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**EXPEDITED APPROACH TO A CARBON TETRACHLORIDE SPILL
INTERIM REMEDIAL ACTION**

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ABSTRACT

Monitored natural attenuation was selected as an interim measure for a carbon tetrachloride spill site where source removal or in situ treatment cannot currently be implemented due to the surrounding infrastructure. Rather than delay action until the site is more accessible to an interim action, this more expedited approach would support a final action.

Individual Hazardous Substance Site (IHSS) 118.1 is a former underground storage tank at Rocky Flats Environmental Technology Site (RFETS) that stored carbon tetrachloride for process use. Inadvertent releases associated with filling and failure of the tank system resulted in an accumulation of carbon tetrachloride in a bedrock depression around a group of former process waste tanks. Access to the source of contamination is obstructed by numerous utilities, the process waste tanks, and other components of the site infrastructure that limit the ability to conduct an effective remedial action. A pre-remedial field investigation was conducted in September 1997 to identify and delineate the extent of the dense non-aqueous phase liquid (DNAPL) in the subsurface. Data collected from the investigation revealed that natural processes might be limiting the migration of contaminants from the source area.

I. INTRODUCTION

RFETS is a former Department of Energy nuclear weapons manufacturing facility approximately sixteen miles northwest of Denver, Colorado. IHSS 118.1 is located within the Industrial Area of RFETS, and is ranked number eight (of over 200 sites) in the Environmental

Restoration (ER) Ranking, (DOE, 1996a). The ground-water plume associated with IHSS 118.1 is ranked eighteenth. Rocky Flats was formerly the largest volume user of carbon tetrachloride in the United States. The 1974 Harmful Materials Inventory listed 12,500 kilograms of carbon tetrachloride as being stored at Rocky Flats (CDH, 1992). IHSS 118.1 is the result of releases that occurred in the 1960s, 1970s, and early 1980s associated with the operation of one 5,000-gallon underground carbon tetrachloride storage tank (see Figure 1). Over this time period, an unknown quantity of carbon tetrachloride was released into the environment. Remedial investigation results indicate that carbon tetrachloride has accumulated below the water table in a bedrock depression encompassing a group of subsurface process waste tanks (Tanks T-9 and T-10) located adjacent to the former carbon tetrachloride tank. The carbon tetrachloride partially displaced the groundwater to create a zone of dense non-aqueous phase liquid (DNAPL) at the base of the Tanks T-9 and T-10. Because the DNAPL zone is situated in a heterogeneous fill material with mixed permeabilities underlain by a low permeability bedrock, movement of DNAPL is constrained both on the inside and outside of this zone.

Based on remedial investigation results, the decision was made to evaluate an Interim Measure/Interim Remedial Action. The objectives of the interim action were to protect surface water and to support a final action for the site. Because the groundwater around IHSS 118.1 daylights to the north, protection of surface water extends to groundwater in the area.

