



Age Dating PCE Releases at a Dry Cleaner Site

In This Issue

- Age Dating PCE Releases at a Dry Cleaner Site
- Isotope Method Distinguishes Dry Cleaning Solvent Plumes
- Sources of PCE Releases at Dry Cleaners
- Discharges Due to Equipment Failure
- PCE and Solvent Stabilizers
- Application of Scanning Electron Microscopy (SEM)

ZymaX Forensics

71 Zaca Lane, Ste 110
San Luis Obispo, CA 93401
Tel. (805) 544-4696
Fax (805) 544-8226
Alan Jeffrey, Ph.D.

DPRA San Marcos

100 E. San Marcos Blvd. Ste 308
San Marcos, CA 92069
Tel. (760) 752-8342
Fax (760) 752-8377
Gary Vargas, PG, CHG

Numerous forensic techniques are available to age date the release of PCE (perchloroethylene) at a dry cleaning site and includes advanced analytical techniques (stable isotope analysis, identification of stabilizing compounds), molar ratio analysis of PCE and its degradation products and the presence of surrogate compounds detected with PCE that are indicative of an activity with a unique time of operation. The majority of these techniques require the proper selection and chemical analysis of environmental samples as well as a detailed knowledge (if available) of the historical use of equipment and services offered. For example, in the early 1980s Dow Chemical introduced 1,1,1-trichloroethane (TCA) as a solvent for use for leather cleaning, although it proved to be unstable and caused equipment corrosion. The presence of TCA and PCE, for example, in the subsurface along with the knowledge of when a dry cleaner offered leather cleaning may provide a means to bracket when a release(s) occurred.

Other dry cleaner services may be associated with a particular owner/tenant or time frame that can be used to age date a release. For example, a dry cleaner may have also offered garment-treating services, such as waterproofing, flame retardants, stain repellants and fabric conditioners. TCA, for example, was used along with petroleum naphtha as a carrying agent for stain retardants on fabrics while flame retardant chemicals such as decabromodiphenyl oxide, organo-phosphates and phosphated ethers were commonly used.

The presence of solvents used by dry cleaners and their presence in the environmental samples can similarly be employed for age dating. Carbon tetrachloride was the primary dry cleaning solvent from the 1920s until the early 1950's. By the 1960s, PCE surpassed carbon tetrachloride for use in dry cleaning operations. The presence of non PCE solvents in environmental samples can often provide evidence regarding when

Continued on page 2

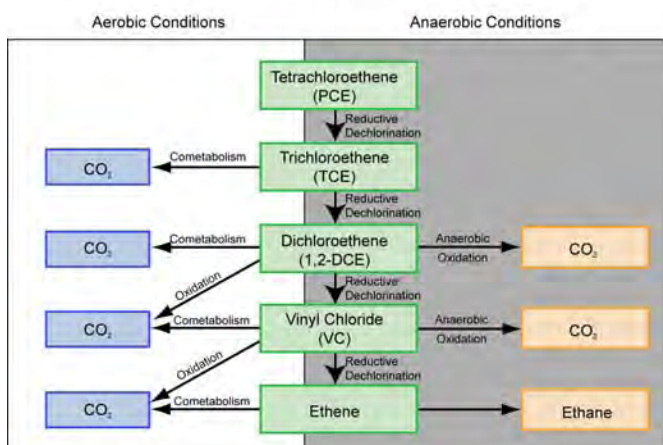
DRY CLEANER FACTS:

