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Environmental Forensic Characterization of Chlorinated Solvent DNAPL Sources

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ABSTRACT: Environmental Forensics entails the application of several techniques for identifying and characterizing the historical sources of releases at sites with hazardous substances in the soil and/or ground water. They can be particularly useful in better characterizing DNAPL and chlorinated solvent sites. The techniques include chemical fingerprinting, interviews, research of historical documents and industrial processes, examination of historical aerial photographs, waste volume calculations, degradation studies and fate and transport evaluations. Currently, the authors are working with others to develop environmental forensic guidance. This paper illustrates their application for site characterization and, in particular, in characterizing sources of DNAPL and chlorinated solvents. These techniques were applied as part of litigation concerning cost allocation and are discussed from both a technical and legally defensible perspective.

INTRODUCTION

Environmental forensics has evolved to be a useful tool in the identification and characterization of historical sources of releases of hazardous substances. In particular, environmental forensics is often applied within the context of litigation concerning remedial cost allocation where questions arise concerning the age of a release. Environmental forensic techniques have evolved to include not only the application of chemical fingerprinting but also historical research concerning questions of who produced or used what products when, how were the associated wastes managed, and what were the waste characteristics. Answers to these questions often drive issues related to how to allocate remediation costs for old manufacturing or waste disposal sites.

Evolution of Environmental Forensics. Environmental forensics has evolved over the last 10 to 15 years to include a number of techniques beyond just chemical fingerprinting. Environmental forensics evolved out of the oil industry's attempts to identify or fingerprint the sources of oil and to differentiate similar petroleum products (Stout and Uhler 1999). However, chemical fingerprinting is not sufficient alone to characterize the history or age of a release and/or the source(s) of the release. For that reason, other investigative techniques have been adapted to help in answering these questions. Such techniques have been used in environmental site assessments and include the following: historical research (e.g., interviews, review of historical aerial photographs, research of historical documents and industrial processes), geological and hydrogeological studies, chemical degradation studies and fate and transport evaluations. Chemical fingerprinting has also evolved to include new and more advanced techniques.

Case Study. To illustrate the importance of these techniques, this paper outlines how the application of several different environmental forensic techniques when combined

together served to provide sound basis to allocate among DNAPL sources. The case study site has a long history of operations (since the 1930s). A recent environmental assessment associated with the potential sale of the property identified an environmental problem – the presence of multiple chlorinated solvent plumes at the site that needed remediation. The primary constituents identified were trichloroethene (TCE) and 1,1,1-trichloroethane (TCA) and their various breakdown products. In general, the amount of TCE reported present at the site was greater than that for TCA, with some areas of the site having only TCE reported present, some areas having only TCA reported present, and some areas having both reported present. The current owners, who bought the facility in 1962, then turned to former owners to pay for most if not all of the remediation cost. The basic question came down to who used what solvents when and where at the site. The current owners initially claimed to have never used chlorinated solvents but later agreed they had used some TCA but continued to claim they had never used TCE.

Given the age of this site, over 70 years old, the timing of the last sale, over 40 years ago, and a lack of historical documents, allocating liability is difficult. No one technique should be expected to be the magic bullet and give the definitive answer. Age dating and fingerprinting are inherently qualitative because of the many environmental factors that may affect the results. To arrive at accurate conclusions requires the development of multiple lines of evidence which taken together corroborate and support the conclusions. In this way, the various questions and theories to be answered can be tested in a variety of way to give a more complete and defensible characterization of past history.

Site History. Depositional testimony and interviews with current and former employees and historical facility documents were reviewed to establish a basic understanding of the site history, what types of manufacturing activities took place, and the potential uses for solvents at the site. This history was then interpreted along with other information from a review of historical aerial photographs, historical information regarding the chlorinated solvent industry, and site investigation results and additional chemical fingerprinting studies to assess the issue of which solvents were likely used by which party. The facility of interest, consisting of about 19 acres, manufactured electrical devices from ~1920 to 1960s. Chlorinated solvents, primarily TCE, were used as part of a plating operation and in the washing and cleaning of metal parts. The facility was sold in 1962 to new owners. After 1962 the facility was primarily used for the manufacture and assembly of residential lighting fixtures, initially from pre-finished parts. In 1965 the business expanded to included custom color fixtures which required a spray booth for painting parts and a degreaser for preparing the raw parts to be painted, which were added to the operations. In the late 1960s, the facility switched from lead to water-based paint and added a vapor degreaser to facilitate degreasing operations. In the late 1980s an ultrasonic cleaner for cleaning glass was installed. The new owners utilized several buildings that were also used by the former owners. In particular, Building No. 5 housed the assembly line and shipping activities, while Buildings No. 6, 7, and 8 were used for storage of raw parts – glass and metal. Chemical usage by the new owners included solvents for degreasers, paint and paint thinner. According to testimony, chemicals at various times were stored inside the work area, on the loading dock, and/or on a covered dock adjacent to the assembly area during occupancy of Building No. 5. The new owners ceased production at

the facility and moved the lighting operations to new facility in 1991. Subsequently, Buildings No. 5, 6, and 7 were demolished. Building No. 8 was destroyed by fire in 1978.

