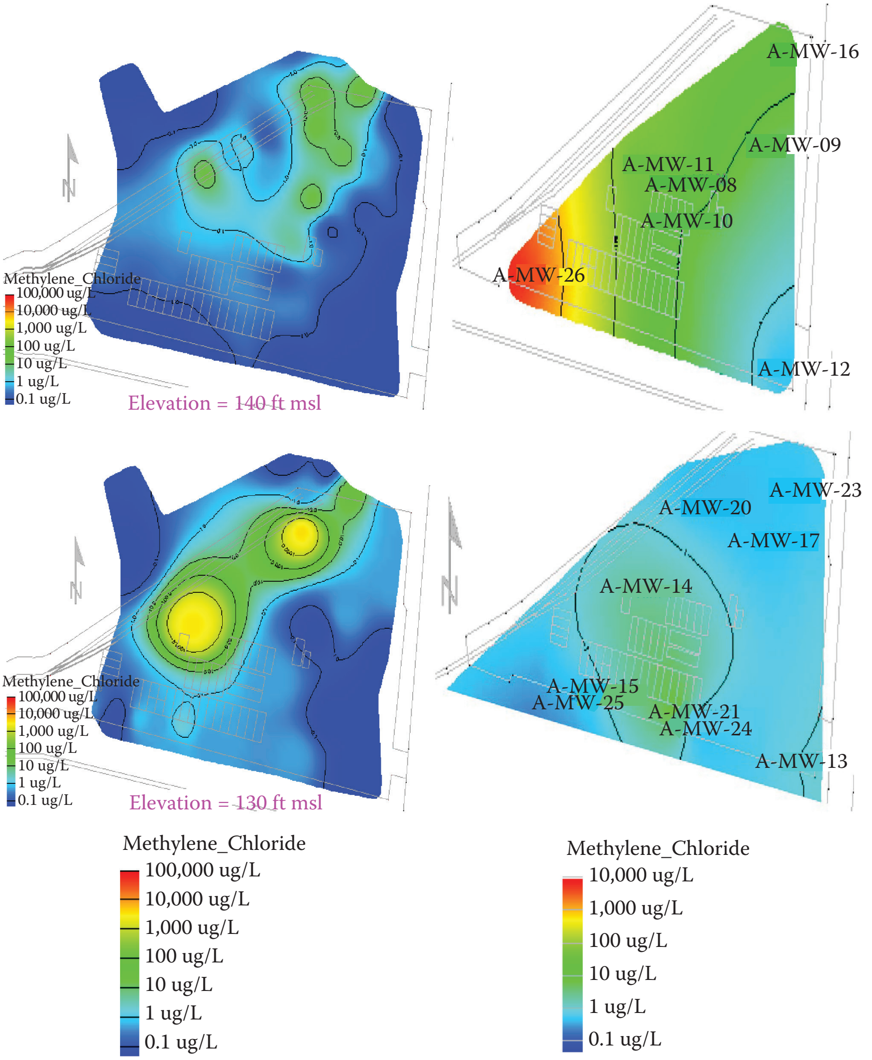
COLOR FIGURE 5.2
1,1,1-TCA chemical fingerprints in shallow subsurface at a site in Southern California.



