STTR/SBIR Phase II
Final Report

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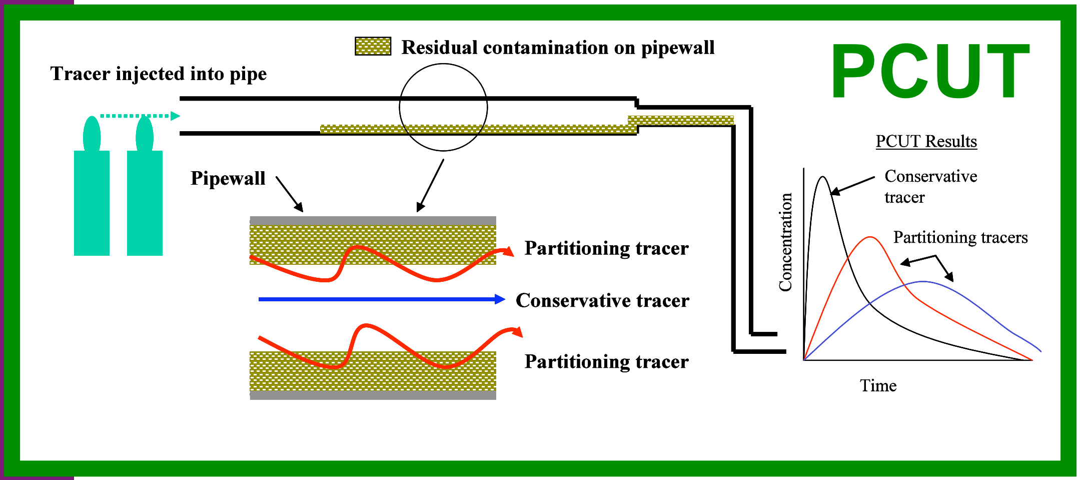
Using Tracer Technology to Characterize Contaminated Pipelines



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SMALL BUSINESS TECHNOLOGY TRANSFER
SMALL BUSINESS INNOVATION RESEARCH PROGRAM

U.S. Department of Energy

VISTA ENGINEERING
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1. *Introduction*

During the course of weapons and nuclear fuel production, fuel reprocessing, and waste disposal, the U.S. Department of Energy (DOE) and its predecessor agencies, have constructed over 20,000 facilities at more than 10 sites across the United States (DDFA, 2000). These facilities include buildings, structures, tanks, pipelines, ductwork, etc. Many of these facilities are contaminated with hazardous chemicals, such as chlorinated solvents, radioactive materials including plutonium and tritium, heavy metals like mercury and lead, or mixtures of the above and more. With the shift in DOE's mission from production to environmental management, several of the facilities are no longer being used, and many have exceeded their design life. The contaminants in these facilities can pose a serious threat to human health and the environment if left unmitigated. DOE Environmental Management (EM) plans to deactivate and decommission (D&D) most of these facilities in order to reduce the costs associated with monitoring and maintaining them and to decrease the potential for release of radioactive, hazardous, or mixed waste to the environment. It is estimated that the total cost to stabilize, deactivate, and decommission these facilities and structures is on the order of $21 billion dollars (DDFA, 2000).

A similar problem exists in industrial and chemical/petroleum facilities that are taken out of service for closure or for maintenance and cleaning. Chlorinated solvents such as trichlorethylene (TCE) and carbon tetrachloride (CCl_4), which were used as degreasers at many industrial complexes, both within the DOE and the Department of Defense (DOD) facilities, are examples. Petroleum fuels are another example of a common hazardous pipeline fluid. Many of the piping systems or large sections of these piping systems are inaccessible, and external inspection techniques that require access or safe access to the outside wall of the pipe cannot be used. Many of the pipes are buried underground, or are located beneath the floor of a building or a paved area. Because direct access to the external pipe wall is not frequently possible, whether for safety or physical reasons, methods that involve internal inspection of the pipe need to be used. In general, these methods generally require that any liquid in the pipe be removed, and some physical device needs to be inserted into the pipe.

To address the need for improved remote characterization of pipelines and ducts, a novel characterization technique that determines the amount of contaminant present in a given pipeline or ductwork was demonstrated in the Phase I effort. PCUT, *Pipeline Characterization Using Tracers*, can be used in support of deactivation and decommissioning (D&D) of piping and ducts that may have been contaminated with hazardous chemicals such as chlorinated solvents, petroleum products, radioactive materials, or heavy metals. The method will work on fluid flow systems in which the liquid contents have been removed. These contaminants may accumulate as a liquid or slurry in the low spots in the pipe, at appurtenances and geometric or flow constrictions in the pipe, or as a film, residue, or particulate build-up on the walls of the pipe. This method has immediate application for D&D activities at the U. S. Department of Energy's (DOE's) nuclear sites, such as the Hanford Site, and various industrial and petroleum facilities.

The PCUT technology injects a conservative tracer and one or more interactive (partitioning or reactive) tracers at one end of the pipe and transports these tracers at a known or constant flow velocity along the pipe using a gas that does not interact with the contaminant or any of the tracers. A gas chromatograph (GC) or other analytical instrument is used to measure the elution curves of tracer concentration at the other end of the pipe as a function of time. The conservative tracer, which is selected because it does not interact with the contamination, acts as a reference. The interactive tracer is selected, because it interacts with the contamination of interest as it flows along the pipe. Detection, quantification, and location are accomplished by comparison of the conservative and interactive elution curves of concentration.

The advantages of using this innovative approach for characterizing pipelines and ductwork are numerous. The first advantage of PCUT is that the same procedure will work on pipes (or ducts) of any size and nearly any length. Gas tracers are just as easily injected into a small diameter pipe (e.g., 0.5 in.) as they are into larger diameter pipe (e.g., 12 in.). Other remote pipe inspection equipment, which transport cameras or monitors by crawlers into a pipe, require pipe diameters of 4 in. or larger for entry and operation. Many of the pipelines within building systems are on the order of 0.5 to 2.0 inches making inspection using mechanical equipment very difficult.

The second advantage of PCUT is that the injected tracers can easily navigate pipe (or duct) bends and other pipe irregularities with ease compared to remotely operated inspection equipment. Tight bends and changes in diameter are not a problem for the tracer gases, yet represent major hurdles for other characterization techniques. Gas tracers also inspect the entire surface of the pipe, including any crevices or nooks that may be difficult to inspect using video approaches or various sensors, especially for square ductwork. This will result in a more complete and thorough inspection of the pipe (or duct).

The third advantage of PCUT is that there are no moving parts or equipment that has to enter the pipe. For pipes or ducts that may contain explosive vapors or contaminants that could ignite, the partitioning tracer technique offers a characterization approach that remains safe. In addition, since no mechanical equipment enters the pipe, this eliminates the possibility of equipment malfunction or getting “stuck” and “plugging” the pipe (or duct).

The fourth advantage is that equipment contamination and de-contamination is avoided. This has both safety and cost implications. Because no equipment enters the pipe, there is no equipment that must be decontaminated when it exits the pipes. This reduces the amount of investigation-derived wastes that require disposal.

The fifth advantage of PCUT is that it can be operated more cost effectively and more safely than other techniques without sacrificing performance. In fact, the performance of PCUT should be better than the more conventional methods.

In addition to being a very advantageous approach for the end users, PCUT has application in a variety of detection and measurement scenarios. The most common scenario is to characterize a pipeline or duct system to determine if the pipeline has any residual contamination that must be removed before the pipe or duct can be decommissioned or released. PCUT can also be used before and after a decontamination event to validate the amount of contamination that has been removed from the pipeline by a particular decontamination technology. Finally, PCUT can also be used to routinely monitor pipelines and ductwork for residual buildup of contaminants that could reduce efficiency of the pipeline.

The technique of Pipeline Characterization Using Tracers (PCUT) can also be used to determine if and when the decontamination efforts have reached acceptable levels. The Phase II work addressed in this report expands on the Phase I work by using partition tracers, reactive tracers, and conservative tracers to detect, quantify, and locate contamination within a pipeline or ductwork. Laboratory testing was conducted on simulated pipelines to demonstrate the technique and to evaluate the accuracy of the approach. These tests used pipelines with hydrocarbon contamination, chlorinated solvent contamination, heavy metal contamination and tritium as the target contamination to demonstrate the wide use of the PCUT approach.

2. *Potential DOE Applications and Needs*

Contaminated pipelines and ductwork within the DOE facilities are a significant component of the D&D plans. Pipelines were used to transport various types of contaminated fluid (liquids and gases) from one location to another. Ductwork was used to move air, such as fume hood effluent, for radiological work. It is estimated that there are several thousand miles of pipelines and ductwork awaiting D&D. Based on their usage and lifespan, it is likely they contain significant quantities of hazardous, radiological, and mixed wastes, and in multiple forms (liquids, sludges, salt cake, crystallized solids, etc.). Before D&D operations commence, characterization of the pipelines and duct systems is critical in order to make this operation more cost effective and to appropriately protect workers performing D&D activities. EM has identified several characterization and remediation needs across the DOE complex related to pipelines and ductwork (DDFA, 2000). These needs are listed in Table 1.

Internal inspection techniques are generally required for characterization when the pipe or ductwork are inaccessible, and these techniques require the insertion of some mechanical device into the pipe or duct to perform the characterization. For piping, a common approach for evaluating whether or not contamination still exists is to sample the liquid, such as water, that is being used to clean the pipe. This approach can miss low spots in the pipe containing contamination. In general, other characterization approaches are needed and are usually combined with this approach.

A common measurement approach for determining whether or not a pipe of duct is contaminated is to use a camera to inspect the inside of the pipe. For short sections of pipe, a small camera can be inserted into the pipe on a cable. Such methods can work over distances of several hundred feet. A camera, as well as other sensors, can be mounted on a robotic vehicle, which is inserted into the pipe (or duct) and allowed to move down the pipe. Many of these robotic systems are limited for use in piping of diameters of 3- to 4-in., or more. This approach is acceptable for larger diameter piping, but for small piping, the robotic vehicle may be too large to be used or not be able to move past bends and constrictions in the pipe. For those instances where access to the pipe is not possible or the pipe geometry limits inspection, the pipe is typically cut and analyzed for contamination in the laboratory at additional expense. A need exists for techniques or equipment that can characterize these small diameter or inaccessible pipes in an economical and quick manner.

Table 1. Summary of Decontamination and Decommissioning Focus Area Needs Relating to Pipeline and Duct Inspection

Need ID	Site	Need Title and Technology Description
NV09-0001-09	Nevada	Non-intrusive Surveys in Pipes and Vessels.
RL-DD031	Richland	Non-Intrusive Detection of Pipe Contents for 233-S. A non-intrusive method to detect liquids or explosive gases in closed piping system is needed.
RL-DD046	Richland	Clean-out of Isolated Piping Systems in Building 324. Methods are needed to perform the decontamination of individual pipes, piping systems, and tanks the are inaccessible because they are either in a high-radiation area, an enclosed pipe chase or vault, and/or they are encased in concrete.
Al-00-01-02-DD	Albuquerque	Characterization Technologies for Verifying Presence or Absence of Contamination in Structures Scheduled for D&D.
ID-7.2.25	Idaho	Decontamination of Metal Pipes. To develop new or significantly improved decontamination techniques for metal pipes in a variety of sizes in contaminated nuclear facilities.
RL-DD03	Richland	Terminal Clean-Out and TRU Waste Decontamination of PFP. Techniques are needed to remove and stabilize plutonium that are held-up within PFP process systems, including piping, ducting, glove boxes, etc.
RL-DD038	Richland	Characterization of Liquids in Equipment (e.g. tanks) and Pipes. Characterization technology is needed to detect and quantify the contaminants of concern in liquids.
RL-DD077	Richland	Duct Cleaning for Building 324 and 327. Systems are needed to remove radioactive, dispersible contamination from ventilation exhaust ducting systems (mostly comprised of stainless steel pipelines) in Building 324 and 327.