Historical Aerial Photographic Study. Historical aerial photographs of the site were obtained and reviewed to assess the site history. Buildings that were only in existence during the time of the former owners, the current owners or both were noted. Soil and ground water analytical data were then reviewed to identify what constituents were associated with the buildings that had unique or common ownership. The data indicated that no historic releases were associated with two of three pre-1962 buildings and that the TCE release near the third might have originated from storage tanks that appeared before and after 1962. The storage tanks on aerial photographs contradicted statements by the current owner that they had been demolished before 1962. The data also indicated that a post-1962 building was located near releases of both TCE and TCA while another was located near a release of TCE. This data, while not conclusive, were consistent with the use of TCE by the owner of the site after 1962.

HISTORICAL USE OF CHLORINATED SOLVENTS

Due to a lack of facility documents identifying the type of solvents used historically and conflicting statements by former and current company officials, a review of the historical chlorinated solvents industry and, in particular TCE/TCA use, was conducted to put the potential use of solvents at the facility in the proper historical perspective. This review indicated that is was more likely that the new owner of the facility used TCE rather than TCA in the vapor degreasing operations at the facility starting in the late 1960s and continuing into the 1980s. The history of production and use of TCE and TCA has been documented by others (Doherty, 2000a, b; Morrison, 2000; and Morrison and Murphy, 2002). Additional information on the historical uses of TCE and TCA, their relative prices, their production and availability were assessed by reviewing historical industrial journals, historical chemical engineering references, and public industry production records. TCE and TCA, along with perchloroethene (PCE) and cloroethene (CT) were widely used as cleaning and degreasing solvents due to their rapid evaporation rates, their low flammability and reactivity, and their ability to quickly and efficiently dissolve a wide range of organic compounds (Doherty, 2000a). The growth of the dry cleaning and degreasing industries created a demand for growth in the organic chemical industry, which was influenced by a number of historic events (e.g., military use and environmental regulations) and economic factors, as noted below.

TCE. Over the past 50 years, TCE was used worldwide as the preferred solvent degreaser (Morrison, 2000). It was the most predominant chlorinated solvent used in the United States for vapor degreasing (Morrison and Murphy, 2002). Due to its effectiveness, non-corrosivity, non-flammability and ease of recycling, no solvents matched the performance of TCE in cleaning and degreasing (Doherty, 2000b). Historically, for most types of vapor degreasing operations, such as the type added to the subject facility in the late 1960s, TCE was considered the preferred vapor degreasing solvent because it exhibited chemical and operational characteristics that made it the most suitable and stable solvent for use in cleaning operations that required heating the cleaning solvent to high temperatures. TCA and PCE were not preferred for degreasing at high temperatures. In

addition to being more suitable for use at high temperatures, TCE's other highly preferred characteristics such as excellent solvency, low flammability, high vapor density (4.5 times that of air), non-corrosivity to most metals, and narrow boiling range made it the solvent of choice for vapor degreasing. These same factors also contributed to its success in other solvent cleaning applications such as cold cleaning and dry cleaning.

By 1960, TCE's performance and price (TCE was typically cheaper than TCA) made it the most popular vapor degreasing solvent in the United States (Doherty, 2000b) and by 1970, TCE reportedly accounted for 82% of all chlorinated solvents used in vapor degreasing, although by 1976 its share had declined to 42% (Grayson and Eckroth, 1979). This was due to the impact of environmental regulations and a number of economic factors. By the mid 1970s, several local and state smog-related regulations in the United States had been promulgated and enforced to restrict the use of TCE. The Clean Air Act controlled TCE usage due to its suspected contribution to ozone and smog formation. As a result, limitations on TCE emissions were placed on users in non-attainment areas which resulted in users switching to TCA as a degreaser. It was as a result of these regulatory pressures that TCA's production rates increased rapidly starting in the mid-1970s and peaking around 1985.