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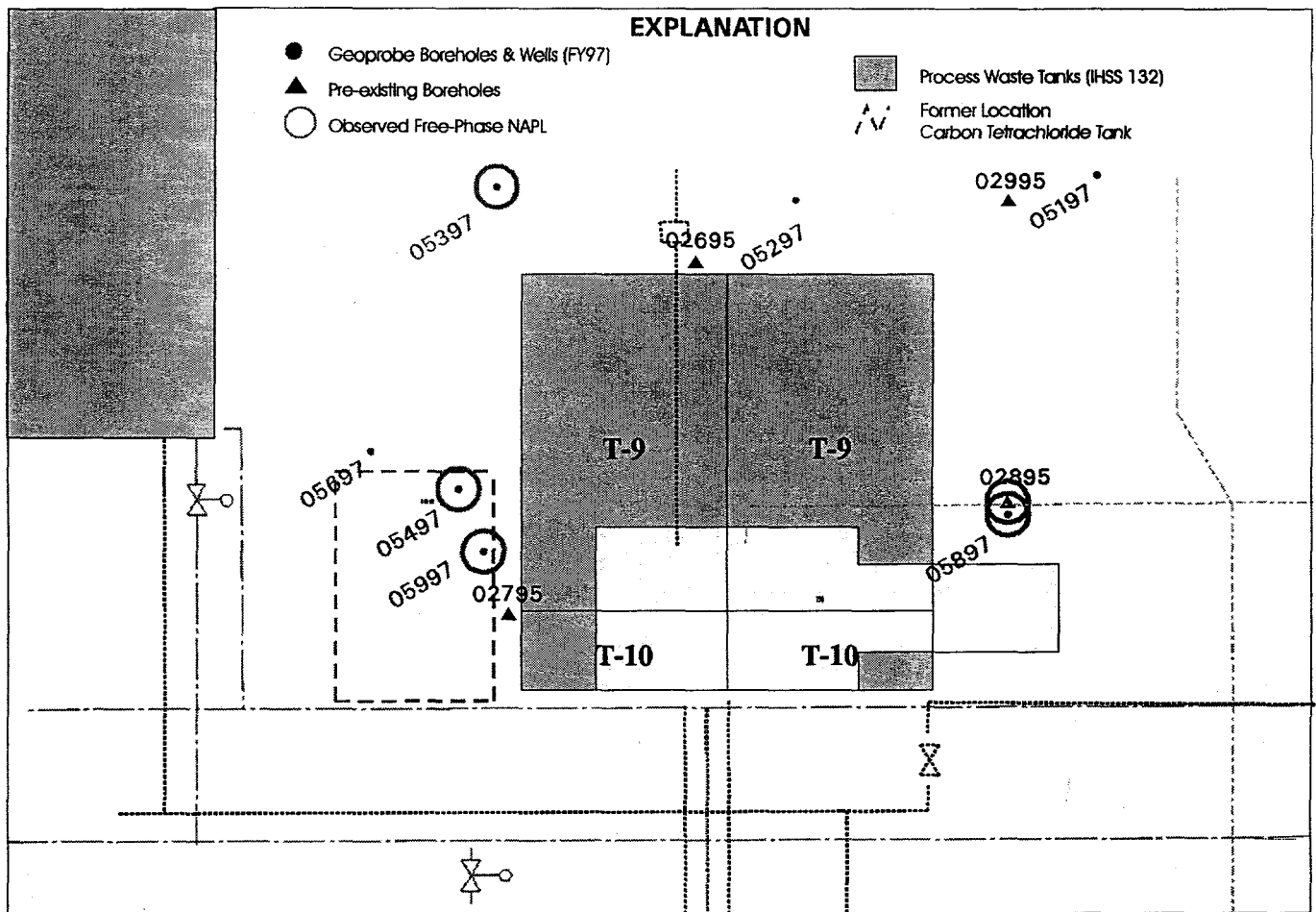


Figure 1 Site Location Map showing location of the former carbon tetrachloride storage tank

II. BACKGROUND

The location of IHSS 118.1, Multiple Solvent Spills West of Building 730, is shown on Figure 1. There have been multiple releases from the tank and associated piping throughout its period of operation from approximately 1963 to 1981. The tank was subsequently removed in 1981 (DOE, 1992).

There are numerous utilities and structures underground and overhead in the IHSS 118.1 area including vitreous clay sanitary sewer lines, electrical lines, tunnels between buildings, and process waste tanks. Four feet east of the former carbon tetrachloride storage tank is a group of four process waste tanks referred to as tank groups T-9 and T-10. Tank T-9 consists of two-22,500 gallon process waste underground storage tanks. T-10 consists of two-4,500 gallon concrete underground tanks. No releases from either set of tanks have been documented (DOE, 1992).

The upper strata in the vicinity of IHSS 118.1 is comprised of 8 to 14 feet of surficial materials immediately underlain by weathered bedrock of the Arapahoe Formation. The surficial materials consist of artificial fill composed of reworked Rocky Flats Alluvium with some undisturbed Rocky Flats Alluvium. The alluvium is primarily composed of clay with interspersed unconsolidated gravels and sands (RMRS, 1997a). The weathered bedrock lithology in most locations is claystone or siltstone; however, Arapahoe Formation sandstones (i.e., Arapahoe No. 1 Sandstone) have been observed east of the IHSS near the Solar Evaporation Ponds (EG&G, 1995).