3. Report Outline

This report presents the detailed results from the Phase II evaluation of the PCUT technology. The report is organized into nine major sections. Section 1 presents an introduction to the technology and the innovative uses of tracers for pipeline characterization. Section 2 presents information about the need for improved pipeline characterization technologies from a DOE perspective. Section 3 covers the report outline. Section 4 covers the Phase II project work plan that was executed to conduct this evaluation of the PCUT technology. Section 5 presents background information on both partitioning tracers as well as reactive tracers. Section 6 presents the measurement results obtained during the Phase II investigation. Section 7 presents the development of a numerical model of the PCUT process that can be used for test design and evaluation of complex pipelines. Section 8 presents a summary of the results as well as details the important conclusion for the Phase II efforts. Section 9 is the reference section.

4. *Phase II Work Plan Description*

The technical effort for Phase II focused on 1) experimental work to verify the contamination quantity estimation procedures, 2) demonstration testing procedures to locate the contaminant within the pipeline, and 3) selecting and developing potential tracers for key DOE contaminants of interest. The effort was divided into six tasks which built on the results of the Phase I effort. Each task is focused on the objective of demonstrating the approach and techniques for pipeline characterization using tracers to detect, quantify, and locate contamination that might be contained within a specified pipeline or ductwork system.

4.1. Task 1 - Project Kick-Off

A project kick-off meeting was held shortly after contract award and involved personnel from both PNNL and Vista Engineering. At the project kick-off meeting we outlined the technical objectives and expected schedule for the project. Scope was clearly defined for the two organizations. The key Vista Engineering scope items consisted of all project management, evaluation of the PCUT method in general in terms of defining the detection limits and quantification accuracies. This testing would be done with both petroleum projects and well as chlorinated solvents. Vista Engineering was also scoped with determination of methodologies for locating contamination along pipeline as well as all aspects of reactive tracer development. PNNL was scoped with assistance on selected and evaluation of partitioning tracers for the chlorinated solvents as well testing of the approach for evaluating tritium contaminated pipelines. All technical aspects of the project were outlined early on then additional meetings were held periodically during the course of the project to ensure that the project was tracking according to plans, as well as permit improvements to be incorporated into the working processes.

4.2. Task 2 - Laboratory Testing

Laboratory testing was conducted using both partitioning and reactive tracers. Suites of tests were conducted using partitioning tracers to characterize hydrocarbons and chlorinated solvents. An analysis of reactive tracers was conducted to determine a viable tracer for heavy metal characterization. The testing effort has focused on three major aspects. The first aspect was to better understanding the capability for quantifying the amount of contamination in the pipeline. The second aspect was to better understand the detection limit and quantities that could be detected. The third objective was to validate the proposed methods for locating the contamination along the pipeline. An analysis of reactive tracers was conducted to determine a viable tracer for heavy metal characterization.

4.3. Task 3 - Numerical Modeling

Numerical modeling was conducted to predict transport of tracers through the pipeline and partitioning characteristics of the contaminants and tracers. The goal of the model is to develop a design tool that can be used for field demonstrations to estimate appropriate flow rates and the diffusion spreading that may be occurring in a given pipe of different dimensions. This effort was geared at developing a design tool that can help with the planning of field testing services.

4.4. Task 4 - Tracer Development

Under task 4, tracers for contaminants of interest for the DOE were identified, evaluated, and prepared for use in the PCUT method. The focus of the effort was to research partitioning tracers for Carbon Tetrachloride (CCl_4) and Trichloroethylene (TCE). Existing tracers were evaluated along with new tracer compounds in order to develop an appropriate range of partitioning coefficients from zero (conservative tracers) to approximately 100. For many contaminated sites, the contaminants are usually a mixture of various chlorinated solvents and other compounds (admixture). Tracers that selectively partition into one component of the mixture can also be used. This approach will provide a means to determine which specific chemical compounds may be contaminating the pipeline.

In addition to TCE and CCl_4, tracers were evaluated for heavy metals. Currently, there are no known tracers for these compounds. A variety of compounds that may partition with these contaminants based upon unique characteristics of each contaminant such as polarity, molecular weight, etc were evaluated.

4.5. Task 5 - Field Demonstration

A field scale demonstration of the technology was originally planned as part of the additional scope and would involved testing of the approach at a DOE facility on a line that would likely contain both radionuclides and other contamination. Since the additional scope effort has not been funded, the field demonstration has not occurred. As described in the results section of the report, we have done a significant amount of testing in various pipelines of different materials and lengths that we are comfortable that technology will be successful in most pipelines. We are still in discussions with DOE to execute a field demonstration, preferably at a DOE site when the funding for the additional scope is released.

4.6. Task 6 - Reporting

Reporting of the progress of this work was submitted semi-annually throughout the duration of the project. This document serves as the final report documenting all activities of the project. This report includes testing procedures, test results, analysis, numerical model formulations and results, and conclusions from both Vista Engineering and our research institute, PNNL.

Any non-federal use of funding for additional development will be documented and tracked by Vista Engineering for a period of three years after the conclusion of the Phase II effort. Any licenses that are issued based upon the technology will be documented and tracked for the same required three year period as the sales and development funding.

5. *Background on Tracers*

During the course of the project two different types of interactive tracers were investigated and studied. The first type of tracer was a partitioning tracer that would be absorbed into the contamination and then when the vapor concentration above the contaminate reduced, the tracer would desorb out of the contaminant and back into the air stream. The amount of tracer that would be adsorbed into the contaminant was a function of the partitioning coefficient of the tracer with the contaminant. The second type of interactive tracer that was studied was reactive tracers. These tracers react with the contaminant and either are bonded to the contaminant or change forms and come out of the pipe as a different compound. A more detailed description of both types of tracers are discussed in the following sections.

5.1. Partitioning Tracers

The PCUT technique uses conservative and partitioning tracers to remotely determine the amount of contaminant within a run of piping or ductwork. The PCUT system was motivated by a method that has been successfully used to characterize subsurface soil contaminants (Jin, et al., 1995a&b, Dwarakanath, 1997, and Deeds, 1999) and is similar in operation to that of a gas chromatography column. By injecting a "slug" of both conservative and partitioning tracers at one end (or section) of the piping and measuring the time history of the concentration of the tracers at the other end (or another section) of the pipe, the presence, location, and amount of contaminant within the pipe or duct can be determined. The tracers are transported along the pipe or duct by a gas flow field, typically air or nitrogen, which has a velocity that is slow enough so that the partitioning tracer has time to interact with the contaminant before the tracer slug completely passes over the contaminate region. A schematic of the PCUT concept is presented in Figure 1.

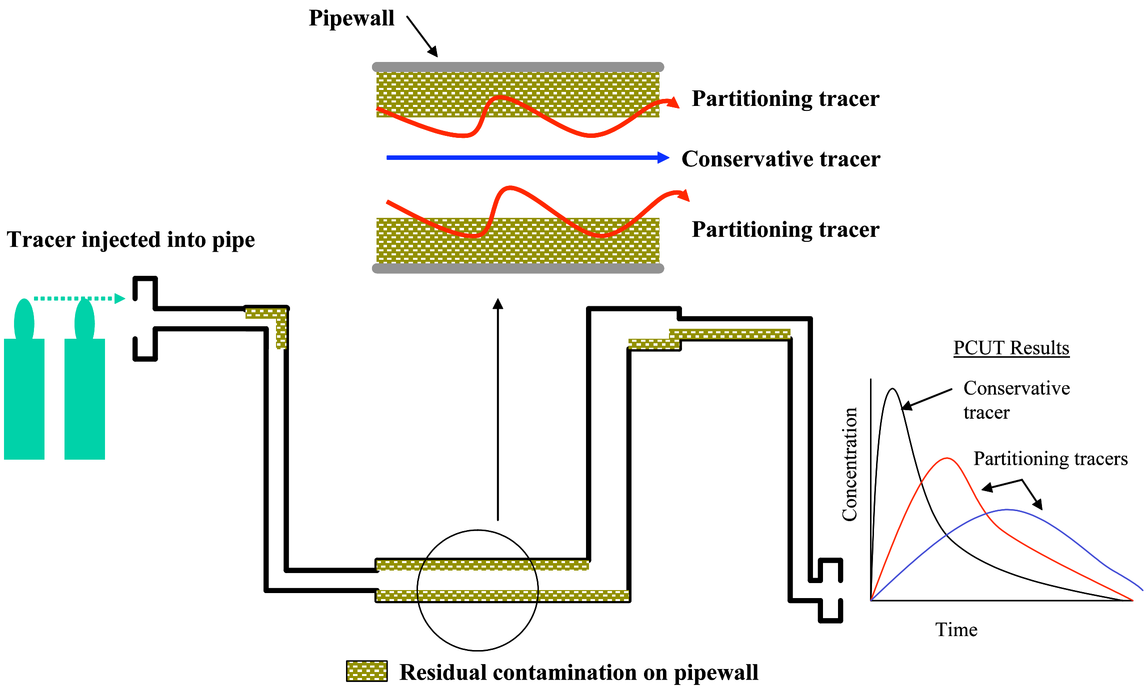


Figure 1. Schematic of partitioning tracer concept deployed for pipeline characterization. The elution curves of concentration for both the conservative and partitioning tracers are also shown.

Partitioning tracers are gaseous and maintain the most significant benefit of the PCUT technique which is that nearly any size pipe can be investigated and the tracer gases spread to contact all the interior surface of the pipe or duct, ensuring that no contamination is missed. The tracers easily accommodate any bends, corners, or pipe diameter changes that may exist in the line. Also, since no physical materials are inserted into the pipeline, there is no chance of equipment plugging the line or equipment that needs to be decontaminated at the end of the test. Finally, gaseous tracers can be very beneficial in hazardous environments, where mechanical equipment could pose a potential sparking event leading to an explosion. For these instances the tracer method is the only safe technique to approach the problem.

The measurement process employed for partitioning tracers is similar to the one that occurs within a standard gas chromatography column. The conservative tracer flows through the column (or pipeline/duct) without reacting with the phase on the column surface (i.e., the contamination on the inside of the pipe). The partitioning tracers, on the other hand, will partition into the contamination on the inside surface of the pipeline, and therefore, will be delayed in time at the exit of the pipe in comparison to the conservative tracer.

The PCUT technique uses the principle of chromatographic separation through partitioning-induced flow retardation of tracers to quantify substances of interest in the air swept volume of the pipe or duct. The elution curves of tracer concentration provide near real time determination of the presence of contamination (within the first 10 hours of the test) as shown in Figure 2. By continuing the test and monitoring the elution of the partitioning tracers until the concentrations return to near zero, quantitative estimates of the volume of contaminant within the pipeline can be determined. Finally, with either testing control procedures or complex numerical simulation, the general location of the contaminant within the pipeline can also be determined. Detection, quantification, and location have all been demonstrated as part of the laboratory testing and are presented in Section 6 of this report.