TCA. TCA became more widely used in the late 1970s and 1980s as it replaced PCE, CT, and TCE in the degreasing and cleaning applications. TCA offered satisfactory solvency for greases, oils, tars, waxes and many other organic materials, and was considered less toxic than the chemicals it was recommended to replace. TCA is the historical solvent of choice in cold cleaning. It was, however, frequently used in vapor degreasing and ultrasonic cleaning of metal parts for the removal of greases, oils and waxes after TCE lost favor because of its smog-related regulatory costs and potential carcinogenicity in the late 1970s (Doherty, 2000b). TCA was found to react vigorously with some metals and formed corrosive byproducts. As a result, un-stabilized TCA could not be used with certain metals.

Stabilizers as Chemical Fingerprints. Stabilizers are chemicals that were added in small amounts to change the properties or prevent solvent degradation. Different stabilizers were used in different time frames for different solvents for differing purposes:

- As a reaction inhibitor that deactivates the surface and complexes salts that form;
- As an acid acceptor that neutralizes trace amounts of acid formed during degreasing which may cause corrosion of the degreased part; and
- As an antioxidant that reduces the solvent's potential to form oxidation products.

By 1954 a patent application was filed to use 1,4-dioxane as a TCA stabilizer to reduce the corrosivity of TCA, and it was found that TCA could be used with aluminum, zinc, and iron with the addition of about 4% 1, 4-dioxane to TCA (Doherty, 2000b). The stabilized formulation of TCA increased its use in vapor degreasing, but TCE remained the preferred solvent of choice for vapor degreasing due to its superior properties. A wide variety of other chemicals were later used as stabilizers of TCA, and include 1,3-dioxolane, 1,2-butylene oxide, N-methyl-pyrrole, methyl ethyl ketone, ethyl acetate, acrylonitrile, nitromethane, dialkyl sulfoxides, sulfides and sulfites, tetraethyl lead,

tert- and sec-butyl alcohol, isopropyl alcohol, morpholine, tetrahydrofuran, and toluene (Standen, 1964; Mcketta and Cunningham, 1979; Archer, 1984; Kroschwitz and Howe-Grant, 1991). The development of stabilized formulations of TCA in the mid 1950s opened up new markets for TCA (Mcketta and Cunningham, 1979), and by late 1957, TCA was considered to have gained widespread acceptance as a replacement for CT, primarily in cold cleaning applications (C&EN, 1957), but it had no impact on TCE use.

Even after the introduction of stabilizers, the preference for the use of TCE versus TCA for vapor degreasing was reflected in historical advertisements in trade journals that presented TCE as the solvent of choice for vapor degreasing. TCE is described under the process of vapor degreasing as "optimum for most soils and metals", while TCA is described as "not generally used for vapor degreasing" (Kearney, 1970; Metal Finishing, December 1964). A PPG ad for vapor degreasing use lists "top 12 reasons" to use their TCE, and also lists other PPG solvents for metal working, but cites their TCA only for cold degreasing, maintenance clean-up, and ultrasonic cleaning (Metal Finishing, 1965). An article in Metal Finishing Guidebook 1970 provides a summary table of typical applications (7 listed) for vapor-degreasing solvents. TCE is listed under three applications (removal of soils, rocket components, and ultrasonic cleaning) with corresponding factors affecting the selection listed as "most commonly used degreasing solvent", "parts that must be free of soils or residues which might react with oxidizers" and "for cleaning efficiency beyond that obtained from standard vapor degreasing." An ultrasonic process was added at subject facility in 1988. TCA is listed under only one application, cleaning coils and motors, with a selection citation that reads "Solvent must not damage wire coating or sealing agents. Requires special equipment design" (Kearney, 1970). There was no report of such cleaning application at the subject site.

CHEMICAL FINGERPRINTING

Forensic techniques for age dating and source identification of chlorinated solvents include: additive identification, isotopic analysis and degradation models. Stabilizers and other additives used in different time frames provide an opportunity to date the timing and /or origin of a solvent release. Additives were blended with chlorinated solvents as corrosion inhibitors, metal inhibitors, and antioxidants. Elements exist in various molecular states called isotopes. Different isotopes of an element have the same number of protons but different molecular weights. In forensic fingerprinting, isotopes can be used to identify multiple sources and distinguish between solvent manufactures. As previously noted, the presence of additives in chlorinated solvents is useful for age dating and source identification and have been used to distinguish between sources of solvents in ground water. The fact that different manufacturers used different additives for identical solvents is useful in determining the origin of a solvent. In the current case study the results obtained were not definitive, probably because solvent use had ended by ~1990 at the site and natural biodegradation had reduced concentrations substantially.