Groundwater flow in the IHSS 118.1 area is generally to the north and northwest towards the North Walnut Creek drainage (EG&G, 1995). Groundwater is present 6 to 9 feet below the ground surface. Building 771 to the north, Building 774 to the northeast, and Building 776 to the south have below grade construction 20 to 30 feet below ground surface (RMRS, 1997b). These buildings

Table 1 Groundwater/DNAPL VOC Results For IHSS 118.1 Investigation ($\mu\text{g/L}$) and Corresponding RFCA Action Levels.

	Methylene Chloride	Chloroform	Carbon Tetrachloride
Groundwater Action Levels ($\mu\text{g/L}$)	500	11000	500
Groundwater Samples	1,900 J B - 32,000 JB	3,500 - <5,000,000	6,600 E - 1,100,000 E
DNAPL Samples	2,500,000 - 3,600,000	2,700,000 - 3,800,000 J	130,000,000 - 250,000,000 E

E - estimated value, concentration outside of calibration range

J - estimated value, concentration is below the detection limit

B - analyte also detected in the blank analysis.

and their foundation drains are likely to have a strong influence over local groundwater flow. Due to its proximity to IHSS 118.1, the Building 771 foundation drain may exert the strongest influence on flow.

Several remedial investigations have been conducted in the vicinity of the contaminant source area. DNAPL was originally detected during the investigation of T-9/T-10 process waste tanks in 1995. A non-aqueous liquid was observed in the fluid sample collected from a borehole on the east side of the process waste tanks that was tentatively identified as carbon tetrachloride. The highest concentration of carbon tetrachloride in groundwater samples was only 2,000 micrograms per liter ($\mu\text{g/L}$); however, three subsurface soil samples collected from near bedrock had carbon tetrachloride concentrations as high as eight percent.

Sampling and analysis was conducted again in September of 1997 to determine the nature and extent of the contamination detected during the tank investigation. Nine boreholes were situated around the perimeter of the T-9/T-10 process waste tanks. Carbon tetrachloride concentrations in the soil ranged up to an estimated concentration of 390 milligrams/kilogram (mg/kg). Although the primary contaminant detected in soil in the investigation area was carbon tetrachloride, lesser amounts of chloroform and methylene chloride (possible reductive dehalogenation products of carbon tetrachloride) were also detected. Other volatiles detected in soil were naphthalene, tetrachloroethene, hexachlorobutadiene, acetone, carbon disulfide, and hexachloroethane.

Six boreholes were converted to monitoring wells and liquid samples were taken including DNAPL samples from four locations. Again carbon tetrachloride was the primary contaminant with lesser amounts of methylene chloride and chloroform. Table 1 gives the ranges of concentrations for the liquid samples for these three contaminants.

A light non-aqueous phase liquid (LNAPL) was detected in two of the samples. The samples were then analyzed for total petroleum hydrocarbons and it was determined that the LNAPL is a semi-volatile hydrocarbon that is likely a fuel oil or fuel-like mixture of hydrocarbons such as Number 2 (diesel) fuel oil. The original source of the LNAPL is unknown. Figure 2 is a photograph of a single sample showing the three separate liquid phases.

III. EVIDENCE OF NATURAL ATTENUATION

Natural attenuation includes physical, chemical and biological processes that limits or controls contaminants in the environment. At IHSS 118.1, dilution, dispersion, biodegradation, sorption, volatilization, and chemical transformation could all possibly play key roles in reducing downgradient contaminant concentrations.

Physical processes could be as effective as degradation in controlling contaminants. The geometry of the bedrock depression containing the DNAPL likely limits contaminant migration to that which can diffuse out of the depression into the groundwater flow in the Rocky Flats Alluvium. As illustrated by the cross-section (Figure 3), the impermeable claystone bedrock limits the vertical migration of carbon tetrachloride and the depression created in the bedrock surface limits the areal extent of the DNAPL zone. Because both the DNAPL samples and high concentrations in soil are found only near the bottom of the excavation, the DNAPL zone is thought to occur in an interval, approximately one-foot thick above the bedrock surface at the bottom of the depression. Based on investigation results and engineering drawings, it is likely that this interval lies beneath the process water tanks and is perched on undisturbed bedrock claystone (RMRS, 1997a), the lowest point is expected to be directly beneath the sump at the center of the process waste tanks.