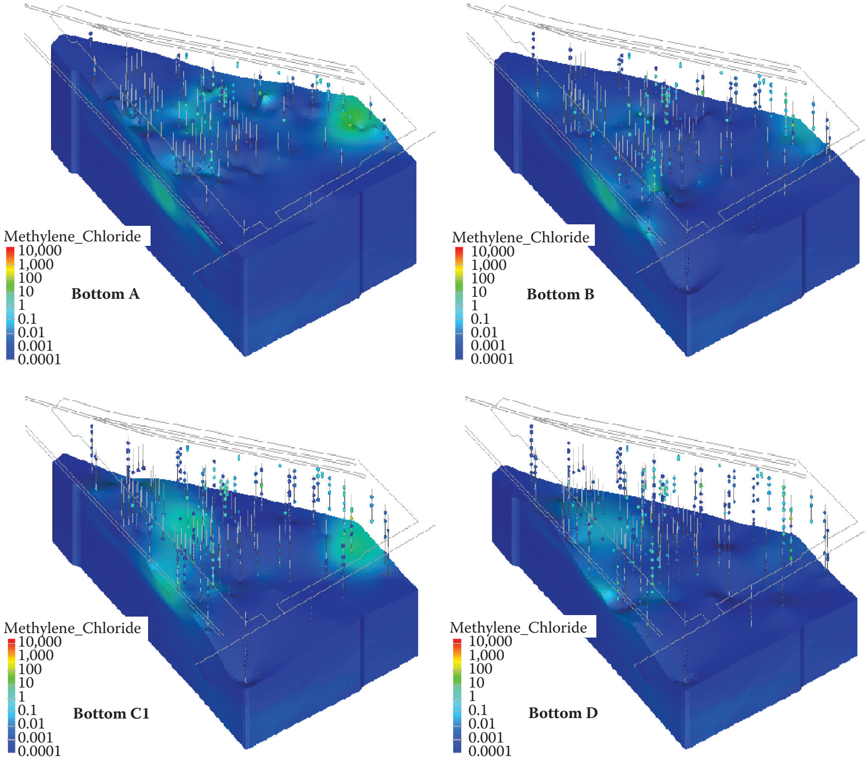
COLOR FIGURE 5.9
Examples of 2D representations of soil vapor plumes (left images) and groundwater plumes (right images) of a contaminant (1,1,1-TCA) at a site with recorded releases in Southern California. The top left image shows 1,1,1-TCA soil vapor plume at 10 ft bgs; the bottom left image shows 1,1,1-TCA soil vapor plume at 20 ft bgs. The top right image shows the 1,1,1-TCA shallow groundwater plume; the bottom right image shows the 1,1,1-TCA deeper groundwater plume. Note the differences between soil vapor and groundwater scales.



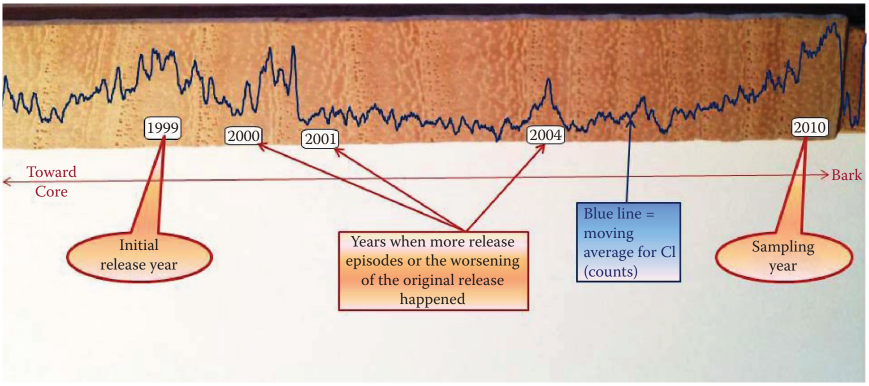
COLOR FIGURE 5.10
Examples of 3D representations of a contaminant (1,1,1-TCA) soil plumes within distinct lithological layers at a site with recorded releases in Southern California. The soil plumes are shown within the same soil "slice," expanding from the surface to approximately 80 ft bgs. Specifically, the four images show color-coded 1,1,1-TCA soil plumes at the bottom depth of four distinct lithological layers expanding from the surface down (from top left toward bottom right, with layer A being the surface layer and layer D being the deepest layer). Note that the color code scale in each individual image ranges from 10,000 to 0.0001 μg/kg as color changes from red to blue (nondetects).



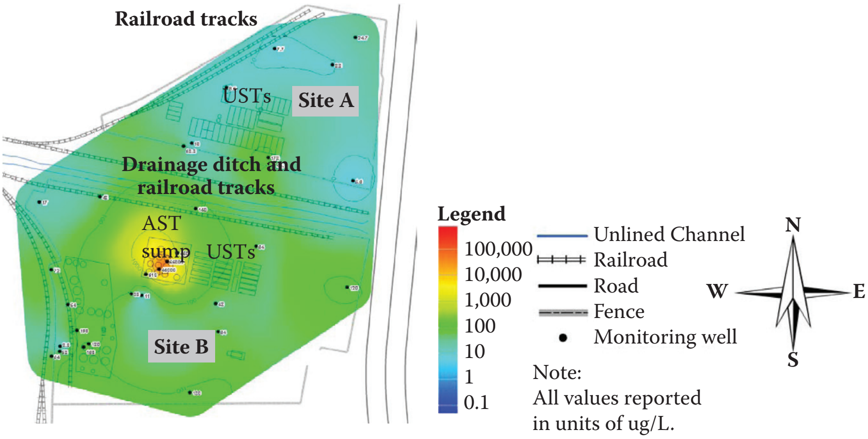
COLOR FIGURE 5.12
Examples of 2D representations of soil vapor plumes (left images) and groundwater plumes (right images) of another contaminant (methylene chloride, MC) at the site with recorded releases in Southern California also displayed in previous figures. The top left image shows the MC soil vapor plume at 10 ft bgs; the bottom left image shows the MC soil vapor plume at 20 ft bgs. The top right image shows the MC shallow groundwater plume; the bottom right image shows the MC deeper groundwater plume. Note the differences between soil vapor and groundwater scales.