Isotopes. Stable isotopic analysis is being increasingly applied to investigate and monitor the sources, transport, and fates of organic constituents in environmental systems. This interest has resulted from recent demonstrations of the ability of isotopic analysis to differentiate sources of and to demonstrate the degradation of organic compounds in the environment. Isotopic analysis of a number of organic constituents has shown that

different sources of chlorinated ethenes can have different stable carbon and chlorine isotopic compositions of fingerprints (van Warmerdam., 2000; Jendrzejewski, 2001). Volatile organic compounds (VOCs) are isotopically fractionated during degradation (Slater, 2003). Current evidence shows that nondegradative subsurface processes such as volatilization and sorption do not significantly fractionate these compounds. Thus isotopic analysis can offer definitive demonstration of the degradation of these compounds in the environment independent of mass loss due to other processes. Stable carbon isotope ratios ($R = {}^{13}C/{}^{12}C$) are expressed in "delta" notation ($\delta^{13}C = (R_{sample}/R_{standard} - 1) \times 1000$) in units of permil ($^{0}/_{00}$). In the case of carbon, the internationally accepted standard is Vienna Pee-Dee Belemnite (VPDB), where $\delta^{13}C$ is taken to be $-31\ ^{0}/_{00}$. Chlorine isotope ratios ($^{37}CL/^{35}Cl$) are compared to the international standard SMOC (Standard Mean Ocean Chloride) (Slater, 2003; Philp, 2002). The effectiveness of this technique depends on its reliability to identify differences in isotopic ratios between samples. During an isotopically fractionating process molecules containing the lighter isotope react at a slightly faster rate that those containing the heavier isotope. This difference in reaction rate is caused by the greater energy required to break bonds containing the heavier isotope. The result of this difference in the reaction rate is that the residual reactant pool becomes relatively enriched in the heavier isotope, while the product pool is relatively depleted in the heavier isotope. That is, the δ value of the reactant pool becomes more positive than its initial δ value, and the δ value of the product pool is more negative than the initial δ of the reactant pool (Slater, 2003).

Correlations on the basis of isotopic compositions utilize either the bulk isotopic compositions or the isotopic composition of individual compounds as determined by gas chromatography – isotope ratio mass spectrometry (GCIRMS). In complex mixtures, the bulk isotopic composition of the mixture will reflect the isotopic compositions of the components in the mixture and their relative proportions. (Philp, 2002).

For the current case study soil samples were collected from two borings (MB-9 and MB-10) which were installed adjacent to former Building No. 5 where the current owner conducted its lighting assembly operations. The borings were installed up-gradient and down-gradient of the reported location of the current owner's degreasing operations. The analyses noted TCE, cis-1,2-dichloroethene (cis-DCE), tetrachloroethene (PCE), and xylene at MB-9 and TCE and cis-DCE at MB-10. Isotope samples were submitted to University of Oklahoma (carbon isotopes) and the University of Illinois Chicago (chlorine analyses using SPME-CF-IRMS). Chlorine isotope analyses indicated the presence of TCE. The carbon isotope results, $\delta^{13}C$, for MB-9 (11-12 ft) (3.6-3.7 m) were $-22\ ^{0}/_{00}$ and for MB-10 (10-11 ft)(3.0-3.6 m) were $-26\ ^{0}/_{00}$. The $\delta^{13}C$ result for MB-10 is within the published and scientifically accepted ranges of TCE source data, i.e., -24 to $-51\ ^{0}/_{00}$, (Jendrzejewski et al., 2001), -24 to $-51\ ^{0}/_{00}$ (Slater 2003), and -26 to $-31\ ^{0}/_{00}$ (Philip personal communication), and is not indicative of a lengthy period of environmental exposure.

Degradation Model. Fate and transport modeling has been used for many settings as a tool to estimate the age of a release by backwards modeling a known plume to characterize a date of release. Modeling performed for the subject site was found to be consistent with more recent releases given the relatively high rates of ground water movement and relatively high rates of biodegradation and natural attenuation.

SUMMARY

For the subject case study, the application of environmental forensic techniques provided multiple lines of evidence that each corroborated a conclusion that TCE had been used in significant quantities at the site after its sell in 1962, contrary to the statements of the current owner. Such use of multiple lines of evidence provides a sound basis for meeting the threshold for acceptance of expert opinions at trial.

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