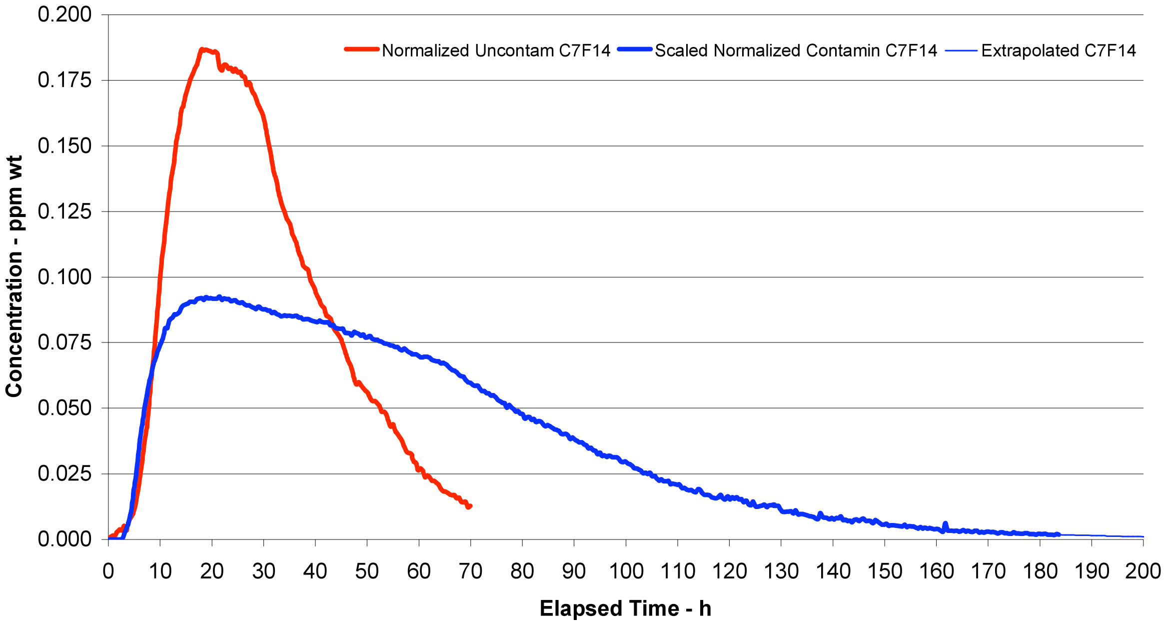


Figure 2. PCUT results from Phase I testing. The red curve is tracer response curve without contamination present in the pipe and the blue curve is the response curve with contamination in the pipe.

A key feature of the PCUT technique is that a suite of tracers are transported down a length of pipe and come in contact with any and all possible contamination within the pipe. The conservative tracer will not interact with the contamination inside the pipe, and therefore, it has a partition coefficient of zero relative to the contamination. The partitioning tracers on the other hand will interact with the contamination, and therefore, have a non-zero partitioning coefficient. The partitioning coefficient (K_i) is defined as

$$K_i = C_{i,D} / C_{i,M} \tag{1}$$

where $C_{i,D}$ is the concentration of the "i"th tracer in the contamination and $C_{i,M}$ is the concentration of the "i"th tracer in the mobile phase, i.e. the air transporting the tracer. The retardation of the tracers by the contamination inside the pipe is given by

$$R_f = \frac{\langle t_p \rangle}{\langle t_c \rangle} = 1 + \frac{K_i S_D}{(1 - S_D)} \tag{2}$$

where $<t_p>$ is the mean time of travel of the partitioning tracer, $<t_c>$ is the mean time of travel of the conservative (i.e., non-partitioning) tracer, and S_D is the average contamination saturation, i.e. the fraction of the volume occupied by contamination in the total swept volume of the pipe. An empirical constant, α, has been incorporated in the solution of Equation 2 for the unique situation of contamination within a pipeline as shown in Equation 3. During the Phase I effort it was postulated that α should be approximately equal to 2 for flow in a pipe since only the top of the contaminant layer can interact with the tracer. The values of $<t_p>$ and $<t_c>$ can be determined from the centroid of the elution curves of tracer concentration during a pipe test, and K_i can be determined in laboratory calibration tests referred to as static partitioning tests. Further research during the Phase II effort has determined that α should be 1 and that the limited surface area does not affect the quantification results.

An estimate of the volume of the contamination can be estimated by solving Eqs. (1) and (2) for S_{Dpipe}, assuming $S_{Dpipe} = \alpha\, S_D$.

$$S_{DPipe} = \alpha \frac{R_f - 1}{K_i + (R_f - 1)} = \alpha \frac{\dfrac{\langle t_p \rangle}{\langle t_c \rangle} - 1}{K_i + \left(\dfrac{\langle t_p \rangle}{\langle t_c \rangle}\right) - 1}, \tag{3}$$

The partitioning tracers undergo retardation due to their partitioning into and out of the contamination, while the conservative tracers are unaffected by the presence of the contamination. The chromatographic separation of the partitioning tracers at the end of the pipeline for the feasibility demonstration testing is presented in Figure 2. The difference between the red (no contamination) and blue curves (contamination) in this figure, on page 7, is due to contamination present in the pipe. There is both an amplitude and a temporal change in the concentration time history of the two tracers due to the presence of contaminant in the pipe.

The partitioning process is caused by the mass transfer of the partitioning tracers into the contaminant until equilibrium partitioning has been reached. For this reason, the flow rate of the tracers must be designed so that sufficient time exists to allow the partitioning tracers to interact with the contaminant. Once the tracer slug has passed the contamination, the partitioning tracer elutes back into the flow field as dictated by the partitioning coefficient. Therefore, the net flux of the partitioning tracers will be from the contaminant back into the flow field to preserve the equilibrium partitioning dictated by the particular coefficient for the tracer. Thus, recovery of the partitioning tracers at the extraction point is delayed (i.e. retarded) relative to the recovery of the conservative tracer. Since the retardation factor of each partitioning tracer, R_f (as defined in

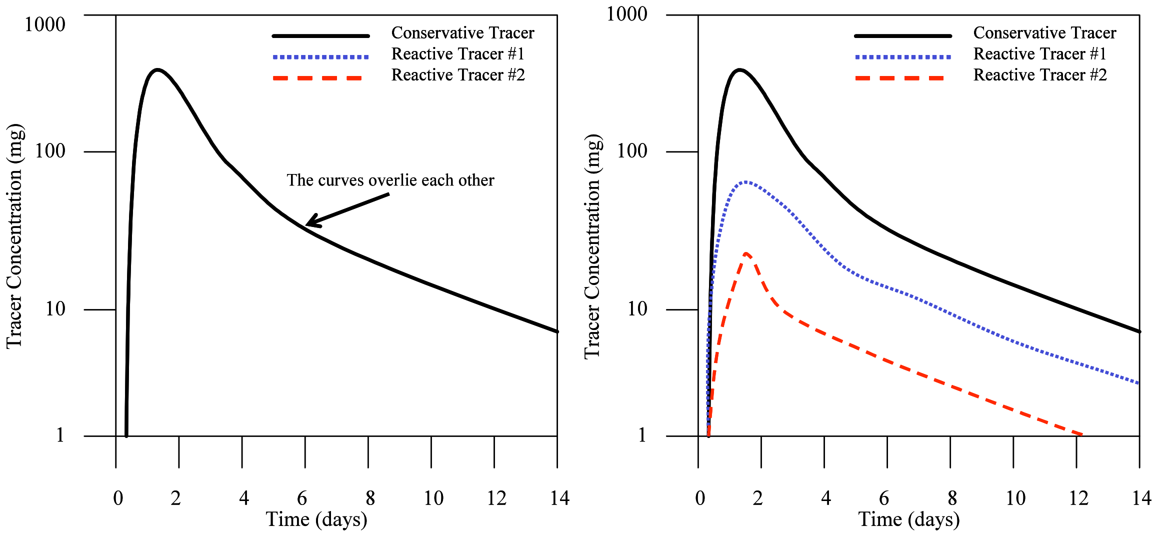
Eq. 2), is a function of both the partition coefficient (K_i,) and the average contamination saturation, S_D, of the contaminant(s) in the pipeline, the contamination saturation can be solved for by measuring R_f for the various tracers pairs with known partitioning coefficients, K_i.

5.2. Reactive Tracers

Reactive tracers are a broader category of tracers that includes partitioning tracers but also includes those gases that change forms when exposed to certain contaminates such as heavy metals and radionuclides. Partitioning tracers offer the advantage that they are retarded by the contaminant of interest and then diffuse out of the contaminant until no tracers remain within the contaminant. This process simplifies detection and provides a source that continuously elutes until no more tracer remains. However, tracers with this unique behavior of partitioning into the contaminant of interest and re-eluting after the tracer slug has passed over the contaminated region may be difficult to find or may not exist for some chemical compounds.

The use of reactive tracers for pipeline and ductwork characterization maintains all of the key benefits from the partitioning tracer approach except location. Reactive Tracers offer two major advantages over partitioning tracers. First the application and availability of finding tracers is much broader using a reactive tracer since more contaminates of interest can be tested. Secondly, reactive tracers have a higher reaction rate and therefore the test can be conducted in a shorter time period.

The reactive tracers would be used in a similar manner as the partitioning tracers. A suite of tracers consisting of at least one tracer that is conservative (i.e. does not react with the contaminant of interest) and one or more reactive tracers would be injected as a slug into the front section of pipe. The tracer slug would be transported through the pipeline or ductwork by an established flow field. In this manner the tracer slugs comes in contact will all the contamination within the pipeline. However, rather than partitioning into the contaminant and diffusing out of the contamination, the reactive tracers would react with the contaminant of interest and either change form or be consumed by the contamination. Figure 3 presents a schematic for the contaminated and uncontaminated results from a reactive tracer test. Note how the clean and contaminated figures for the reactive tracers have the same time scale whereas the time scale is different between the clean and contaminated test using partitioning tracers. This figure points out one of the additional advantages of the reactive tracer test, which is that the test should be shorter because the partitioning tracers do not have to diffuse out of the contamination.



a) Reactive tracer concentration curves when there is no contamination present

b) Reactive tracer concentration curves when contamination is encountered in the test zone

Figure 3. Reactive tracer elution time histories: A) without contamination and B) with contamination present.

For the scenario where the tracers are not completely consumed by the contaminant, it may still be possible to estimate the contaminant volume based upon the amount of tracer detected in the effluent of the pipe. The ratio between the injected concentration and the measured concentration should be related to the amount of contamination present, with consideration given to the effects of the reaction rate. When more contamination is present the concentration should be reduced from the scenario of both a clean pipe and a pipe with a small amount of contamination.

For the scenario where a tracer reacts with the contaminant of interest and changes form, determination of the contamination volume is more difficult. This work focused on finding ways to simply detect the presence of the contaminant by using a conservative tracer and at least one reactive tracer. The presence of the conservative tracer provides the time base for test control as well as the percent recovery to ensure that the flow field is fully captured. Ideally, the reaction between the tracer and the contaminant will be quick, and the change will only occur while the tracer slug is in contact with the contaminant. Slow reactions may take a while to elute from the system.

