This Guidance Document has been developed as a supplement to the Remediation Closure Guide (RCG). Use of this guidance will aid in the development of a conceptual site model (CSM) for sites that used or are using dry cleaning solvents. This guidance may also have useful information to address chlorinated solvent releases from sources other than dry cleaning facilities.

Introduction

When investigating a dry cleaning site, a good working knowledge of past and present operations is needed. Several key pieces of information are necessary prior to conducting any active investigation work:

- A determination of the age of the facility and periods of operation. This information will help develop a sampling plan and can provide information on potential types of contamination.
- Location of the waste handling areas (this should include the location of the trash dumpster). A well developed sampling plan will include these areas.
- Types of equipment used and how they are tied into site infrastructure (special attention should be given to sewer lines).
- Proximity to other structures (needed when conducting a vapor intrusion study).

Much of this document is based on research that includes references (intended for further reading) compiled by the State Coalition for Remediation of Drycleaners in two documents published by that organization. These documents are:
History of Dry Cleaning Processes

Over the past 130 years a number of different chemicals were utilized as dry cleaning solvents. These included: camphor oil, turpentine spirits, benzene, kerosene, white gasoline, petroleum solvents (mainly petroleum naphtha), chloroform, carbon tetrachloride, perchloroethylene, trichloroethylene, 1,1,2-trichlorotrifluoroethane, glycol ethers, 1,1,1-trichloroethane, decamethylcyclopentasiloxane, n-propyl bromide, and liquid carbon dioxide. If the dates of operation are available, a detailed list of contaminants of concern (COCs) can be developed. The next section provides a brief history of dry cleaning operations and date ranges for when certain solvents were used.

Early dry cleaning solvents were petroleum-based. In 1924 (due in part to fire risk) the petroleum-based solvents were replaced with the less flammable Stoddard solvent. This solvent was the primary chemical used from the late 1920s to the late 1950s.

In the 1930s trichloroethylene (TCE) was introduced as a non flammable replacement, but was never widely used as a primary dry cleaning solvent. TCE is still used as a pre-cleaning or spotting agent and is used in some water repellent agents.

Carbon tetrachloride was used for dry cleaning in the 1940s and 1950s. Because of its high toxicity and tendency to contribute to machinery corrosion, carbon tetrachloride is no longer used. It was phased out in the late 1950s and replaced with perchloroethylene (PCE).

1,1,2-trichlorotrifluoroethane (Freon 113) was used for a short period in the 1960s. This chemical was later found to be an ozone depleter and is no longer used.

1,1,1-trichloroethane (TCA) was introduced in the 1980s but was never widely used. One of its main uses was for leather cleaning. It has also been used as a spotting agent and in waterproofing agents and stain repellents, such as:

- Glycol ethers
- Decamethylcyclopentasiloxane (GreenEarth™)
- n-Propyl Bromide
- PureDry™ and
- Liquid Carbon Dioxide.
In the early 1990s new petroleum-based solvents were developed. These include:

- Dry Cleaning Fluid-2000 or DF-2000
- EcoSolv®,
- Hydroclene, and
- Shell Sol 140 HT.

Perchloroethylene (PCE) is currently the dry cleaning solvent used in most dry cleaning operations. USEPA has scheduled PCE to be phased out of use by 2030.

**Pre-Cleaning / Spotting Agents**

Numerous chemicals are used for pre-cleaning and spot cleaning. Prior to placement in the dry cleaning machine, heavily stained garments are pre-cleaned. Most pre-cleaning solvents are also used in the primary dry cleaning cycle. There are three main categories of pre-cleaners:

- Wet-side Spotting Agents,
- Dry-side Spotting Agents, and
- Bleaches

**Garment Treatment Chemicals**

There are a variety of chemicals that are used to treat garments for various reasons. There are four main categories of garment treating chemicals:

- Waterproofing chemicals,
- Flame retardant chemicals,
- Fabric conditioning chemicals, and
- Stain repellent chemicals.

**POTENTIAL SOURCE AREAS**

When evaluating a dry cleaning facility for potential source areas, many investigators assume that releases occur near the dry cleaning equipment. While this is true, other potential sources need to be investigated as well. These potential source areas include:

- Solvent recovery systems (distillation units, filters, traps),
- Areas around service doors,
- The sanitary sewer / septic tank and leach field,
- ASTs and USTs,
- Storm sewers,
• Dumpsters and trash cans,
• Spotting Board area,
• Blind drains or sumps,
• Air handling equipment (especially areas where these devices discharge to the outside),
• Storage buildings, and
• Unique treatment units (for example discharging separator water to the outside through a mister unit).

