

## INTRODUCTION TO ENVIRONMENTAL FORENSICS

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### **Summary**

*Environmental forensics is the systematic and scientific evaluation of physical, chemical, and historical information for the purpose of developing defensible scientific and legal conclusions regarding the source or age of a contaminant released into the environment.* As such, there is a multitude of forensic techniques available for contaminant age dating and source identification including, but not limited to aerial photo interpretation/photogrammetry, chemicals associated with discrete chemical processes, identification of the manufacturer of a particular product, chemical additives and/or impurities, chemical profiling, degradation modeling, corrosion models, contaminant transport modeling, surrogate chemical analysis, chronological changes in chemical processes resulting in diagnostic markers, compound specific isotopic analysis, polychlorinated biphenyl (PCB) congener analysis and degradation product ratio analysis. Given the range of available environmental forensic techniques, selected methods are presented to illustrate the applications of environmental forensics to identify the age and source of a contaminant release.

## **1. Introduction to Environmental Forensics**

### **1.1 Definitions**

Environmental forensics is defined as the systematic and scientific evaluation of physical, chemical and historical information for the purpose of developing defensible scientific and legal conclusions regarding the source or age of a contaminant release into the environment.

### **1.2 Historical Perspective**

Environmental forensics evolved in the 1980s as a result of the potential liability (as defined by laws in the United States) of parties who allegedly released a contaminant into the environment. Since this time, other countries, such as those in the European Union, have enacted similar laws requiring the same environmental tools provided by environmental forensics.

### **1.3 Applications**

Applications of environmental forensic techniques include their use for identifying the responsibility for areas of known contamination, to allocate responsibility for remediation in areas of mixed waste streams from multiple parties, identification of historical property owners responsible for a contaminant release, developing the probability that chemical exposure caused manifest or latent injuries, distinguishing between anthropogenic and anthropomorphic contaminants, and for marine oil pollution, determining the spill source.

## **2. Generic Forensics Techniques for Contaminant Age Dating and Source Identification**

The following sections describe generic forensic techniques that may be useful in determining the age and source of a release. There is no technique that applies perfectly to every chemical released at every site. The forensic investigator must identify the

methods most likely to assist the progression towards scientifically valid and defensible conclusions.

## 2.1 Underground Storage Tank Corrosion Models

A common environmental forensic question regarding the allocation of responsibility for a contaminant release is when potential contaminants, sometimes stored in an underground storage tank, were first released. In most instances, tank corrosion models can provide probability statistics to produce a range of likely release dates, as corrosion pitting and perforation leak data is normally distributed.

The corrosion rate of an underground storage tank and associated piping is influenced by the thickness of the metal and the electrical resistivity of the soil. The thicker the tank or piping wall, the longer it takes for corrosion to occur. Soil with resistivity values below 10 000 ohm-centimeters are corrosive, respective to steel while soil with resistivity values of 2 000 ohm-centimeters are five times more corrosive than 10 000 ohm-centimeter soils. Soil with resistivity values below 1 000 ohm-centimeters are considered extremely corrosive, although rarely encountered.

The primary soil measurements typically used in underground storage tank corrosion models include the following:

- Soil moisture content;
- Soil resistivity;
- Water soluble chloride and sulfate concentrations (the higher the chloride and sulfate content, the greater the corrosion rate for steel tanks);
- pH, and
- Bicarbonate concentration.

Generally, the evaluation of these five soil parameters along with information specific to the tank construction and materials, provide the analytical framework for determining the likely corrosion rate. Examples of corrosion models for underground storage tanks include the Mean Time to Corrosion Failure (MTCF), the Tank Environmental Profiling (TEP) and the Tank Suitability Study (TSS) methods, and the Rossum Pitting model. Of these models, the Rossum Pitting Model is frequently used to estimate when an underground storage tank began leaking in environmental forensic investigations and is therefore selected to examine in detail.