6. Measurement Results

6.1. Partitioning Tracers with Hydrocarbons

The Phase II laboratory testing effort focused on three major aspects of the PCUT technology. The first aspect was to better understand the capability for quantifying the amount of contamination in the pipeline. The second aspect was to better understand the detection limit and quantities that could be detected. The third objective was to validate the proposed methods for locating the contamination along the pipeline. The first suite of laboratory testing was conducted using the partitioning tracer method on hydrocarbon contaminants. Weathered diesel fuel was selected as the contaminant because it was easy to handle and tracers and tracer properties were previously established in the Phase I effort. Table 2 lists the tests conducted using the hydrocarbon contaminant and some of the testing conditions.

Table 2. Summary of PCUT Pipeline Laboratory Tests with Hydrocarbon Contaminant.

Test #	Pipe	Tray	Contaminate	Injection Method	Notes
1	Short	None	None	End	Baseline Test
2	Long	None	None	End	Baseline Test
3	long	3 round trays	30 ml of Diesel	End	Volume too small - no partitioning
4	short	wide	300 ml of Diesel	End	Quantification Test
5	short	wide	300 ml of Diesel	End	Flow rate 18-20 ml/min
6	short	wide	300 ml of Diesel	End	Quantification Test
7	long	wide	300 ml of Diesel	End	Location Test
8	long	wide	300 ml of Diesel	End	Location Test
9	short	tall	300 ml of Diesel	End	Bad test - equipment difficulties in the middle of the test
10	long	wide	300 ml of Diesel	Flood	Location test - No SF6 to estimate volumes
11	short	cardboard	10gms of dried glue	Flood	Semi-Solid/Solid Contaminant Test
12	long	cardboard	21.5 gms of dried glue	Flood	Can't estimate volume due to flood procedure
12a	long	cardboard	33.5 gms of dried glue	Flood	Higher Tracer Concentration - No volumes due to flood
13	short	tall	300 ml of Diesel	End	Quantification Test
14	short	tall	300 ml of Diesel	End	Tracer conc. was 100 instead of 10
15	short	wide	150 ml of Diesel	End	Detection Limit Test
16	short	wide	150 ml of Diesel	End	Detection Limit Test
17	short	wide	145 ml of Diesel	End	Detection Limit Test
18	short	tall	300 ml of Diesel	End	Good data
19	short	wide	250 ml of Diesel	End	Flow data not collected due to PRB programming efforts
20	short	wide	250 ml of Diesel	End	Blind Testing
21	short	wide	225 ml of Diesel	End	Blind Testing
22	long	wide	300 ml of Diesel	End	Blind Testing
23	long	wide	300 ml of Diesel	Flood	Location Test - Flood so can't quantify
24	long	2 trays	300 & 300 ml of Diesel	Flood	Bad Test - Large pipe leak due to missing o-ring in compression joint
25	long	2 trays	300 & 300 ml of Diesel	End	2 Contamination Zones
26	short	wide	300 ml of Diesel	End	Quantification Test
27	long	wide	300 & 300 ml of Diesel	Flood	2 Contamination Zones
35	Short	wide	300 ml Diesel	End	Old steel pipe as opposed to PVC
36	Short	none	none	End	Old steel pipe as opposed to PVC

Testing was conducted in three pipeline configurations. The first configuration was a short pipeline consisting of an 8 foot section of 2 inch PVC pipe followed by a 4 foot section of 3 inch PVC pipe followed by another 3 foot section of 2 inch PVC pipe. The second configuration was a longer pipeline constructed of 66 feet of 2 inch PCV, followed by a 4 foot section of 3 inch PVC, followed by another 45 foot of 2 inch PVC. The longer pipeline is more representative of the configurations expected to be encountered in actual application of the technology. Additionally, a third pipeline was constructed containing two 3 inch PVC sections for placing contamination at multiple locations within the pipeline. The various configurations are shown in Figure 3. Pipe similar to the short pipeline were also made out of copper and steel to evaluate other pipeline materials. All testing, include some old steel pipe, showed no significant influence of the pipe material on the PCUT methodology.

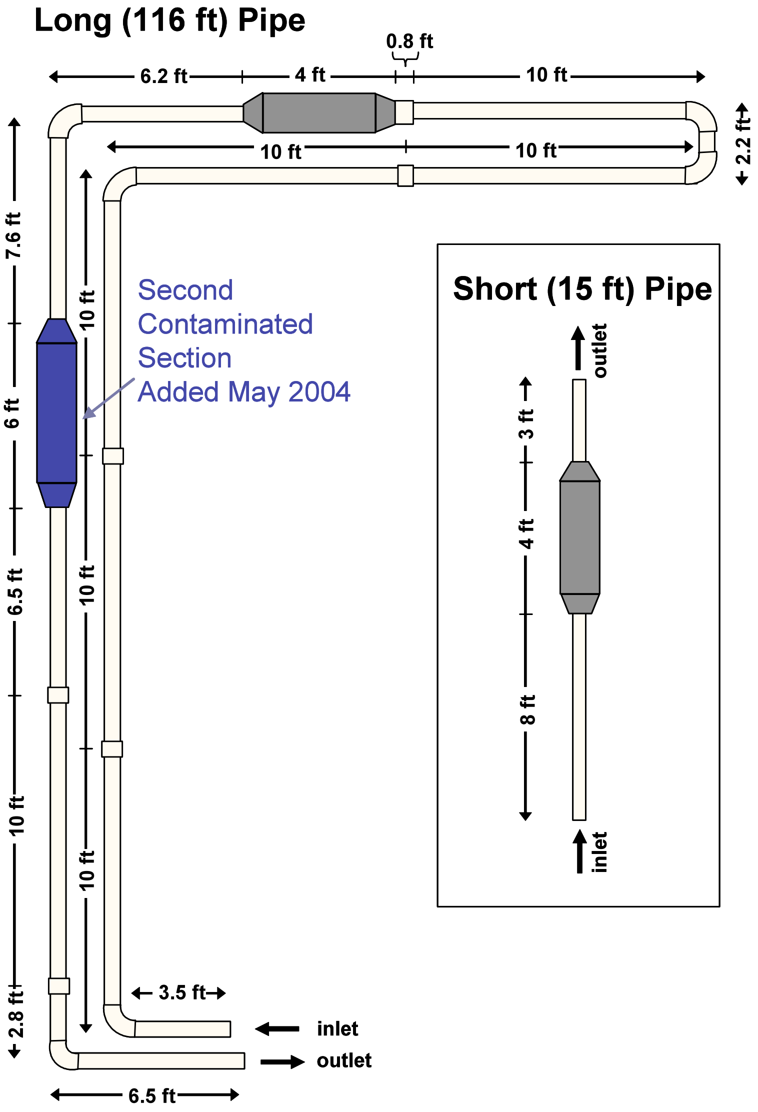


Figure 3. Schematic of Pipelines used in Laboratory Testing.

Each 3 inch section of PVC pipe has a screw connection such that it can be opened to accept trays of contamination. This makes the pipeline more versatile and allows the contamination to be easily removed or changed for different tests. The contaminant was placed in a tray and inserted into the 3 inch diameter sections of pipe. Two types of contamination trays were used in the testing, each was 3 feet long. The shallow trays had a width of 1.625 inches. The tall trays had a width of 0.8125 inches. This allowed the same volume of contaminant to be used in each test, but changed the surface area of the product that was exposed to the tracer gases. These trays were used to evaluate surface area effects as well as facilitate contaminant change outs.

6.2. Laboratory Testing for Volume Estimating

Four series of tests were conducted as described below. The tests were designed to study the effects of product surface area and product volume on the partitioning effects of the tracers. For each test a weathered diesel product was used as the contaminant of interest.

The testing procedure for estimating the volume of contaminant consisted of placing a known volume of contaminant in one of the trays and placing it in the 3 inch PVC section of the pipeline. A known volume of a specific concentration of tracer gases (both conservative and multiple partitioning tracers combined) was injected into one end of the pipeline (shown as “end” in the Injection Method column of Table 2.) Once the tracer was injected, a slow, constant flow of inert gas, nitrogen in this testing, was started and continued for the duration of the test. The inert gas flow forced the traced gas through the pipeline, past the contaminant, to the gas chromatograph on the outlet end of the pipeline.

300 ml Shallow Tray Test Series: The first series of tests was run with 300 ml of contaminant in a shallow tray that has a width of 1.625 inches. This consisted of Pipe Tests 4, 5 and 6 in Table 2. The results were encouraging and are presented in Table 3. The average errors in the volume estimates were 5.9% using the C_7F_{14} tracer and 7.4% using the C_8F_{16} tracer. All estimates were less than the actual volume. Figure 4 presents the tracer response curve from pipe test #4. The blue curve is the conservative tracer and indicates the non-partitioned flow through the pipe. The pink and green curves show the partitioning tracers. The different shape of the two curves is due to the differing partitioning coefficients. The lower peak indicates that the tracer partitioned into the contaminant. The longer tail of the two curves shows that the tracers then eluted for the contaminant after the initial tracer slug passed the location of the contamination. The results from pipe test #5 are postulated to be below average because of the increase in the average flow rate from 8-12 ml/min up to around 20 ml/min. It is believed that this did not allow sufficient time for the tracers to partition into the contaminant.

Table 3. Volumetric test results using shallow tray.

	C_7F_{14}		C_8F_{16}	
Test ID	Vol (ml)	Error (%)	Vol (ml)	Error (%)
Pipe Test #4	283.6	-5.5%	296.4	-1.2%
Pipe Test #5*	271.6	-9.5%	261.7	-12.8%
Pipe Test #6	291.6	-2.8%	275.4	-8.2%
Average	**282.3**	**-5.9%**	**277.8**	**-7.4%**

* Flow rate for this test is nearly double the flow rates of Test #4 and Test #6

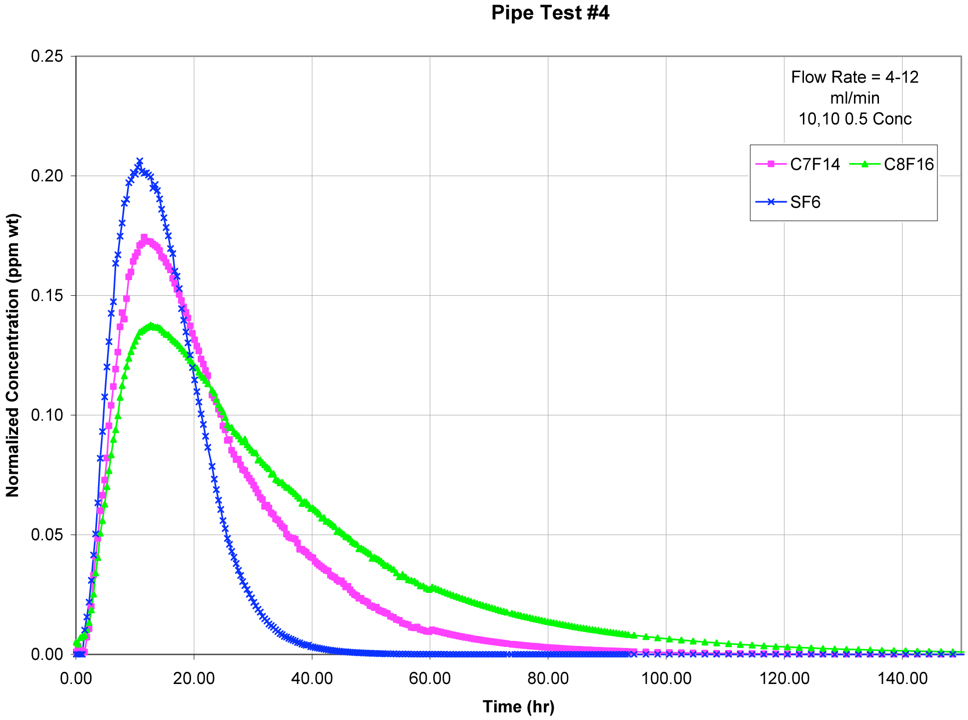


Figure 4. PCUT test results from pipe test #4 with 300 ml of diesel.