HOW TO INVESTIGATE

Proper planning can make the difference between collecting the information needed to develop a meaningful CSM and having to remobilize to collect additional information. Planning should start with conducting a thorough Phase I Site Assessment. Although similar, this list is not intended to include all requirements for conducting Phase I Environmental Site Assessments per 40 CFR 312.21 (AAI) and ASTM Standard E1527-05.

A Phase I Site Assessment for a dry cleaner has the following elements:

• Historical documentation, including but not limited to:
  o City directory searches (this can include crisscross, phone books, and city directories),
  o Review of historical aerial photographs (these photos could be from several different sources),
  o Review of topographical maps,
  o Historical fire insurance maps (such as the Sanborn® and Baist maps),
  o Full title search back to when the property was first developed,
  o Interviews with current/past managers of the facility to identify solvent and waste handling practices.

• Review of other nearby remediation projects that are active or are complete. This information could be useful if a contributing off-site source is present.

• Review any facility as-built drawings and/or emergency plans. These will provide information about locations of processes and waste handling areas.

• Obtain utility records. Check with the city, town, or municipality for records and maps of the underground utilities (man-made preferential pathways) that may be affected by contamination from the site. Identify any current or historical septic systems.
Once the historical information is compiled, assess the on-site and near site features. A site reconnaissance should include:

- Identification of sensitive receptors that may be affected by a release from the site. Sensitive receptors can include:
  - Residences,
  - Day care centers,
  - Hospitals,
  - Nursing homes,
  - Schools,
  - Water supply wells, and
  - Natural features (like rivers, lakes, karst, and habitat of endangered species).

- Review any operation records stored on-site. These records could give clues where to conduct sampling.

- Canvas the businesses around the area to determine if other sources are present that may account for contamination found in unlikely locations.

- Review locations of the dry cleaning equipment as well as other areas where solvents may have been used. This should include:
  - The dry cleaning machine,
  - The distillation unit,
  - Solvent storage tanks,
  - Waste storage areas,
  - Spotting boards,
  - Vacuum units,
  - ASTs,
  - USTs,
  - Floor drains,
  - Sump pits,
  - Mop buckets, and
  - Dumpsters and trash cans.

- Evaluate historical waste management practices. This should include a list of wastes generated by the dry cleaning process.

- Determine how solvents were delivered to the facility and how spent solvents were managed.

- Determine how the dry cleaning machine was filled. The methods used to load and un-load a dry cleaning machine account for most of the contamination detected at a dry cleaning facility.
• Review waste water management. This should include a detailed description on the use of drain lines and floor maintenance (floor cleaning).

• Determine the locations of air handling system vents to the outside.

• Follow all piping to the terminus and account for all discharges from them.

• Inspect the condition of flooring throughout the facility.

It may not be possible to determine much of this information if the dry cleaner is no longer operating. At this point historical records and employee interviews (if possible) are vital.

After the Phase I Investigation and the Site visit are completed, develop a CSM to best determine an investigation and drilling plan. This model will be used to guide the Phase II Site Assessment. Elements of the CSM include:

• Geological setting (this should include information on unsaturated soils, saturated soils, ground water and bedrock);

• Surface and likely ground water flow, including local conditions that alter the flow (i.e. high capacity water wells);

• Identification of preferential pathways for contaminant migration (this should include natural and man-made features);

• Identification of potential receptors (the more information provided the better the assessment will be); and

• A list of the contaminants of concern and all of their physical and chemical properties.

CONDUCTING THE SITE ASSESSMENT (Phase II Investigation)

In general, chlorinated solvent contamination plumes are larger (deeper and of greater areal extent) than contaminant plumes associated with petroleum contamination. Dry cleaning solvents are denser than water so they will sink vertically and spread horizontally until a confining unit is encountered. They are also less viscous than water so they will spread farther. The plumes can be thinner than petroleum plumes and have a center of mass well below the water table. A majority of the time, contamination associated with dry cleaning solvents will extend off-site. This off-site extent needs to be taken into account when developing an exposure assessment and remedial strategy.
To be successful in assessing chlorinated solvent contamination, the site stratigraphy needs to be defined. Information gathered from site stratigraphy can provide information on preferential flow paths and the nature and extent of confining layers.