Rossum developed Equation 1 to solve the time when a leak first occurs in a pipe or outer surface of an underground storage tank:

$$T_L = (\rho/10 - pH)(z/K_n K_a)^{1/n} (1/A)^{a/n} \quad (1)$$

Where  $T_L$  is the time for the first leak to occur;  $\rho$  is the resistivity in ohms-centimeter;  $pH$  is a measure of acidity or alkalinity of the soil;  $z$  is the wall thickness of the metal;  $K_n$  is an empirical constant equal to 170 for soil with good aeration, 222 for soil with fair aeration and 355 for soil with poor aeration;  $K_a$  is the relative pit depth, equal to 1

for wrought iron, 1.06 for steel and 1.4 for cast iron;  $A$  is the area of exposed pipe or underground storage tank surface;  $a$  is an empirical constant for wrought iron equal to 0.13, for steel 0.16, and for cast iron 0.22; and  $n$  is an empirical constant for soils with good aeration, equal to 1/6, for soil with fair aeration equal to 1/3 and for poor aeration equal to 1/2.

Rossum also provided a solution for the number of leaks that can occur at any time as expressed by Equation 2:

$$L = A(K_n K_a / z)^{1/a} [t(10 - pH) / \rho]^{n/a} \quad (2)$$

Where  $L$  is the number of leaks and  $t$  is time.

Given that the parameter values used in the Rossum model are available or are reasonably estimated, the forensic scientist can estimate when a leak first occurred. The ability to provide a range of values for Equations 1 and 2 also provides the ability to use probability statistics to assign confidence levels to estimate when a release first occurred.

The Rossum Pitting model, as with other corrosion models, presents a simplified expression for estimating when an underground storage tank began leaking and the number of leaks. Other considerations influencing the corrosion rate include the following:

- the presence of cathodic protection, a sacrificial anode, which can retard the corrosion rate estimate by the model;
- the presence of inter-connected tanks and piping of different composition and wall thickness;
- the presence of a surface coating on the exterior of the tank, often similar to asphalt;
- the historical presence of a fluctuating groundwater table which was in contact with the tank and associated piping for some portion of time each year, and
- evidence that leakage occurred from tank overfilling/spills as opposed to tank corrosion.

The final consideration can be examined by identifying whether soil at the ground surface, and especially near the fill port of the underground storage tank, indicates the presence of the same contaminants that are identified at depth in samples adjacent to or below the underground storage tank. Care must be exercised when reaching conclusions regarding the source of the contaminants detected in soils adjacent to the underground storage tank and piping and whether the contaminant distribution reflects a combination of surface and tank failure releases.

## 2.2 Commercial Availability of a Chemical

A forensic investigator can sometimes use the commercial availability of a chemical to age date a contaminant release and sometimes to distinguish between potentially responsible parties. This indirect linkage to a particular party can sometimes be the only

means available to bracket ownership or site operation timeframes with possible chemical use and release. This approach is not applicable only to chemicals with relatively narrow availabilities. Chemicals with broad historical availability can often be further differentiated by the presence and/or concentration of additives (reaction inhibitors, antioxidants, light inhibitors, oxygenates, stabilizers, etc.), which can sometimes be associated with relatively narrow timeframes that parallel evolving industrial practices or regulations. Commercial availability analysis is particularly useful for fuel additives, chlorinated solvents, pesticides, herbicides, fungicides, and chlorofluorocarbons. Table 1 summarizes when several commonly encountered contaminants became commercially available.

<b>Contaminant</b>	<b>Year</b>
<b>Chlorinated Solvents</b>	
Carbon tetrachloride	1907
Chloroform	1922
Tetrachloroethene (PCE)	1925
Trichloroethene (TCE)	1908
1,1,1-Trichloroethane (TCA)	1946
1,1,2-Trichloroethane	1941
1,2-Dichloroethane	1922
<b>Pesticides / Herbicides / Fungicides</b>	
Aldrin	1948
Bromacil	1963
Chlordane	1947
DDT	1942
Dibromochloropropane (DBCP)	1955
Dieldrin	1948
Dinoseb	1945
Parathion	1947
Phorate	1954
Toxaphene	1947
Trifluralin	1960
<b>Polychlorinated biphenyls (PCBs)</b>	
PCBs (non-specific)	1929
Aroclor 1016	1971
“Late production” Aroclor 1254	1974
<b>Gasoline additives</b>	
Ethanol	1930
Tetra-ethyl lead (TEL)	1923
Ethylene dibromide (EDB)	1928
Methyl-tertiary-butyl ether (MTBE)	1979
Ethyle-tertiary-butyl ether (ETBE)	1969

Table 1. Commercial availability of select contaminants.