It is likely that DNAPL is in pockets within the DNAPL zone due to the mixed permeability of the fill, as

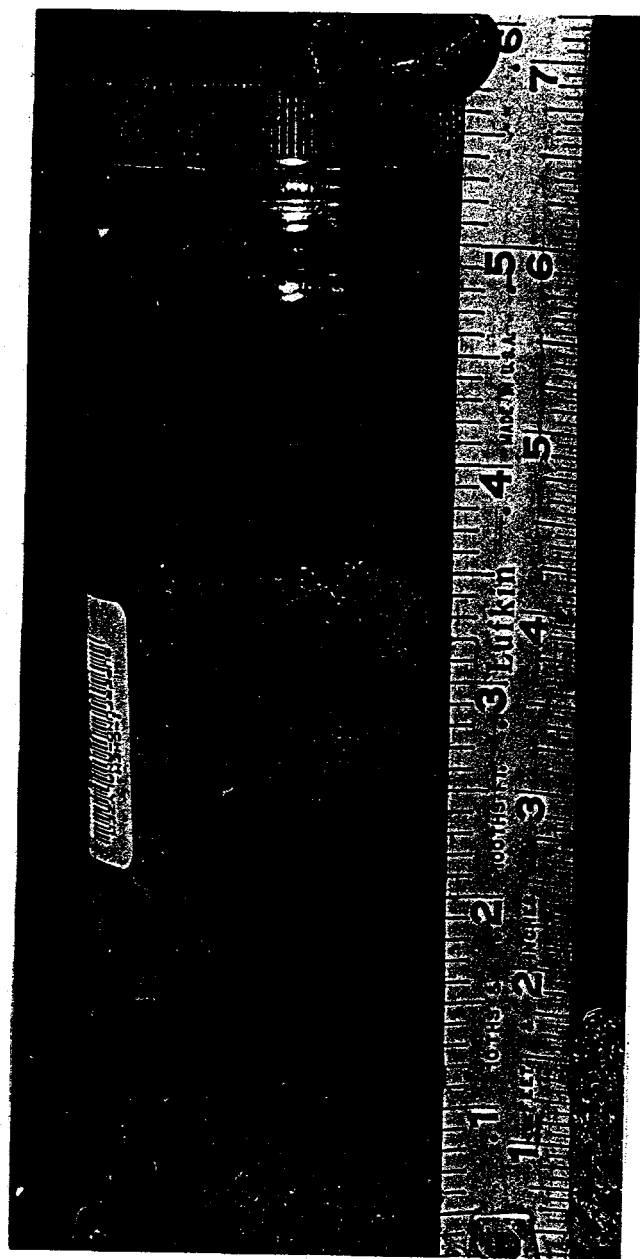


Figure 2 Sample from IHSS 118.1 showing three liquid phases

opposed to a continuous shallow layer. The zone where the DNAPL resides is comprised of two liquid phases: the groundwater that has not been displaced and the DNAPL that is trapped in pores and fractures. Because water is the wetting fluid, it is not completely displaced by the DNAPL in this zone. The migration of DNAPL through these pores is controlled by capillary pressure which holds the DNAPL in porous media. This capillary pressure is particularly significant in fine grained media.

The vertical migration of DNAPL into bedrock at RFETS was evaluated by an earlier study, which

concluded that there is no apparent threat to surface water or to deeper aquifers (RMRS, 1996). All occurrences of the DNAPL layer are at depths too great to migrate along utility corridors or along the original bedrock surface. Therefore, the only risk to surface water is through migration of the dissolved phase in groundwater (RMRS, 1997a).