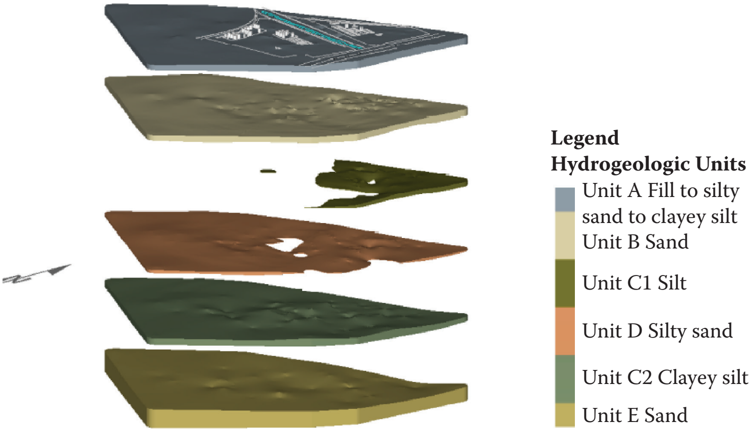
COLOR FIGURE 5.13
Examples of 3D representations of another contaminant (methylene chloride, MC) soil plumes within distinct lithological layers at the site with recorded releases in Southern California shown in previous figures. The soil plumes are shown within the same soil slice, expanding from the surface to approximately 80 ft bgs. Specifically, the four images show color-coded MC soil plumes at the bottom depth of four distinct lithological layers expanding from the surface down (from top left toward bottom right, with layer A being the surface layer and layer D being the deepest layer); note that the color code scale in each individual image ranges from 10,000 to 0.0001 µg/kg as color changes from red (highest concentration) to blue (nondetects).



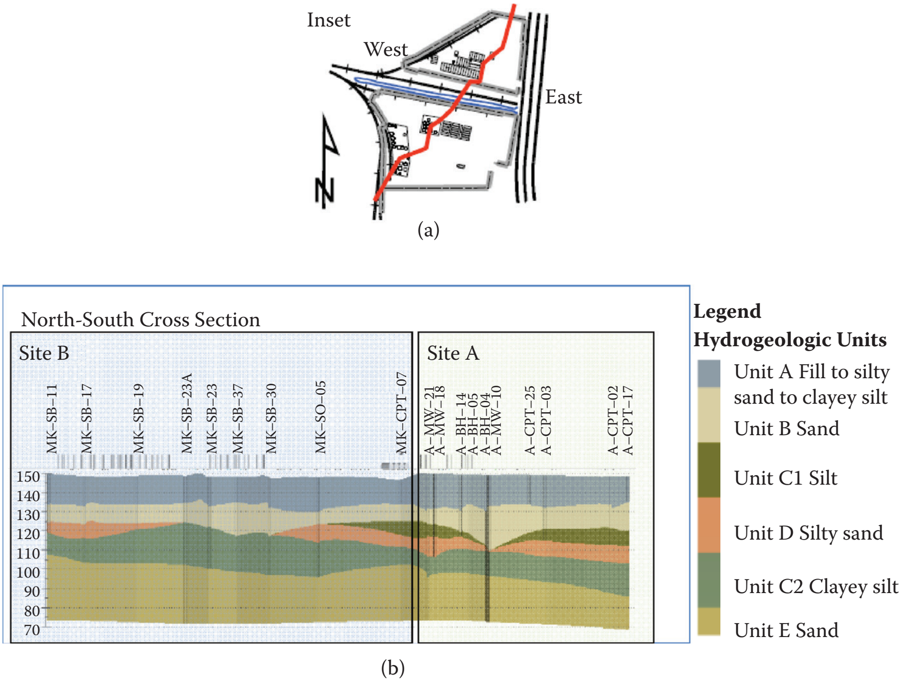
COLOR FIGURE 6.8
Example of tree-ring data evaluation in a hypothetical case study. The results of chemical elemental analysis for Cl are superimposed on the magnified core image after proper calibration; to the left is the core or so-called pith of the tree, and to the right is the tree bark.