### 2.3 Chemicals Unique to a Manufacturing Activity

While chemical availability and usage trends are easily identified, they cannot be exclusively used as the only evidence of chemical use at a facility. For many chemical families, a high degree of overlapping availability and usage timeframes makes it unreliable as a stand-alone link between operations and chemical use. The infrastructure required for different manufacturing activities may provide insight into potential source locations. The point at which a contaminant is allowed entry into the environment (i.e. floor drains, sumps, transfer piping, storage areas, underground storage tanks, equipment outlets or overflows, etc.) is often related to site activities for a given timeframe. In a scenario where manufacturing activities have changed over time due to change in ownership or tenancy, existing infrastructure may sit unused whereas other newly constructed infrastructure is installed. These unique operational features are often the best or only evidence that can be examined alongside contaminant distribution to develop causal relationships.

Unique formulations of chemicals can be indicative of the manufacturing requirements and can sometimes be used to date the timing and/or origin of a release. A stabilizing chemical such as 1,4-dioxane in TCA can be used to date a release and to suggest likely manufacturing activities. Unstabilized TCA is unsuitable for many metal cleaning operations, particularly in the heated environment of a vapor degreaser. 1,4-dioxane was first incorporated into TCA products by Dow in May 1960, designed to prevent corrosion of aluminum, iron, and zinc surfaces. The coincidence of TCA and 1,4-dioxane in an environmental sample may therefore suggest a post-1960 release from an operation involving degreasing metals which are reactive with unstabilized TCA.

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gasoline in groundwater, includes measured half-life values for various related chlorinated and BTEX compounds and discussion of using BTEX ratios to age-date a hydrocarbon.]

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McCarty, P. and L. Semprini (1994). In *Handbook of Bioremediation*. Eds. Robert Norris, Lewis Publishers, Boca Raton, FL, p.87. [Introduces bioremediation concepts and provides information relative to topics that are used in environment forensics such as chemical degradation pathways of chlorinated solvents, including the transformation of TCA to 1,1-DCE.]

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[Introduces and explores the application of environmental forensics to chlorinated solvents and provides information relative to chlorinated solvent chemistry, production, commercial applications and availabilities.]

Morrison, R. D., and J. R. Hone (2010). Age dating the release of PCE, TCE, and TCA using stabilizers and feedstock impurities as indicators, In: *Environmental Forensics, Proceedings of the 2009 INEF Annual Conference*, Morrison, R., and G. O'Sullivan (Eds.), Royal Society of Chemistry (RSC) Publishing, Cambridge, UK. pp. 289-304. [This manuscript discusses various methods used to age date PCE, TCE, and TCA using stabilizers and feedstock impurities.]

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### **Biographical Sketches**

**Dr. Robert D. Morrison** has a B.S. in Geology, a M.S. in Environmental Studies, an M.S. in Environmental Engineering and a Ph.D. in Soil Physics. Dr. Morrison has worked for 40 years as an environmental consultant on soil and groundwater contamination projects. Dr. Morrison specializes in the forensic review and interpretation of scientific data for the purpose of identifying the source and age of a contaminant release.

Dr. Morrison is considered the “father” of modern environmental forensics and coined the term “environmental forensics” in peer-reviewed literature published in the 1990s. Dr. Morrison is an active member on numerous scientific editorial boards and has published extensively on the subject of environmental forensics. Dr. Morrison is the author of more than 15 books on environmental issues including the first book devoted solely to environmental forensics in 1999 (*Environmental Forensics Principles & Applications*). In 2000, Dr. Morrison established the *Journal of Environmental Forensics* as the premiere peer-reviewed scientific journal on the subject of environmental forensics. Dr. Morrison is also a founder the International Society of Environmental Forensics (ISEF) in 1999 and the International Network of Environmental Forensics (INEF) in 2008. Dr. Morrison is active in establishing environmental forensic programs at universities throughout the world.

**Justin R. Hone, P.G.** is a registered professional geologist in California and has a BS in Geophysics from the University of California at Riverside. Prior to joining the environmental sector in 2004, Mr. Hone acted as president of European operations for an explosive detection technology company where he managed product prototyping, investor relations, and business development. Since then he has focused on expert witness and litigation support as well as forensic site assessment and sampling activities. Mr. Hone utilizes isotopic ratio analyses, interactive geographical information system (GIS) modeling, aerial photography, historical research, and other forensic tools to develop linkages between contaminant releases and responsible parties.