Dilution probably also plays a role as the dissolved contaminants are mixed with cleaner groundwater from other parts of the Industrial Area. Although the DNAPL appears to be confined to the area of the T-9 and T-10 excavation, the dissolved plume is not confined by these physical constraints. As previously stated groundwater appears to be flowing into the Building 771 foundation drain. Although not all of the drains for the 771/774 complex were sampled, samples collected in 1993 from a Building 771 foundation drain to the north had 43 micrograms per liter ($\mu\text{g/L}$). Carbon tetrachloride was not detected in a sample from a foundation drain for Building 774 from about the same time. Since the Building 771 foundation drain is only about 100 feet downgradient of the DNAPL, the low concentrations in the drain suggest that contaminant migration is being severely limited through attenuation process such as dilution or degradation. Due to the complexity of flow through the bedrock depression and unknowns concerning the nature of the DNAPL zone, the reduction in concentration across the IHSS 118.1 source area has a high degree of uncertainty. Nevertheless, there still would be a significant reduction in carbon tetrachloride that could be attributed to attenuation. Additionally, carbon tetrachloride was not detected at the closest surface water location to the out fall for this water.

There are a number of potential chemical/biological mechanisms that could degrade or limit the mobility of carbon tetrachloride at IHSS 118.1. Reductive dechlorination is the most promising of these because it can effectively destroy carbon tetrachloride. Data gathered from past investigations indicate that, not only are there favorable conditions for reductive dechlorination, but also that it is likely that it is occurring.

Evidence of reductive dechlorination includes the following observations:

- ◆ Possible carbon tetrachloride degradation products are present in the soil, groundwater, and the DNAPL. These compounds include chloroform, methylene chloride, and carbon disulfide. It is believed that all of the spills of DNAPL were probably of unused carbon tetrachloride that was an industrial grade and likely contained small amounts of chloroform and