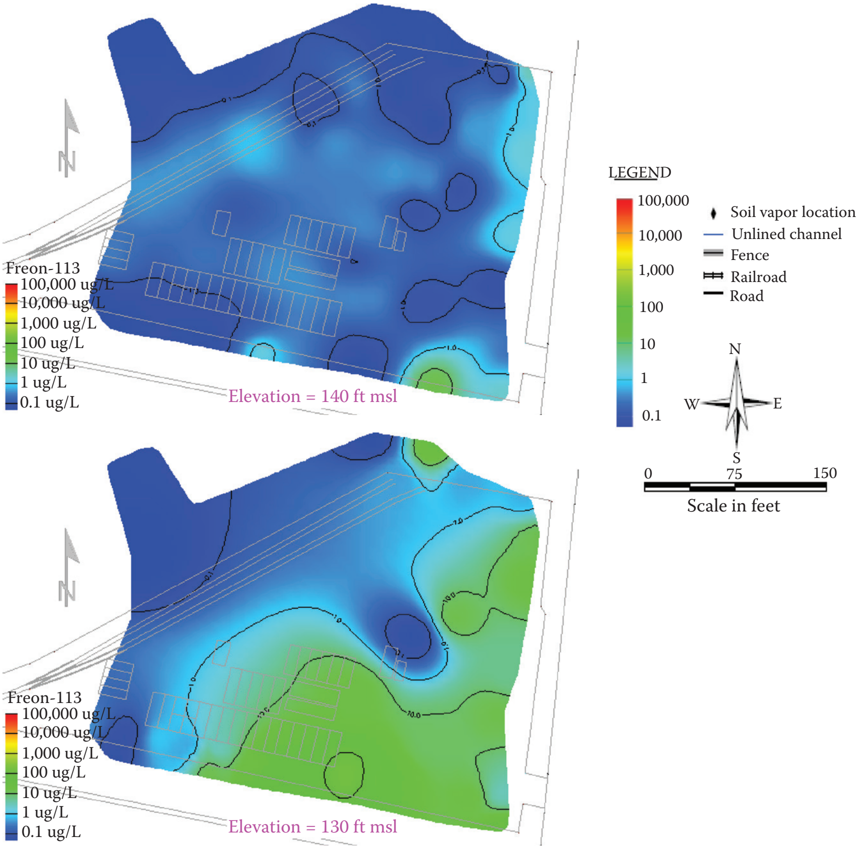
COLOR FIGURE 9.1
Location and main features of Sites A and B, along with TCE concentration in deeper regional groundwater.