300 ml Tall Tray Test Series: For the second test series (Test #13, #14, and #18), the shallow tray was replaced with a tall tray. The volume of contaminant remained the same as for the first series of tests; however the surface area exposed to the tracer was reduced by a factor of two. The results from these tests are presented in Table 4. The flow rates for these tests were similar to pipe tests using the shallow tray, yet the results show smaller estimated quantities and larger errors than the previous shallow tray test series results. Engineering judgment indicates that if a relationship was present between the estimated quantity and the product surface area then the volumes measured in this test series would be a factor of two less than those measured in the previous test series. This isn't the case as shown in Table 4; the estimated volumes using an alpha (α) factor of 1 in Equation 3 are closer to the actual 300 ml, than 150 ml, which would be case if the alpha factor was directly related to surface area of the contaminant. The estimated quantities in Table 4 are generally less and this is believed to be related to the amount of residence time the tracers have over the contamination. With a larger surface area the necessary residence time is less than if the surface area is smaller. For the tall tray, the tracers can only interact through half the surface area to detect the same volume as the first series of tests. It appears that as the residence time is reduced the amount of error in volume estimate increases. This was also observed in other tests using reduced volumes of contamination.

Table 4. Volumetric test results using tall tray.

	C_7F_{14}		C_8F_{16}	
Test ID	Vol (ml)	Error (%)	Vol (ml)	Error (%)
Pipe Test #13	263.4	-12.2%	317.5	5.8%
Pipe Test #14	250.9	-16.4%	220.4	-26.5%
Pipe Test #18	301.3	0.4%	260.6	-13.2%
Average	**271.9**	**-9.4%**	**266.2**	**-11.3%**

150 ml Shallow Tray Test Series: The third test series used the shallow trays again but the total volume placed in the trays was reduced to 150 ml, half that used in the previous tests. Three replicates were again conducted using flow rates between 8 and 12 ml/min. The results are presented in Table 5. In all cases, the quantification errors were larger than the quantification errors obtained from any of the 300 ml test runs. Although quantification of a 150 ml volume of diesel was difficult for the PCUT method as evidence by the quantification errors, the detection or presence of the contamination was easily noted as the partitioning tracer curves were well separated from the conservative tracer curve. See Figure 5. It should be noted that detecting the presence of contamination in a pipeline is significantly easier than accurately quantifying the contamination. Although the PCUT method had an average error of over 25% for quantifying 150 ml of diesel, it can easily detect this volume and could likely detect volumes even smaller given sufficient partitioning time.

Table 5. Volumetric test results using shallow tray and 150 ml of contaminant.

	C_7F_{14}		C_8F_{16}	
Test ID	Vol (ml)	Error (%)	Vol (ml)	Error (%)
Pipe Test #15	124.2	-17.2%	113.6	-24.3%
Pipe Test #16	102.2	-31.8%	96.6	-35.6%
Pipe Test #17	108.8	-24.9%	99.4	-31.5%
Average	**111.7**	**-24.6%**	**103.2**	**-30.5%**

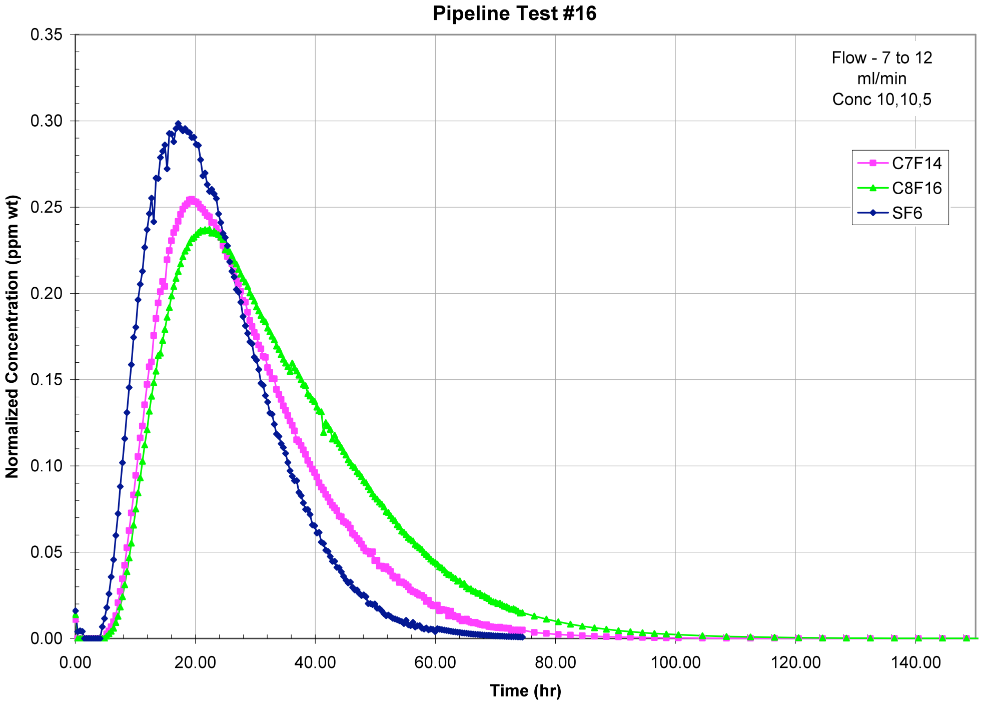


Figure 5. Typical test results from testing with 150 ml showing separation of the conservative and partitioning tracers indicating detection of the contamination.

Blind Test Series: A final, fourth test series was also conducted to confirm the final analysis approach. These tests were conducted in a blind manner to determine how well the method works for unknown scenarios. For these tests, the test operator placed an unknown volume in the tray for each test. After the test was conducted a separate person analyzed the data and determined the volume estimate. Only then were the actual volume placed in each test revealed and compared to the measured volume. These results are presented in Table 6.

Table 6. Blind Volumetric test results.

	C_7F_{14}		C_8F_{16}	
Test ID	Vol (ml)	Error (%)	Vol (ml)	Error (%)
Pipe Test #20 (250 ml)	268.2	7.3%	217.9	-12.8%
Pipe Test #21 (225 ml)	218.0	-3.1%	244.7	-8.7%
Pipe Test #22 (300 ml)	277.8	-7.4%	298.9	-0.4%
Average		**-1.1%**		**-7.2%**

The results from the blind testing strongly support the ability of PCUT method to both accurately detect contamination as well as quantify the amount of contamination present. Using the three blind tests presented in Table 6, a total of six quantifications were made using two partitioning tracers in each test. The average quantification error for each tracer was less than 10 percent, with C_7F_{14} producing an average of 1.1%. These average errors for the blind testing are within the expected range of the other tests done to date and typical of the average test error from all the testing which was not conducted blind.

The various tests conducted using the short pipeline, have clearly demonstrated that that PCUT method is a viable method for detecting and quantifying contamination within pipelines. These tests have established specific testing procedures for conducting the PCUT tests that can be applied to other pipeline scenarios. The major first order effects have been investigated and established as minor in relating to the quantification estimates. Based upon the test results obtained in Phase II, the alpha factor (α) has been determined to be 1. A second order relationship has been noted between the residence time of the portioning tracers and quantification error, implying that sufficient time for the tracer transport should be utilized to obtain accurate contaminant volume estimates. In summary the PCUT test procedures are established and have been proven to be effective for detecting and estimating contamination within a pipeline.

6.3. Laboratory Testing for Detection Limits

In addition to the laboratory testing for evaluating the surface area and volume relationship, additional testing was also conducted for determination of the detection limits of the PCUT approach. The Phase I results demonstrated that the technique easily identified 1.5 liters of weathered diesel contamination in the pipeline with a pipe volume of 17.7 liters. For this situation the contamination was 8.5 percent of the pipe volume. We believe, from the strength of the responses (i.e. reductions in concentration levels and also the change in the centroid of the mass), that detection limits can be much lower. Realizing that detection limits will depend on a variety of factors such as contaminant of interest, selected tracers, distribution of the contamination, some basic tests to attempt to establish boundaries for the detection limits were made.

The pipe to be used for these tests was the long pipe described above (see Figure 3). The pipe is 116 feet long and contains a 4 foot section where contamination can be placed about two thirds of the way along the pipe. The first test in the pipe (test #2) did not have any contamination and was used to confirm that the pipe was clean and to assist in establishing flow rates. The next test (test #3) used three circular tins, each with 10 ml of diesel. This amount of contamination was not detected at a flow rate of 30 to 60 ml/min. It is likely that the 30 ml of contamination was not detected because the tracers were swept through the pipe at too high rates. Had the rate been much closer to the 8-12 ml/min used for the other testing it is possible that the contamination might have been detected.

The next test (test #7) reduced the flow rate to 8 to 20 ml/min and utilized 300 ml of diesel in the shallow tray. This contamination was detected and quantified at 285 ml, which is similar to the results from the short pipe. Figure 6 presents the tracers time histories for this test.

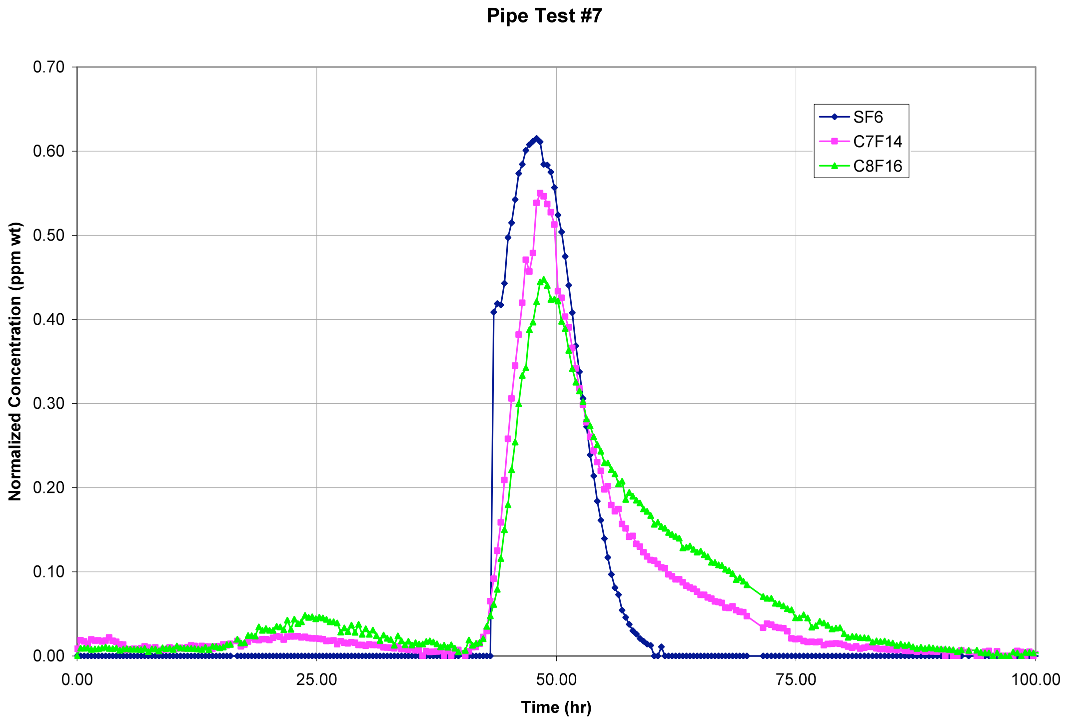


Figure 6. Tracer concentration time histories from the long pipe with 300 ml of diesel located two thirds of the length of the pipe.