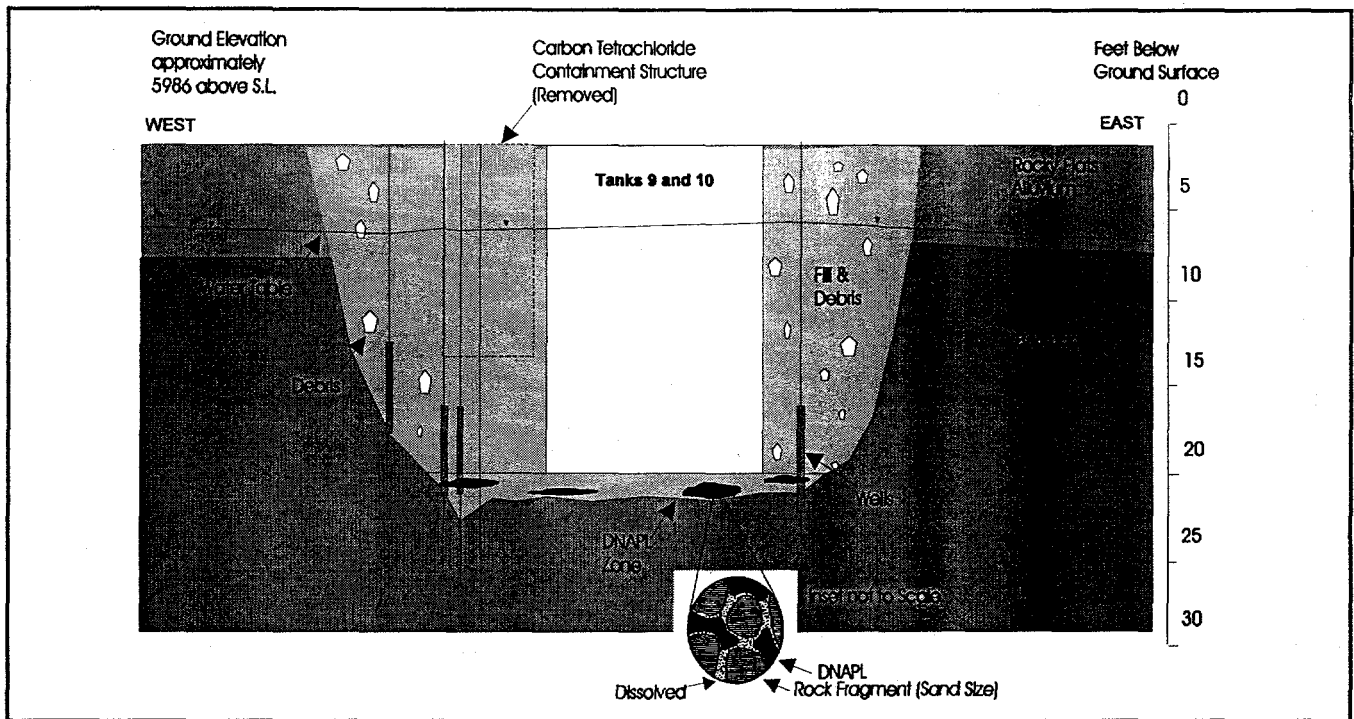


Figure 3 Generalized Hydrogeologic Cross Section of IHSS 118.1. Inset adapted from Pankow and Cherry, 1996.

methylene chloride. However, because the concentrations are high, reductive dehalogenation could also explain the pervasiveness of these compounds in both the aqueous and non-aqueous phases.

- ◆ In addition to single carbon reductive dehalogenation products, significant amounts of hexachloroethane, tetrachloroethene and hexachlorobutadiene were detected in subsurface soils. These multiple carbon compounds could have been produced by dehalogenation occurring in an environment where there isn't sufficient hydrogen to form chloroform and methylene chloride. Instead the chlorine could have been stripped off and carbon-carbon bonds were formed instead of carbon-hydrogen bonds.
- ◆ Non-chlorinated hydrocarbons (No. 2 Diesel) are present that could act as a substrate for biological activity in the water phase. The light non-aqueous phase liquid that was detected provides ideal conditions for the most aggressive biodegradation process (reductive dehalogenation).
- ◆ Oxidized non-chlorinated hydrocarbons, such as carboxylic acids and ketones, were detected that could be the result of aerobic biodegradation.

Figure 4 is a conceptual model showing the interaction between natural attenuation processes at IHSS 118.1.

IV. REMEDIAL STRATEGY

Based on investigation results, an interim remedial action was planned. A two-step process was used to select the best alternative: (1) an initial screening to select the best alternatives, and (2) a comparative analysis of the alternatives. Both the screening and the comparative analysis are based on effectiveness, implementability, and cost.

As part of the alternative screening, thirteen technologies or groups of technologies were evaluated. Three technologies were selected for a final comparison. The other ten were eliminated primarily because of the:

- ◆ Inaccessibility of the DNAPL,
- ◆ Potential damage to the RFETS infrastructure,
- ◆ Technical impracticalities,
- ◆ Undeveloped or unproved effectiveness, and
- ◆ Partial removal of the DNAPL would not be effective in mitigating groundwater contamination because of residual DNAPLs and the effect of partitioning.