- The United States Environmental Protection Agency (EPA) estimates that almost 16,000 dry cleaner sites will probably require environmental investigations and remediation at an estimated cost of \$6 billion dollars.
- In 2004, EPA estimated that potentially 9,000 to 90,000 "inactive sites" dry cleaner sites will require environmental investigations and remediation.
- In 2003, the number of active commercial dry cleaners in the United States was 30,000.
- In 1998, EPA estimated that active dry cleaners in the United States generated nearly 25 million gallons of hazardous waste per year.
- In 1988, an International Fabricare Institute survey of 909 dry cleaner respondents indicated that about 71% indicated that separator water was discharged to either a sanitary sewer or septic tank. Separator water can contain PCE at concentrations up to 200 parts per million.
- A 2004 survey of 334 dry cleaning facilities and 14 wholesale supply facilities in Florida indicated that leaks, spills or discharge of solvents as their facilities had occurred for about 32% of the facilities.
- A study of dry cleaning solvent contamination (primarily PCE) in California concluded that the main discharge point for dry cleaners is the sewer line.
- A study of 150 dry cleaning sites in Florida indicates that the soil beneath the dry cleaning floor slab in the vicinity of the dry cleaning machines/distillation unit was the primary contaminant source area (47.4% of the identified source areas).

Age Dating PCE Releases at a Dry Cleaner Site—continued from page 1

releases occurred or overlapped the discharge of PCE. For example, non-PCE solvents and their date of introduction includes dipropylene glycol tertiary-butyl ether (RYNEX late 1990s), decameethylcyclopentasiloxane (GreenEarth™ late 1990s) or petroleum hydrocarbons along with hydrofluoroethane and /or perfluorocarbons (Pure Dry 2000). Chemical stabilizers (used to minimize corrosion) and impurities may also provide insight regarding the source and timing of a PCE release. For example, the use of reclaimed PCE by a particular owner and its subsequent release into the subsurface may typically contain impurities such as methyl ethyl ketone, toluene, TCA, and butylated hydroxytoluene (a color inhibitor added to some reclaimed PCE). The use of non-reclaimed PCE (99.9% pure), in contrast, would only contain other chlorinated solvents.

Degradation Pathway of PCE



Isotope Method Distinguishes Dry Cleaning Solvent Plumes

DPRA/Zymax Forensics has developed and used a stable isotope technique to determine if PCE (a common dry cleaning solvent) plumes originate from a single or from multiple sources. This involves measuring the carbon isotope ratio of PCE in groundwater or soil. Similar ratios in different plumes would indicate a similar source; different ratios would indicate different sources. The method and case studies using the method were presented at a recent Groundwater Resources Association meeting in California on isotopic methods, and was well received.

Case Study 1

PCE was present in substantial concentrations in soil and groundwater near a dry cleaning store. The dry cleaner had multiple owners over a long period of time, and the main issue was whether the PCE was from one source, associated with a single owner, or from multiple releases, perhaps associated with several owners. The carbon isotope ratios were similar in all the soil and groundwater samples, and it

was even possible to identify the manufacturer of the PCE. This suggested one source for the PCE, but raised another issue: whether a single source meant that the multiple owners used the same PCE supplier.

Case Study 2

PCE was present in substantial concentrations in groundwater at a retail store site. Groundwater flow was to the northeast, and the highest PCE hits were at the southern edge of the site. The owner suspected that PCE from one or more sources had migrated on to the site. The carbon isotope ratios showed significant differences in the three plumes shown on the map. PCE in plumes A and B showed the largest isotopic difference, with PCE in plume C showing intermediate values. From the isotope ratios and groundwater flow direction, it was inferred that PCE in plume A and B were from different sources and plume C represented mixing of these plumes. This also provided isotopic fingerprints that could be used to identify possible offsite sources.