To improve upon the overall time required to conduct a test, another tracer injection method was evaluated in pipe test #10. For all the other tests, the tracers are introduced at the start of the pipe and transported along the pipe over the contamination using and advective flow. For pipe test #10, the pipe was flooded with tracer and then sealed overnight allowing the tracer to reside over the contamination regions (shown as “flood” in the Injection Method column of Table 2.) The next morning the tracer was swept out using a high flow rate and then a lower advective flow was established. As the partitioning tracers are eluted into the advective flow stream they are carried to the GC for measurement. This approach reduced the total time of the test and permitted the location of the contamination to be estimated. The location calculations are discussed in Section 6.5.

6.4. Testing with other Contaminant Materials

In addition to the diesel detection and quantification, three demonstration tests were also performed using dried glue as a semi-solid test material. The glue is a standard epoxy called WELDER, which is manufactured by Homax Products, Inc., and can be purchased at any local building supply store. The glue is 46% by weight Toluene and has a vapor pressure of 22 mm Hg at 68^{o}F as a liquid when first applied. The manufacturer stated that the vapor pressure decreases significantly (<< 1 mm Hg at room temperature) as the glue dries and the toluene evaporates, however the manufacturer does not have a value for the vapor pressure of a dried glue sample.

For the first test (test #11), approximately 10 grams (5 ml) of dried glue were placed in the short pipe previously described. The same tracer suite was advected through the pipe and the tracer elution curves shown in Figure 7 were observed. In this figure, there is clear indication of a partitioning effect occurring as the peaks of Partitioning Tracer #1 and #2 (C_7F_{14} and C_8F_{16} respectively) are not as high has the conservative tracer. In addition, the partitioning tracers clearly continue to emerge even after all the conservative tracer has been swept out of the pipe. The center of mass for both partitioning tracers is also much longer in time than the conservative tracer. It is interesting that both partitioning tracers are nearly identical, indicating that partitioning coefficient for both tracers, which are chemically very similar, are about the same in the dried glue material. This is different than for the aged diesel in the short-pipe test described above, where the partitioning coefficient into diesel for Partitioning Tracer #2 is about three times the partitioning coefficient of that for Partitioning Tracer #1 into the aged diesel. The other two tests (tests #12 and #12a) were conducted in the long pipe and showed similar results, indicating that even small amounts of a semi-solid material can be detected in typical pipe lengths.

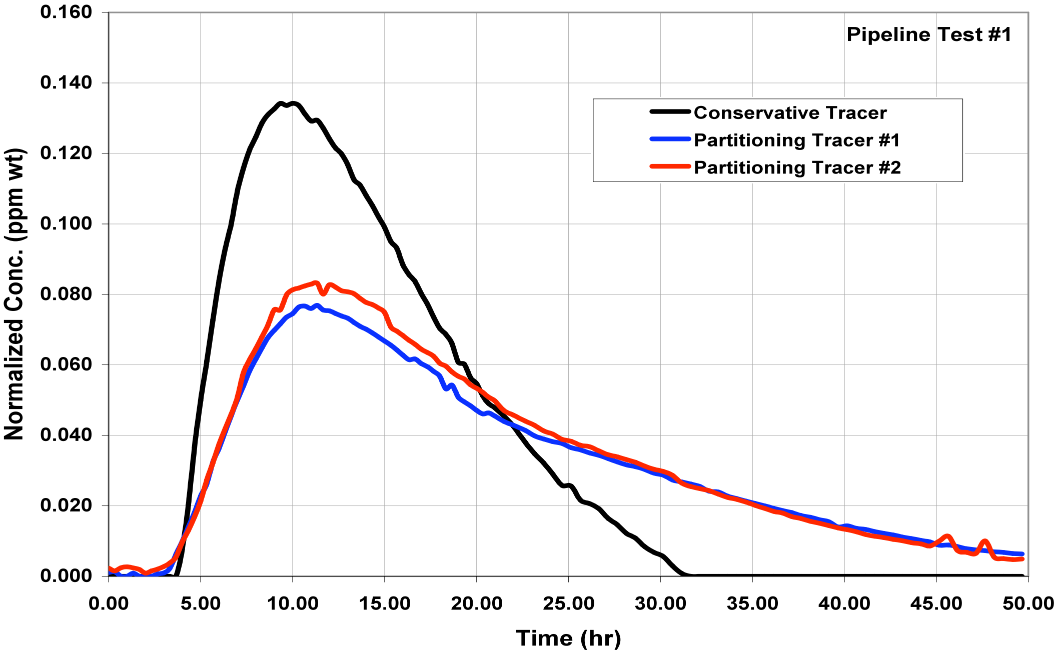


Figure 7. Tracer elution time history for dried glue in a short pipeline test.

6.5. Laboratory Testing for Contaminant Location

The location capability of the PCUT technology was experimentally demonstrated in the laboratory using two partitioning tracers in the long (116 ft) pipe. A 3 foot by 1.625 inch rectangular tray (shallow) was inserted into a 4 foot section of 3 inch diameter PVC pipe whose center position was located 47.5 feet from the end of the pipe where the GC measurements were being made. The tray contained 300 ml of aged diesel fuel. The same two tracers and the same advection gas as used in the detection and quantification tests were used in the location test.

Figure 8 shows the time history of the concentration curves of the two partitioning tracers and the conservative tracer from one of the tests location tests. Superimposed on these curves is the flow rate of the advection gas. The location measurement is made after the detection measurement. The data required for detection is the same as for previous tests except only enough data needs to be collected to define the peak of the conservative tracer. This allows a comparison between the partitioning tracers and the conservative tracer for detection and also allows sufficient time for the tracers to partition into the contaminant. The next step is to rapidly flush the conservative and partitioning tracers through the pipe and then to re-establish the advection flow stream at a known velocity. As shown in Figure 8, the line was flushed at 350 ml/min, which is over 10 times the flow rate of the measurements. Once the flow rate is re-established, the partitioning tracers in the diesel fuel re-enter the flow stream and are advected to the end of the line at a known flow rate. The location of the contamination is then determined from the advection velocity and the arrival time of the tracers. This figure shows the two partitioning tracers arriving at about 63 hours; the advection flow field was re-established at 44 hours.

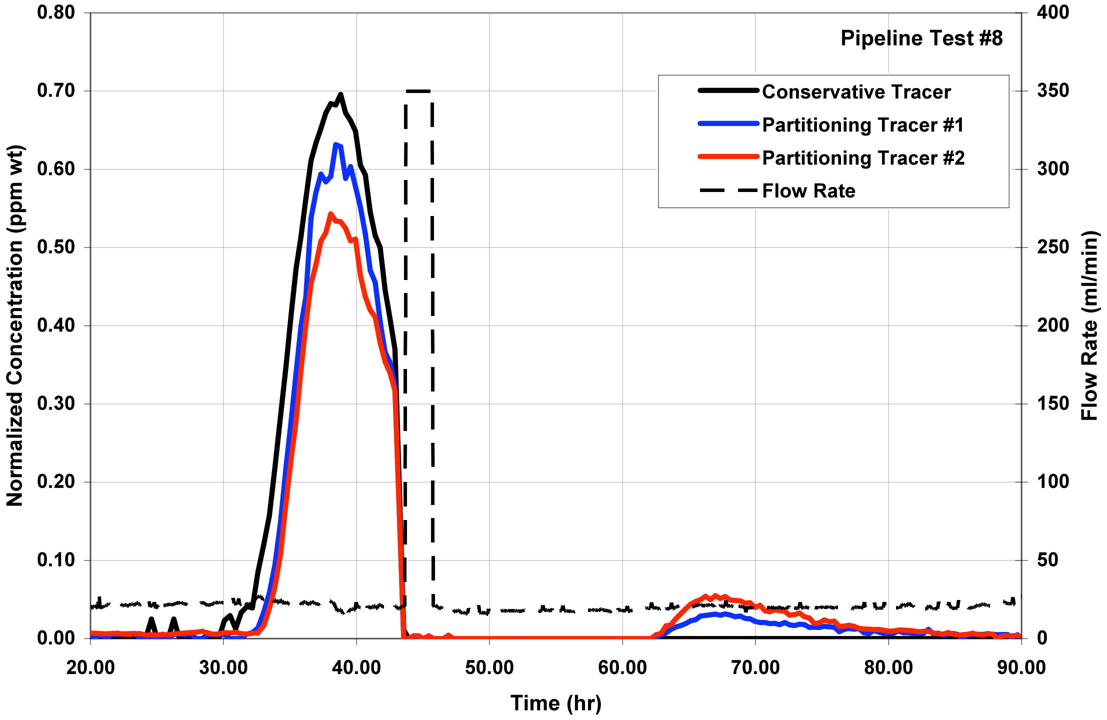


Figure 8. Test results from a test to determine the location of contamination within the long pipe using 300 ml of diesel as the contaminant located two thirds of the pipe length.

Table 7 summarizes the location results. Two methods were used to locate the contamination. Both methods used the time of arrival of the peak of the tracer concentrations. The first method uses only the average velocity within the pipe and the time of arrival of the tracer peak after flushing. The average velocity is computed by dividing the measured volumetric flow rate by the diameter of the pipe. The second method, which does not require a priori information about the diameter or geometry of the pipe, utilizes the ratio of the time of arrival of the peak of the first tracer pulse, which traveled over the full length of the pipe (i.e., 116 feet) and the time of arrival of the second tracer pulse, which traveled only the distance from the contamination to the end of the pipe. After weighting the arrival times by the mean of the measured flow rates, the distance from the tail of the pipe to the contamination can be determined.

Table 7. PCUT estimation of the location of the 300 ml of diesel fuel contamination.

	Method 1		Method 2	
Test	Location (ft)	Error (%)	Location (ft)	Error (%)
Pipe Test #8	51.3	3.3%	53.2	4.9
Pipe Test #10	38.1	6.4%		
Pipe Test #12	45.4	0.1%		
Pipe Test #23	44.7	0.6%		
Average		**2.6%**		

* The actual location of the contamination is centered 47.5 ft from the outlet end of the 116-ft pipe.