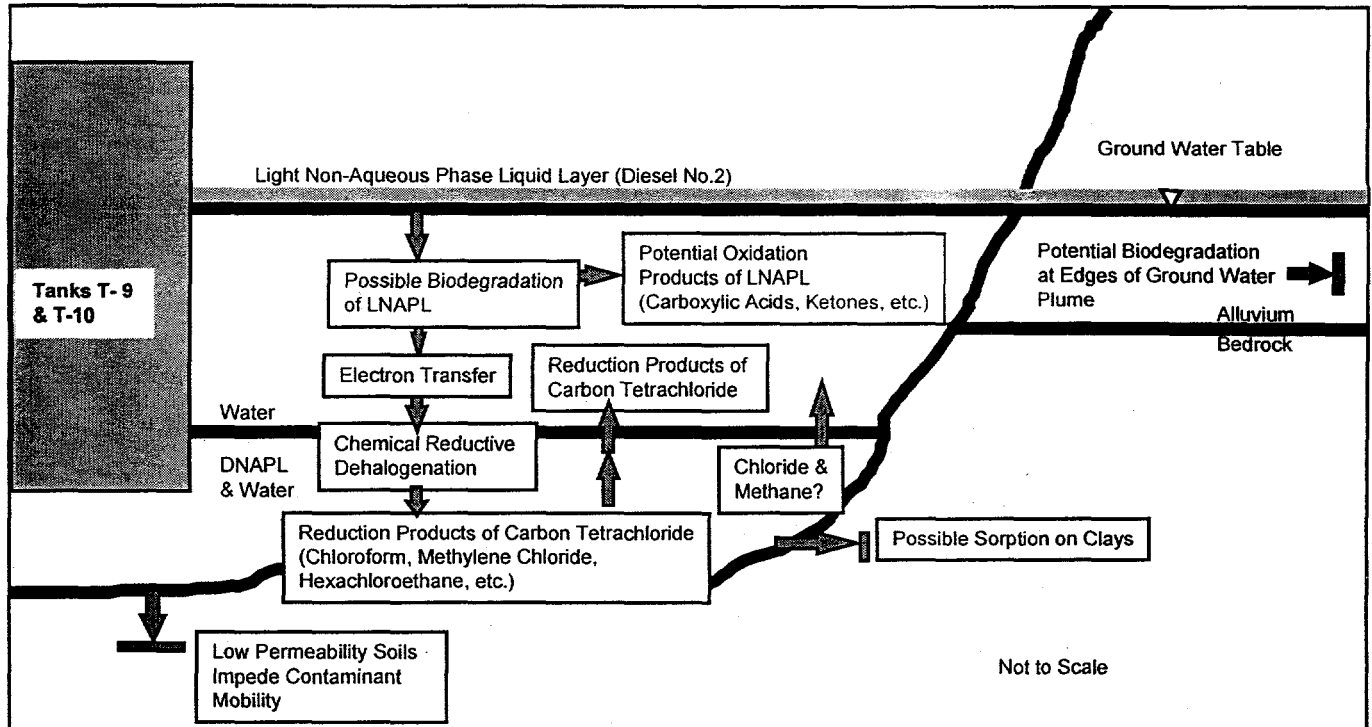


Figure 4 Conceptual Model of Natural Attenuation Processes at IHSS 118.1

The three technologies selected for the comparative analysis of alternatives are:

- ◆ **No Interim Action** - Delay any remedial activity for IHSS 118.1 until a final remedy is selected.
- ◆ **Pump Carbon Tetrachloride** - Install a recovery well and pump system to collect the DNAPL.
- ◆ **Monitored Natural Attenuation** - Demonstrate that existing processes are limiting the migration of contamination

Monitored Natural Attenuation was selected as the best interim action for IHSS 118.1 at this time. Unique site conditions at IHSS 118.1 are very favorable to natural processes that control and limit the migration of carbon tetrachloride. The historical absence of contaminants in nearby surface waters suggests that natural attenuation is effectively limiting the migration of contaminants and thereby protecting surface water. It should be emphasized that Monitored Natural Attenuation is not a final response; the use of monitored natural attenuation does not preclude the utilization of a more effective technology at a later date when the IHSS is more accessible.

The basis for this selection is twofold: first, the most effective technologies, e.g. source excavation, are not feasible at this time due to accessibility and secondly, the objective of the action is to protect surface water and support a final response. None of the alternatives screened and evaluated could effectively remove DNAPL in a manner that is protective of groundwater, and therefore surface water, under current site conditions.

Monitored natural attenuation was selected over no interim action because the contaminant plume will be monitored and evaluated in support of future action. Partial source removal through pumping or other means is ineffective because residual DNAPL would not be completely recovered and would continue to contaminate groundwater. Furthermore, even with complete removal or containment of the carbon tetrachloride at IHSS 118.1, other sources in the Industrial Area would continue to supply carbon tetrachloride to the groundwater plume.

V. PROJECT APPROACH

In order to ensure protection of surface water, monitoring natural attenuation will determine if existing processes mitigates potential risks to surface water posed by the DNAPL. Furthermore, information garnered from studying the natural attenuation process and hydrogeology

will be useful in determining a final response at IHSS 118.1 and possibly in other areas where chlorinated solvents exist at RFETS by providing information on how residual contaminants in the soils and water can be mitigated through natural processes. All activities will be integrated with existing RFETS monitoring activities. Monitoring is planned to continue until enough data is collected to perform trend analysis. The elements of the monitoring program will be as follows:

1. Install four additional downgradient monitoring wells which will be used to sample for carbon tetrachloride and associated indicators of natural attenuation. The wells will be in a east-west line north of the site with an additional well to the east.
2. Install two upgradient wells to determine background concentrations.
3. Analyze groundwater in wells near IHSS 118.1 for reductive dehalogenation products such as chloroform, methylene chloride, and chloromethane in addition to analyzing for chemical conditions favorable for reductive dehalogenation. The analysis will determine whether there are promising trends in the measured parameters.
4. Analyze DNAPL to determine relative ratios of carbon tetrachloride and reductive dehalogenation products and observe if these concentrations change with time.
5. Measure water and DNAPL levels. This would allow the opportunity to further evaluate the nature of the DNAPL in the soil.
6. Evaluate groundwater flow direction and the gradient.
7. Monitoring of IHSS 118.1 will be integrated into the current integrated monitoring program for the site. This will include sampling, analysis, data evaluation, and reporting.

The four downgradient wells will be used to determine if the plume migration is limited by natural attenuation and the degree to which reductive dehalogenation is occurring.

The wells that would be sampled include the six proposed wells plus possibly two of the previously installed wells installed near the T-9/T-10 tanks. Table 2 presents the analytes to be sampled and the basis for each analyte. Some of the analytical indicators in Table 2 such as total organic carbon, alkalinity, dissolved methane,....etc., will also be used to evaluate the

interaction between the diesel and the carbon tetrachloride. It is proposed that the first round of sampling would include all of the analytes. The first round results would be evaluated to determine which analytes were useful for assessing natural attenuation processes. An evaluation report would be prepared documenting this analysis. Sampling would be performed semiannually or annually. At the end of the evaluation period, the sampling results would be evaluated a final time to determine the effectiveness of natural attenuation.

VII. CONCLUSIONS

Use of monitored natural attenuation is a viable option for an expedited response under circumstances where other interim actions are not feasible or are not effective. At a minimum, monitored natural attenuation can be used to monitor and evaluate the migration of contaminants until another action can be implemented. Furthermore, if monitoring can demonstrate that contaminant migration is effectively controlled, it could eliminate or reduce a final action at the site. If a final action is necessary, there are number of other benefits of this approach that support a final action and closure of RFETS in general including:

- ◆ A determination whether natural attenuation is a viable alternative for a final action by itself or in combination with other actions,
- ◆ Additional analytical information that could be used as part of a basis of design for a final remedial action,
- ◆ Information acquired could potentially be used for other DNAPL spill sites at RFETS,
- ◆ Groundwater information that can be used in evaluating and determining a response as part of the sitewide groundwater program, and
- ◆ A baseline can be established for the IHSS that will aid in closure and post-closure monitoring.

VIII. REFERENCES

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Table 2: Analytical Samples for Monitored Natural Attenuation Program

Analyte	Analysis Location	Basis
Volatile Organic Compounds	Laboratory	Characterization of the types and concentration of organic contaminants. Analysis will be done on both water and DNAPL
Sulfates	Laboratory	Electron acceptor, reduced concentrations from background suggests favorable condition for reductive dehalogenation
Sulfides	Laboratory	Reduced form of sulfur - presence is consistent with favorable conditions for reductive dehalogenation
Nitrate	Laboratory	Electron acceptor, reduced concentrations could indicate anaerobic conditions
Iron	Laboratory	Electron acceptor, elevated concentrations could indicate anaerobic conditions
Manganese	Laboratory	Electron acceptor, low concentrations could indicate anaerobic conditions
Chloride	Laboratory	Levels above background are an indication of reductive dehalogenation
pH	Field	Characterization of basic water chemistry
Oxidation Potential	Field	Indicator of aqueous reduction/oxidation potential
Alkalinity	Laboratory	Elevated levels can be associated with oxidation of hydrocarbon to CO ₂ and H ₂ O
Methane	Laboratory	Presence of detectable methane is consistent with redox conditions that favor reductive dehalogenation
Total Organic Carbon	Laboratory	Absence or depressed levels are consistent with active degradation of nonchlorinated hydrocarbons and condition favorable for reductive dehalogenation
Dissolved Oxygen	Field	Higher concentrations would indicate that reduction is not occurring.
Dissolved Hydrogen	Laboratory	Source of hydrogen for reductive dehalogenation
Electrical Conductivity	Field	General water quality parameter
Temperature	Field	General water quality parameter

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