**CONTAMINATED MEDIA**

**Dense Non-aqueous Phase Liquids (DNAPLs)**

Chlorinated solvents (except for vinyl chloride) have a density greater than water; therefore chlorinated solvents can form dense non-aqueous phase liquids (DNAPLs) when product is released to water. When developing a sampling strategy for investigation of a dry cleaning facility the existence of DNAPLs is a possibility. Ground water sampling in areas where DNAPL is suspected needs to include shallow and deep zones in the potentially contaminated aquifer.

**Soils**

Soil sampling provides information about three aspects of the CSM:

- Provides information about the contaminant mass in soil (needed to properly design remedial measures);
- Provides information about the presence of free product in ground water;
- Provides information needed to assess vapor intrusion and;
- Provides information needed to assess the presence of DNAPL.

The investigator should be aware that soil source zones can be small and may appear disconnected from surface sources because chlorinated volatile organic compounds (CVOCs) are less viscous than water and tend to follow soil fractures.

To determine if areas require further testing (soil, ground water, and vapors), there are several locations within a dry cleaning facility where soil sampling should always occur:

- Beneath the dry cleaning machine,
- Outside any service doors,
- The locations of any USTs or ASTs,
- Sanitary sewers (include all inlets and laterals),
- Septic tanks and associated leach fields,
- Storm sewers,
- Floor drains,
- Dumpsters and trash cans,
- Areas around the spotting board(s),
- Areas where mop buckets are stored, and
- Other source areas.
**Ground Water**

Since chlorinated solvents are denser than water, sampling at the water table may miss not only the core of the contaminant plume, but also potential DNAPLs. If free product is suspected, this material could sink to the bottom of the aquifer or may be deflected by less conductive materials. **Contamination from a dry cleaner should never be investigated in the same manner as a release from a petroleum source.**

A good CSM is needed to determine not only where to place monitoring wells but depth(s) where screens are needed to adequately monitor contamination. Unlike petroleum sites, monitoring well screens for chlorinated solvents should be designed to straddle contaminated intervals rather than fluctuations of the water table. Standard 10 foot screens are often inappropriate for these plumes.

**Vapors**

Vapor intrusion involving chlorinated compounds is slightly different than vapor intrusion involving petroleum based contamination. There are no attenuation factors for chlorinated compounds, therefore collecting soil gas samples to assess risk is not necessary. It is best to collect paired sub-slab and indoor air samples. Detailed instructions concerning the collection of chlorinated vapor samples can be found in section 5.4.2 of the new 2012 RCG.

**CLOSURE STRATEGIES**

This technical guidance document provides an overview of the common remediation methods used at dry cleaners in Indiana. Some of the remedial technologies listed may be applicable. This list is by no means exhaustive. IDEM will evaluate other methods of remediation on a case by case basis.

**Excavation**

Excavation can be effective if one of the following conditions is present:

- The release is recent,
- Bedrock is shallow,
- A shallow confining layer is present, and
- There is a thick layer of soil above karstic or fractured bedrock.

If the volume of soil contaminated with chlorinated solvents is large or site conditions will not allow for excavation, in-situ soil remediation methods should be used.
Pump and Treat

Pump and treat systems have been used for years to remediate ground water contamination. Recent data show that these systems may not be the most effective way to remediate chlorinated sites, especially if there is substantial soil contamination or groundwater contamination is at depth. However, pump and treat can be useful when used with additional remedial methods. For example, pump and treat can be used to draw down a water table so that a soil vapor extraction (SVE) system can more effectively treat soil contamination.

Monitored Natural Attenuation (MNA)

USEPA (1999) lays out a general framework for the appropriate implementation of MNA. Pope et al. (2004) summarize that comprehensive framework in the following steps:

- Demonstrate that natural attenuation is occurring according to expectations;
- Monitor environmental conditions for changes (e.g., hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of any of these natural attenuation processes;
- Identify any potentially toxic and/or mobile transformation products;
- Verify that the plume(s) is not expanding down-gradient, laterally or vertically;
- Monitor for new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy;
- Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors; and
- Verify attainment of remediation objectives.

USEPA has observed, "at many sites, the evaluation of trends in concentrations stops with an evaluation of whether MNA is occurring (step 1), and the evaluation does not proceed to the next step." When evaluating MNA it is important to make sure the COCs are fully degrading. It is possible that the process could stall (many factors can lead to stalling the MNA process) and some of the degradation products are more toxic than the original contaminants.