The location test was also repeated using the dried glue sample of approximately 20 grams (10 ml). For this test the pipeline was flooded with tracer overnight and then flushed with 350 ml/min of the advection gas. After the flush, an advective flow stream was established and used to determine the location of the dried glue specimen. The distance from the end of the pipe to the glue sample was calculated to be 49.2 feet which is less that 10% error on the actual value of 47.5 feet.

The ability to detect the location of multiple contamination locations was investigated in test 27. In this test, 300 ml of diesel was placed at two locations within the 116 ft pipeline. The first location was 47.5 ft from the GC where the measurements were taken. The second location was 28.7 ft from the GC. The tracer gas was flooded into the pipeline in the sections of the two contamination locations. The sections were sealed and the system was left alone for 18 hours. After this, the system was flushed with a flow of 400 ml/min of the advection gas. Once the system was flushed, an advection flow of 12 ml/min was established and the output of the pipeline was sampled continuously for partition tracer that was released from the two contamination locations. Figure 9 shows the response for Tracer 1.

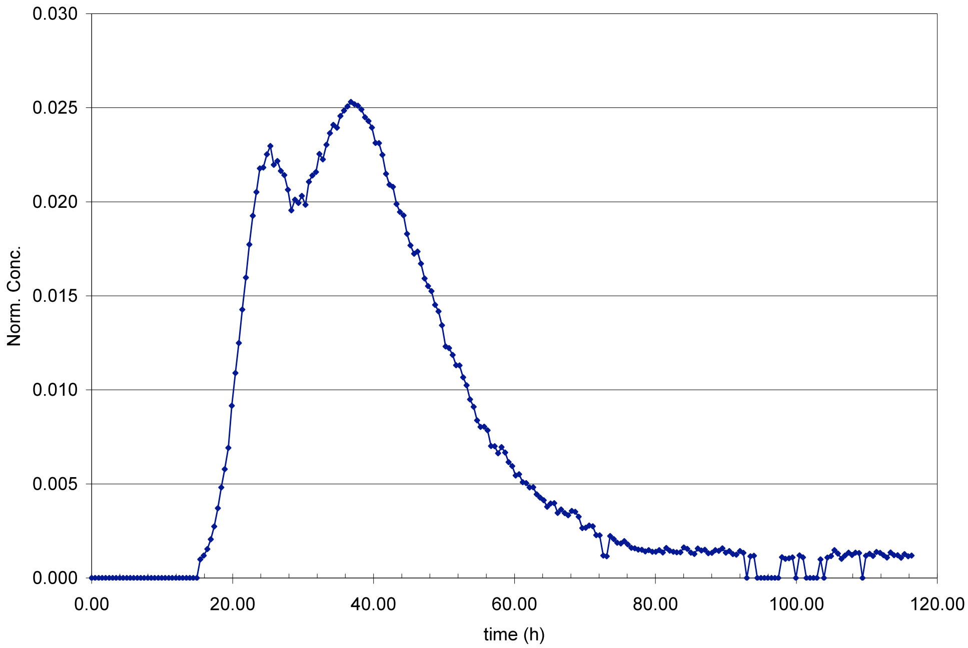


Figure 9. Response of Tracer 1 in the 116 ft pipeline with two contamination locations.

The twin peaks result from the superposition of responses of the released tracer from the two contamination locations. Each of the peaks was estimated using the following exponential decline equation

$$R(t) = Exp(a + \frac{b}{t} + c\ln(t)) \tag{4}$$

where t is time and a, b, and c are fitting parameters. Figure 10 shows the two estimated curves for the two contamination locations. The blue curve is the actual response from the test. The two green curves are the estimates for the two peaks caused by the two contamination locations. The orange curve is the superposition (sum) of the two estimated curves.

The location of the contamination can be determined from the time of arrival of the peak and the advection flow. Table 8 shows the estimated locations of the two contamination sections as determined by test 27. The calculation was performed by determining the volume of advected gas that had exited the pipeline at the times of the two estimated peaks. Dividing this volume by the cross sectional area of the pipeline produces the distance from the end of the pipeline. In all cases, the distance is underpredicted, but all were underpredicted by a similar amount, about 12%. This may be due to difficulties in setting the testing flow rate in the longer pipeline. Our measuring of the flow rate when changing from the flushing flow rate to the advective flow rate may have underpredicted the amount of gas that was forced through the system.

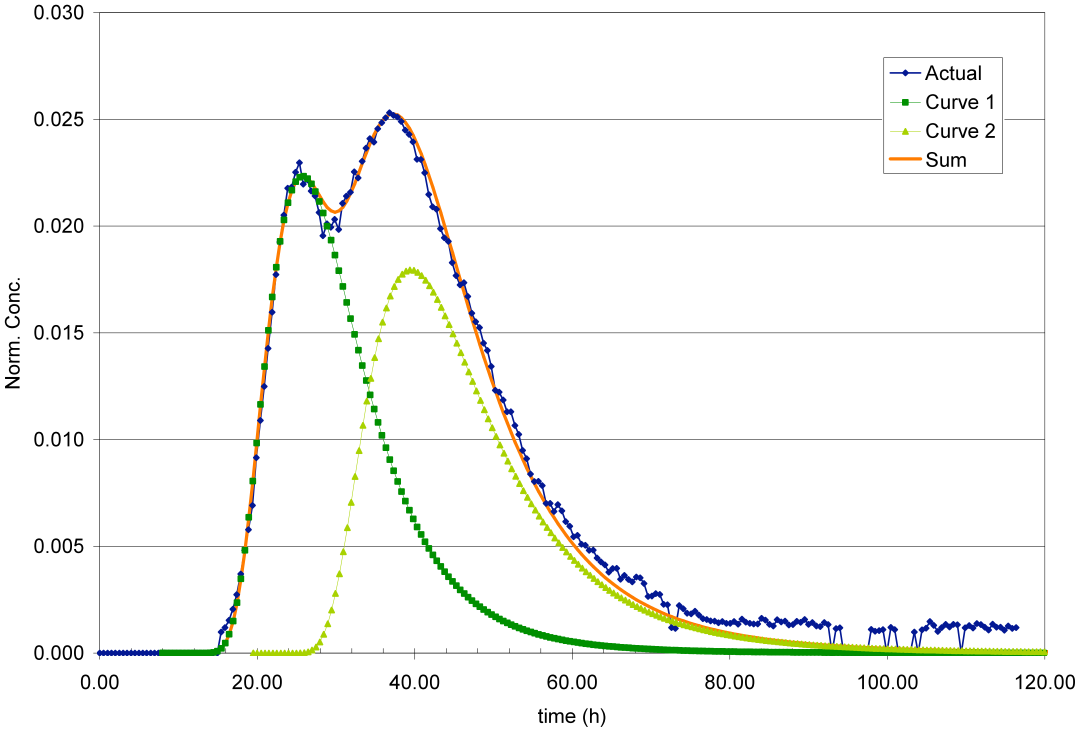


Figure 10. Estimated curves of Tracer 1 due to the two contamination locations.

Table 8. PCUT estimation of the location of multiple contamination locations.

Tracer #	Location 1 (ft)	Error (%)	Location 2 (ft)	Error (%)
1	25.8	-10.5	40.1	-15.6
2	24.73	-14.3	41.8	-12.1

* The actual location of the contaminant is 28.7 ft and 47.5 ft.

6.6. Partitioning Tracers with Chlorinated Solvents

One of the major contaminates of interest to DOE are chlorinated solvents. This task focused on identifying, selecting, and evaluating partitioning tracers for Carbon Tetrachloride (CCl_4) and Trichloroethylene (TCE). For groundwater problems, both alcohol tracers and fluorocarbon tracers, such as those used for the diesel contamination during Phase I and also initially in Phase II have been used. To alleviate problems with natural off-gassing of the chlorinated solvents interfering with the tracer concentration analytical instrument, a set of alcohol tracers were selected. The tracers include 1-methanol as a conservative tracer, 1-heptanol, 1-hexanol, 1-propanol, and 1-pentanol as partitioning tracers. These tracers have not previously been used in vapor phase. Difficulties were encountered in creating stable vapor phase concentrations of the tracers, due to the heavy weight of several of the alcohol compounds. The tracers were unstable and tended to condense on or adhere to the container walls altering the concentrations. When these standards were then analyzed, the analytical results were erratic and stable calibration curves for these tracers were not obtained. After several attempts to improve the vapor phase alcohol stability, it was decided to switch and use the fluorocarbons as tracers for the chlorinated solvents.

Static bag testing was conducted by PNNL to determine the partitioning coefficient for the three partitioning tracers, C_5F_{12}, C_7F_{14}, and C_8F_{16} in each of the chlorinated solvents. Each bag was assembled with 50 ml of the chlorinated solvent (TCE or CCl_4) and 750 ml of a tracer nitrogen gas mixture. Samples from the bag were collected and analyzed with a GC at 4 hour intervals until the tracer concentration in the bags reached a stable value (i.e. equilibrium was reached). Table 9 lists the partitioning coefficients for the three partitioning tracers in TCE and CCl_4. Once a set of conservative and partitioning tracers were established for both TCE and CCl_4, a series of tests were conducted to confirm the tracers partitioning into the contaminant as expected and that these tracers could be used with the PCUT Method. Tests were conducted to evaluate the detection and quantification capabilities of the PCUT Method. These tests are listed in Table 10. Location testing was not performed in the chlorinated solvent series, since this testing was done in a copper pipeline and a long copper pipeline was not available. The procedure will work with chlorinated solvents, as all the same principals still apply from the location testing with diesel in the long PVC pipeline.

Table 9. Partitioning Coefficients for the three partitioning tracers in TCE and CCl_4.

	C_5F_{12}	C_7F_{14}	C_8F_{16}
TCE	26.9	66.5	124.1
CCl_4	24.7	113.8	243.1

Table 10. Summary of tests involving chlorinated solvents.

Test #	Pipe	Tray	Contaminant	Injection Method	Notes
128	short PVC	Wide	200 ml TCE	End	Reaction with contaminant and PCV, test aborted
129	Short copper	Wide	None	End	
130	Short copper	Wide	200 ml TCE	End	Selected conservative tracer not conservative
131	Short copper	Wide	300 ml TCE	Flood	Aborted
132	Short copper	Wide	None	End	
133	Short copper	Wide	200 ml TCE	End	
134	Short copper	Wide	200 ml CCl_4	End	
148	Short copper	Wide	504g soil mixed with 300ml of 100ppmv CCl4 solution	End	Dissolved Phase
149	Short copper	Wide	508.9g soil mixed with 250ml of 800ppmv CCl4 solution	End	Dissolved Phase
150	Short copper	Wide	100ml CCl4 mixed with 250g soil	End	Slurry

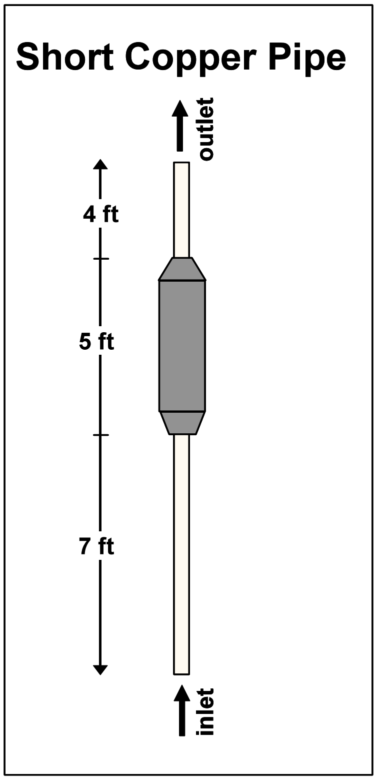


Figure 11. Schematic of Copper Pipeline used in Chlorinated Solvents Testing.