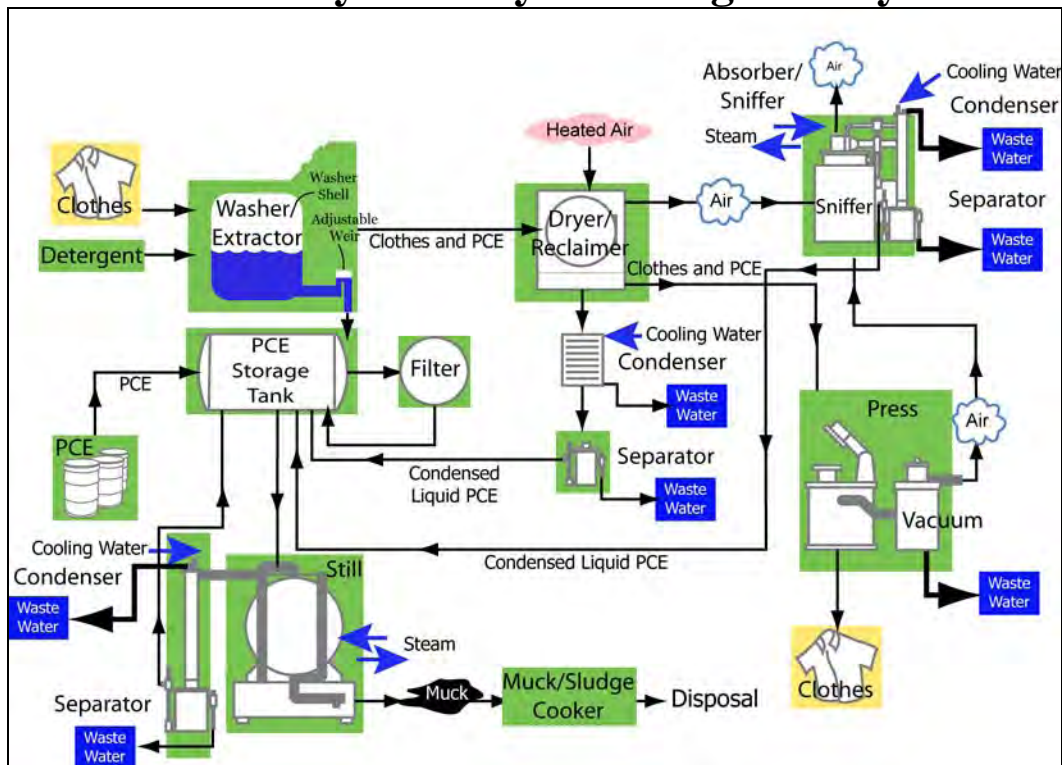
DPRA/Zymax Forensics can measure the carbon isotope ratio of PCE in groundwater at concentrations as low as 20 parts per billion (ppb). The cost is \$300/sample for the isotope ratios of PCE and its degradation products (TCE and DCE). Please contact Dr. Alan Jeffrey, alan.jeffrey@dpra.com, or Dr. River He, river.he@dpra.com for more information.

Forensic Analysis of Samples Collected at a Dry Cleaners

<u>Analysis</u>	<u>Method</u>	<u>Holding Time (days)</u>	<u>Cost (\$)</u>
Volatile Organic Compounds	EPA Method 8260B	14	95
TDS (Total Dissolved Solids)	EPA Method 160.1	7	15
MBAS (Methyl Blue Active Substance)	EPA Method 425.1/425.1M	2	50
Stable Isotopes (carbon)	GC/IRMS	14	300
Fecal Coliform	SM 9221 B	6 hrs	145
SEM (Scanning Electron Microscope)	SEM		Varies
BTEX	EPA Method 8015B (M)	14	85
Major Anions/Cations	EPA Method 300.0/6010B	48 hrs/180 days	75-110
Metals	EPA Method 6010B	180	80-175



Anatomy of a Dry Cleaning Facility



Sources of PCE Releases at Dry Cleaners

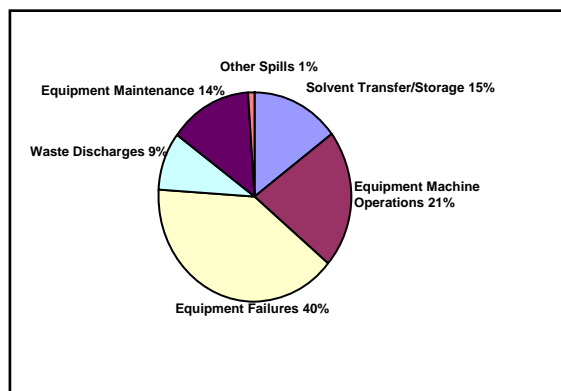
Identification of where to collect samples as well as the proper selection of analytical techniques is critical in the forensic investigation of a dry cleaner facility. EPA has found that the largest number of reported spills/discharges (39.2% of reported discharges) are associated with dry cleaning equipment failure. According to an EPA study, up to 25% of solvent emissions in dry cleaning operations can be attributed to equipment leaks. The types of reported equipment failures included: leaking seals, gaskets, piping, hoses, valves, etc. Equipment leaks can be the result of equipment wear and corrosion; expansion and contraction of metal from temperature changes; and vibration of equipment. In terms of what was specifically identified, leaking door gaskets were the most commonly reported source of solvent leakage.