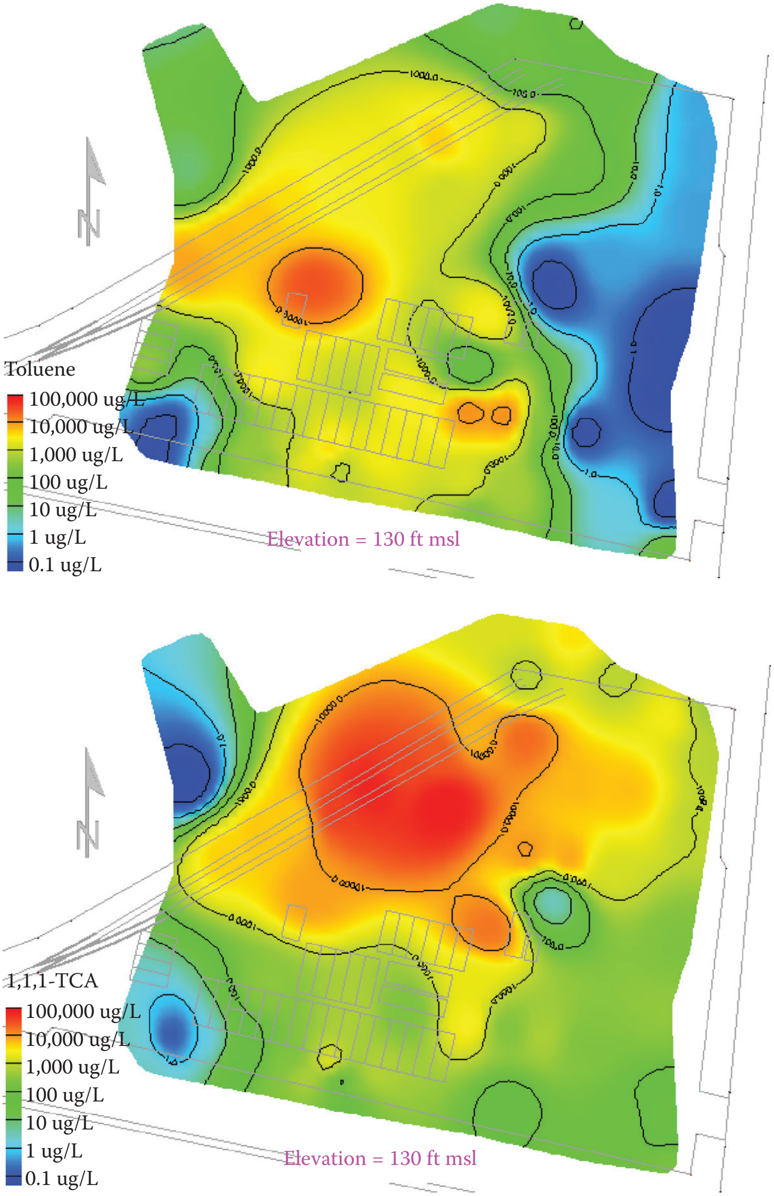
COLOR FIGURE 9.2
Reconstructed lithological layers (below Site A).



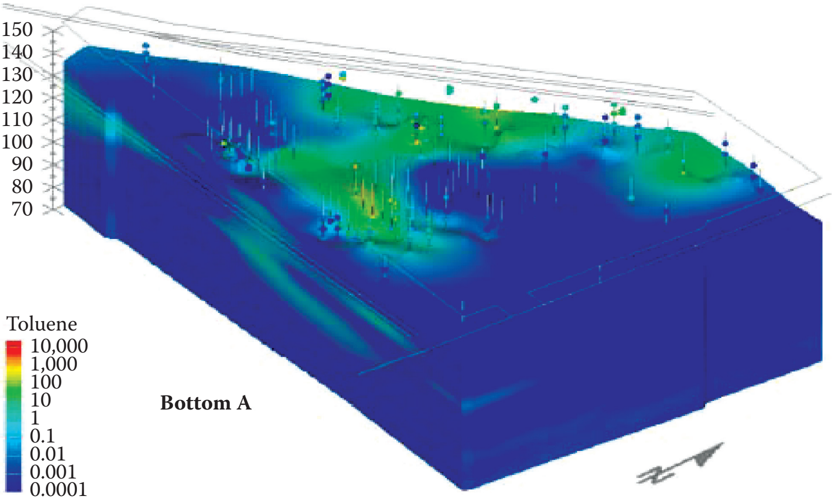
COLOR FIGURE 9.3
(a) North-south cross section location along the two sites (A and B)—note that Site A is toward north of Site B. (b) North-south cross section along the two sites (A and B)—note that north is to the right.

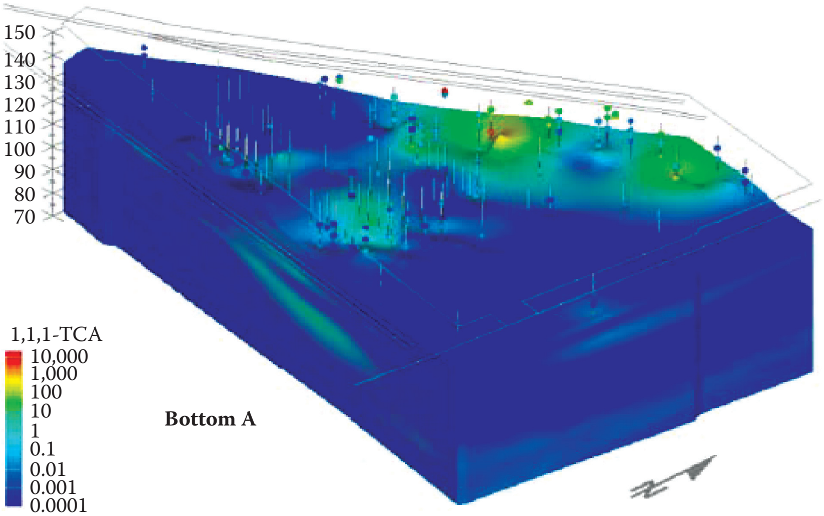


COLOR FIGURE 9.4
Freon 113 detection (isoconcentration plumes) at Site A in soil vapor at 10 ft (top) and 20 ft (bottom) below ground.