Reductive Dechlorination (Bioremediation)

When using methods involving reductive dechlorination, in addition to sampling for PCE, TCE, dichloroethene (DCE), and vinyl chloride (VC) in soil, ground water and vapor, vapor testing needs to include methane. The biodegradation of
CVOCs can be associated with increases in methane gas. In some cases methane can reach explosive levels. Monitoring is needed to evaluate methane build-up and mitigation.

In most cases reductive dechlorination involves injection of key nutrients needed by indigenous micro-organisms to effectively degrade chlorinated solvents. Unlike bioremediation of petroleum related contamination, reductive dechlorination takes place in reducing conditions (i.e. oxygen poor conditions). For a more detailed description of bio-remediation of chlorinated solvents see the Science Services “Technical Memorandum on Bioremediation” (dated March 29, 2010).

**Emulsified Zero Valent Iron (ZVI)**

Since the limiting factor in reductive dechlorination is often due to elevated oxygen levels (i.e. reducing conditions are not present), it is necessary to artificially reduce oxygen levels. A common method to achieve reduced oxygen levels is through the introduction of ZVI. Once oxygen levels are reduced, injection of key nutrients needed by indigenous micro-organisms is applied to the subsurface. For a more detailed description of bio-remediation of chlorinated solvents see the Science Services Technical Memorandum on Bioremediation (dated March 29, 2010).

**Chemical Oxidation**

Chemical oxidation of contaminants involves injecting or emplacing a highly reactive substance to break apart the bonds in a contaminant compound, usually by inserting oxygen to physically destroy the molecule. This is notably different from bioremediation, in which microbes gradually strip off elements for use as food, but leave the rest of the molecule intact.

There are numerous types of in-situ chemical oxidation (ISCO) systems. Geological Services has evaluated various remediation applications using hydrogen peroxide (Fenton’s Reagent), magnesium peroxide, magnesium hydroxide, ozone, calcium peroxide, and sodium persulfate; with or without special catalysts, pH adjustment compounds, and iron supplements. All of these are intended to chemically break down contamination. Some of these have oxygen as a theoretical end product, which may stimulate aerobic microbes (those not killed by the peroxides and toxic secondary chemicals).

These chemical oxidants should not be confused with agents such as Oxygen Release Compound (ORC)™ sold by Regenesis, which is a magnesium peroxide with phosphate added to form time-release crystals. ORC is used to provide oxygen to stimulate microbial action, rather than for chemical oxidation (see Geological Services technical memo on ORC™ applications). For more information on the use of in-situ chemical oxidation, see the Science Services
Thermal Desorption

Thermal desorption is a process that uses electrical heating elements to raise the temperature of subsurface soils and ground water to drive VOCs to a vapor state that can then be captured by a conventional SVE system. These systems have shown that sites can be remediated in a few months, however if large areas are to be treated the cost (requires installation of electrodes and SVE points as well as large quantities of electricity) can be prohibitive.

Electrical Resistive Heating

Electrical resistive heating is similar to thermal desorption, except instead of using heating elements, an electric current is passed through the subsurface materials and it is the resistance of the materials that causes the temperature increase.

Plume Trend Analysis

If the conceptual site model shows that there are no completed exposure pathways, evaluation of the contaminant plume using a plume trend analysis may be an applicable path to site closure. Section 4.7.6 of the RCG provides additional details needed to use this statistically-based demonstration of plume behavior.

Summary and Conclusions

The information in this document was assembled from sites in Indiana, the references provided, and IDEM staff experiences. This document provides a basic outline for investigating dry cleaning sites. More in-depth evaluations should be discussed on a site by site basis. An understanding of the past and present operations and the nature of the materials associated with those operations is needed to develop an accurate CSM. In addition, working knowledge of how ground water interacts with those materials is also needed to develop an accurate CSM.

Further Information

If you have any additional information regarding this subject or any questions about this evaluation, please contact the Technical Evaluation Group at (317) 232-8866 or by email at lsteadha@idem.in.gov. This technical guidance document will be updated periodically or if new information is acquired.
ADDITIONAL READING AND REFERENCES

Dry Cleaning History


Dry Cleaning operation and practices


Hayday, William. 2007. E-mail from William Hayday, Rynex Holdings, Ltd. To William J. Linn, Florida Department of Environmental Protection.


**Vapor Intrusion**


**Chemistry**

Chemical Week, 1953. Tri, Per and Carbon Tet. 72, 56.


Risk Assessment