In a study of 530 dry cleaning facilities in Florida, the percentage of spills or discharges of PCE in the subsurface were associated with the following scenarios.

Discharges Due to Equipment Failure

Given that PCE discharges are predominately associated with the failure of the dry cleaning equipment, the next step is to identify the most likely location for collecting an environmental sample with the highest probability of forensic

value in identifying when the release occurred. As depicted in the figure titled Anatomy of a Dry Cleaning Facility many



possibilities exist. Although the operational history of each site is different, the highest probability locations for collecting meaningful forensic samples are those associated with equipment failure, including the following:

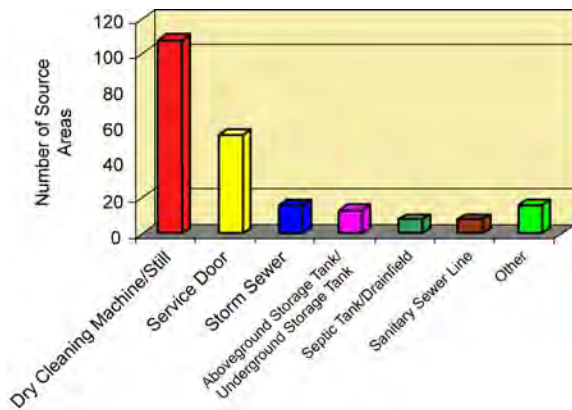
- The current and former location of the front and back of dry cleaning machines and/or distillation units. The former location of machines are often identified by the presence of cut-off lag bolts used for anchoring in the floor slab or concrete patches in the floor slab where the lag bolts were formerly located.
- The presence of coffee-colored stains on the concrete floor is often indicative of where boilovers of



distillation units occurred or still bottoms were spilled during cleanup.

- Cracks or concrete joints in the concrete floor;
- Floor drains;
- Along sanitary sewer laterals (especially at joint locations) and especially near the function of the facility sewer lateral with a larger trunk line;
- The service door of the facility where the transference of solvent to a solvent tank or into the dry cleaning machine occurred; and
- Current and former solvent storage tanks.

In a study of 150 dry cleaning sites in Florida, the most likely source area is the soil beneath the dry cleaning machines or distillation stills (See Bar Chart).

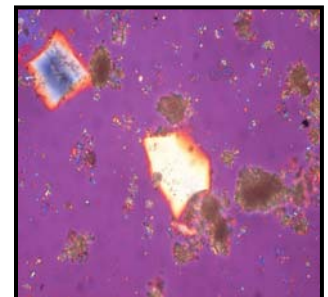


PCE and Solvent Stabilizers

Solvent stabilizers are frequently used to age date or distinguish between different sources of chlorinated solvent contamination. PCE is relatively stable, relative to other chlorinated solvents, and requires only small amounts of stabilizers. As a result, the ability to forensically use PCE solvent stabilizers in environmental investigations is usually quite limited.

Application of Scanning Electron Microscopy (SEM)

Dry cleaning equipment has a unique history relative to its evolution, especially regarding filters. Early equipment often used diatomaceous earth as a filter which was subsequently replaced with activated carbon. Understanding the type of equipment used by an operator and its chronological use can often provide information regarding the discharge of the PCE into the environment. For example, a soil sample with elevated concentrations of PCE along with diatomaceous earth or granules of activated carbon (See SEM slide) can provide insight regarding whether the filter from a particular type of dry cleaning equipment was discharged.



Prst Std
U. S. Postage
PAID
Escondido, CA
Permit 180

DPPRA
Creative People. Smart Solutions.
100 E. San Marcos Blvd., Suite 308
San Marcos, California 92069-2986