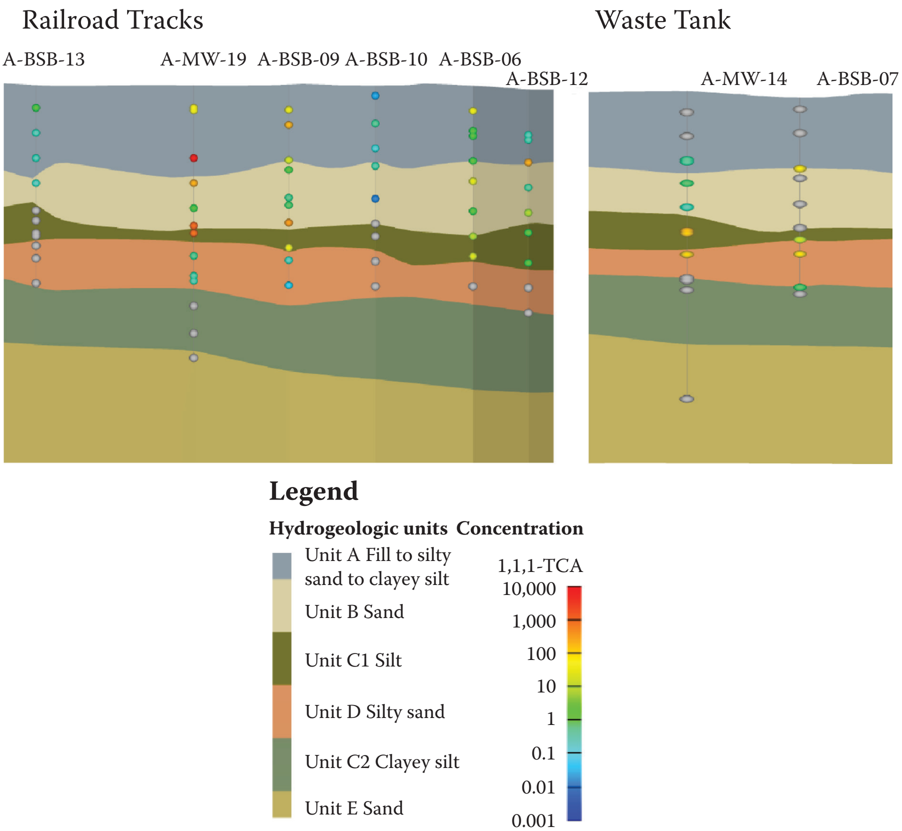


COLOR FIGURE 9.5
Soil vapor concentrations at 20 ft bgs for toluene (top) and 1,1,1-TCA (bottom) at Site A.

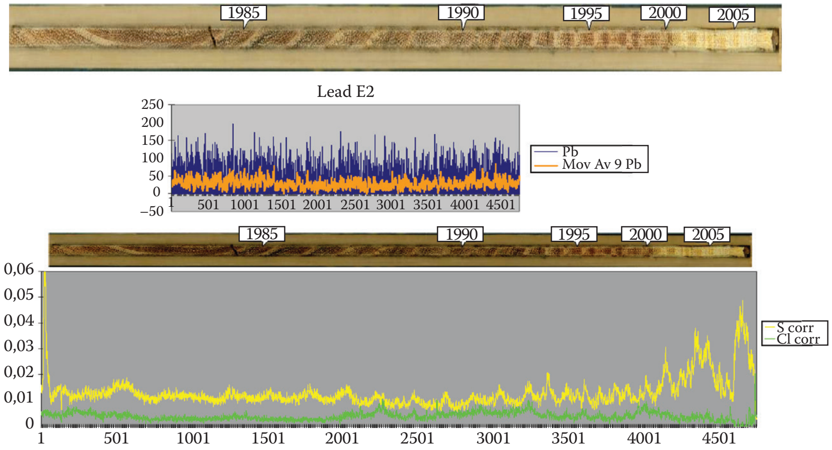




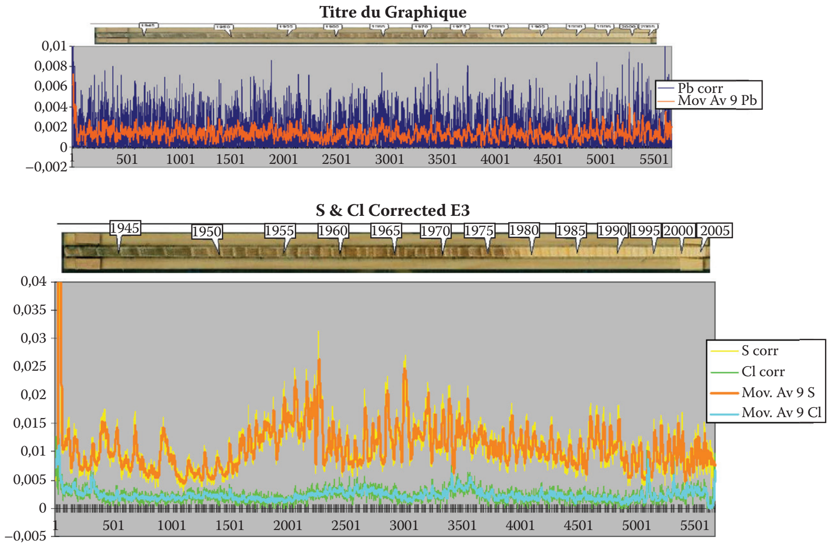
COLOR FIGURE 9.6
Soil concentration profiles (bottom of unit A) for toluene (top) and 1,1,1-TCA (bottom) at Site A (note that in both Figures 9.5 and 9.6, the red color is used to show the highest recorded concentrations, and blue color indicates nondetects).



COLOR FIGURE 9.7
Vertical profile of 1,1,1-TCA in soil at two historically recorded source areas at Site A (see color-coded concentration scale and hydrogeologic units in legend to the left).



COLOR FIGURE 14.4
Selected tree-ring fingerprinting results for tree E2: magnified core image (top), Pb profile across the core (middle), and S and Cl profiles across the core (bottom). The magnified core image is provided again with S and Cl profiles for easier identification of years corresponding to each anomaly (while there are no Pb anomalies, S had an anomaly in years 2002–2003 when a slight Cl anomaly was also observed; these anomalies may be due to the excavation work done in that period at the site, which could have mobilized older fuel oil releases from site soil). EDXRF profile data are in counts; "Mov Av" stands for moving average, which refers to corrected data, with each data point corrected over the two earlier and two later points as explained by Balouet et al. (2007b).



COLOR FIGURE 14.5
Selected tree-ring fingerprinting results for tree E3: Pb profile across the core (top) and S and Cl profiles across the core (bottom) with the magnified core image provided at the top of each profile. While there are no Pb anomalies, there are several S and Cl anomalies as discussed before for the pre-1982 period of interest in this case. EDXRF profile data are in counts; "Mov Av" stands for moving average, which refers to corrected data, with each data point corrected over the two earlier and two later points as explained by Balouet et al. (2007b).

ENVIRONMENTAL TOXICOLOGY

ENVIRONMENTAL FORENSICS FUNDAMENTALS A Practical Guide

A Practical Guide to Environmental Crime Scene Investigations

Releasing contaminants into the environment—whether deliberate or unintentional—can be thought of as a crime against the environment. The role of environmental forensics is to identify and prevent environmental pollution, or crimes. ***Environmental Forensics Fundamentals: A Practical Guide*** examines this growing field, and provides environmental professionals looking to specialize in environmental forensics with the materials they need to effectively investigate and solve crimes against the environment.

Pointing the Finger at Environmental Crime

Environmental forensics uses "fingerprinting" techniques in order to assess and analyze contamination sites. Fingerprinting can reveal the source of contamination, as well as how, where, and when the contamination was released. This handy guidebook outlines the proven techniques, applications, and resources needed to efficiently investigate environmental crimes and become successful in this emerging field.

Learn the Basics from a Single Source

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