Each of the tests involving the chlorinated solvents was conducted in a short pipeline (15ft) and used the wide tray. As Test 128 progressed it was found that the contaminant reacted with the PVC tray and the pipeline material causing the test to be aborted. Following this, a copper pipeline and copper trays were constructed and used for the remaining tests. Figure 11 shows a schematic of the copper pipeline. Test 129 was used to confirm the integrity of the new pipeline and to ensure the partitioning tracers selected were not affected by the components of the new pipeline. In this case no contaminant was placed in the pipeline and the tracer gas mixture was flushed through the system. The response was as expected, each tracer, the conservative and the three partitioning, displayed the classic PCUT response for a system with no contaminant. Each tracer peaked at the same time and decayed down to zero at about the same time. This confirmed that the new pipeline could be used for the remaining tests.

Test 130 was conducted with 200 ml of TCE placed in the copper tray in the center of the 15 ft pipeline. At the conclusion of this test it was found that the tracer selected to be conservative was actually not conservative. The selected conservative tracer, propanol C_3H_7OH, reacted with the TCE. Methane, CH_4, was selected as an alternative to the propanol for the conservative tracer. Pipeline Test 132 used the newly selected conservative tracer, CH_4, and the three partitioning tracers in a clean pipeline test. Once again, each of the tracers showed the classic PCUT response for a clean pipeline, peaking at identical times and decaying to zero at identical times.

Test 133 was conducted with 200 ml of TCE in the wide tray in the short copper pipeline. CH_4 was used as the conservative tracer and C_5F_{12}, C_7F_{14}, and C_8F_{16} were used as partitioning tracers. Figure 12 presents the response curves for Test 133. The dark blue curve represents the conservative tracer. The magenta, orange, and green curves represent C_5F_{12}, C_7F_{14}, and C_8F_{16} respectively and are in order of increasing partition coefficient. Quantification results were calculated for each tracer using the partitioning coefficients determined by PNNL and are presented in Table 11. Partitioning tracer C_7F_{14} produced the best results. Tracer C_5F_{12} has a low partitioning coefficient, 26.9, which allowed very little separation between its response and that of the conservative tracer. Conversely, C_8F_{16} has a high partition coefficient, 124.1, which produces a long tail which takes extended time to reach a concentration of zero.

Additional analysis was done using the known volume of contaminant to back calculate the partitioning coefficient. Using the data gathered during this test, the partitioning coefficient for C_5F_{12} is 8.2, C_7F_{14} is 55.5, and C_8F_{16} is 86.5 each lower than what was determined in the laboratory.

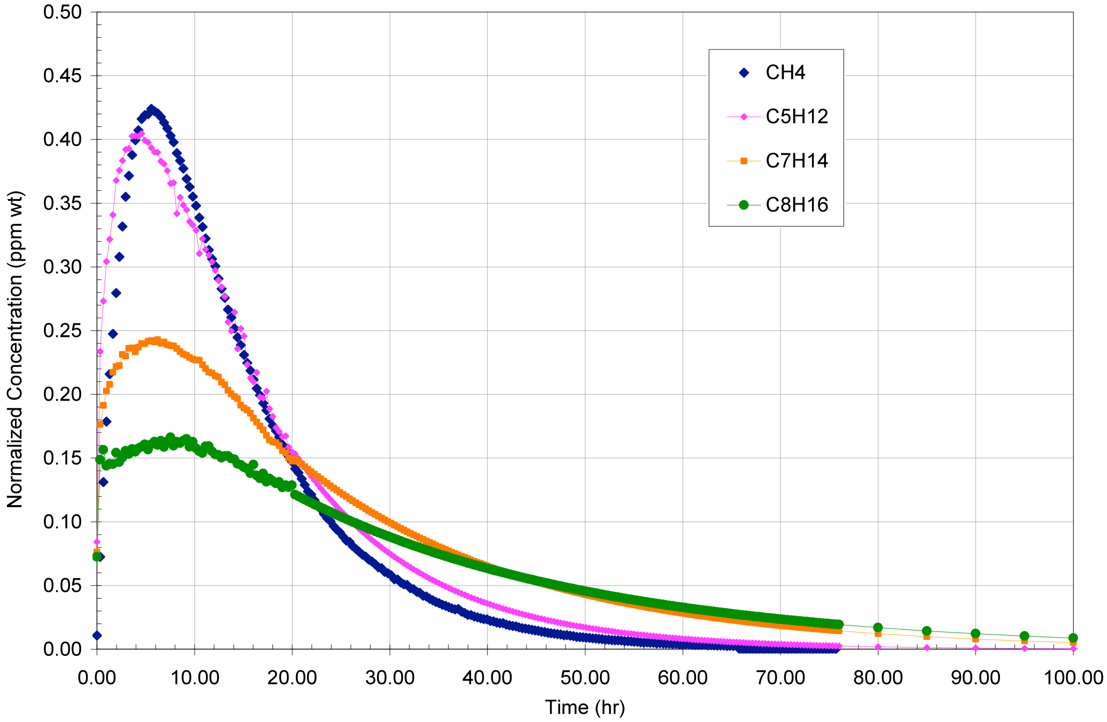


Figure 12. PCUT test results from Pipeline Test 133 with 200 ml of TCE.

Table 11. Volumetric test results of TCE contaminant test.

	Vol (ml)	Error (%)
C_5F_{12}	61.5	-69.2
C_7F_{14}	167.4	-16.4
C_8F_{16}	140.8	-30.0

In addition to testing with TCE as the contaminant, a test was conducted with carbon tetrachloride, CCl_4, as the contaminant. The same conservative and partitioning tracers used in the TCE test were used in the CCl_4 test. Figure 13 shows the results from test 134. As with the TCE, partitioning tracer C_5F_{12} has a low partitioning coefficient of 24.7 in CCl_4, and therefore exhibits very little separation between itself and the conservative tracer. The GC method used for the detection of the tracers also detects the CCl_4 in the gas stream. It was found that the elution time of CCl_4 from the GC column is the roughly the same as the elution time for the C_7F_{14} peak. The CCl_4 peak masked the detection of the C_7F_{14} peak and did not allow the C_7F_{14} to be used for quantification. This does not mean C_7F_{14} may not be used as a partitioning tracer for CCl_4 in other test. To be able to detect the C_7F_{14} in a system that contains CCl_4 would require adjusting the GC method to separate the response of the CCl_4 and C_7F_{14}. The partitioning coefficient for C_8F_{16} in CCl_4 is very large, 243.1, and is indicated by a very long tail in the response curve. This curve is extrapolated using an exponential curve and does not stop detecting the C_8F_{16} in the sample stream until after 200 hours.

Additional work on the actual chemical detection methods will have to be done to configure the GC method to utilize the PCUT technology to detect CCl_4 in pipelines. Tracer C_7F_{14} performed well for TCE and it is expected to perform well for CCl_4 once the GC method is modified to allow it to be detected separated from the CCl_4. Additionally, other compounds can be identified as possible partitioning tracers for pipelines contaminated with CCl_4 and other chlorinated solvents.

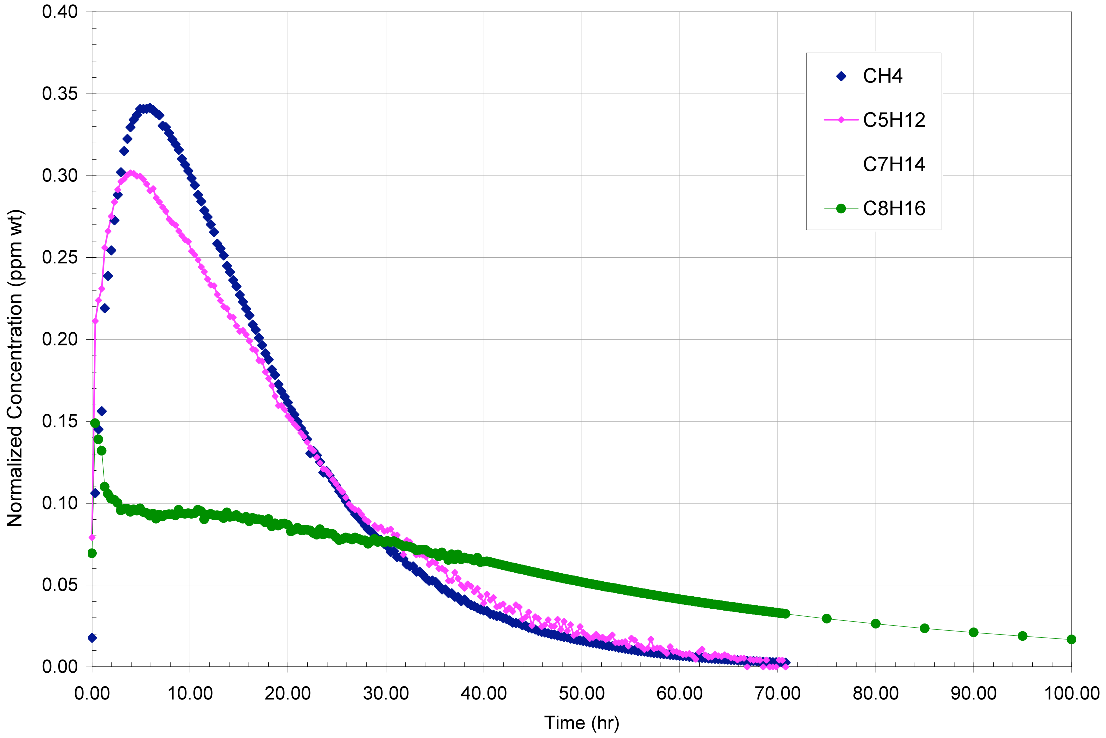


Figure 13. PCUT results from Test 134 using CCl_4 as the contaminant.

Three tests (tests #148, #149, and #150) were conducted using CCl_4 in a dissolved phase as opposed to pure product to determine how the tracers will behave with the lower concentrations of contaminant. In the three tests, the CCl_4 was mixed with soil to produce a slurry which was placed in the trays within the pipeline. Test #148 combined a 100ppm by volume solution of CCl_4 with 504g of soil. Tracer gases were injected in the end of the pipeline and slowly flowed over the slurry mixture. The response of the tracers showed no temporal separation at the output of the pipeline. This indicates that there was no partitioning of the tracers into the contaminant at this low concentration. A second test was run (test #149) with a higher concentration of CCl_4, 800ppm by volume. 800ppmv is the maximum concentration of dissolved phase CCl_4. The results of this pipeline test were similar to the previous in that there was no temporal separation of the tracers. The results of test #149 are shown in Figure 14. The third test (test #150) combined pure CCl_4 with soil to form the slurry. In this case, partitioning is clearly present. See Figure 15. These three tests indicate, in the case of CCl_4, concentrations greater then the dissolved phase limit are required for detection. It also indicates that product can be detected when combined into a slurry form.

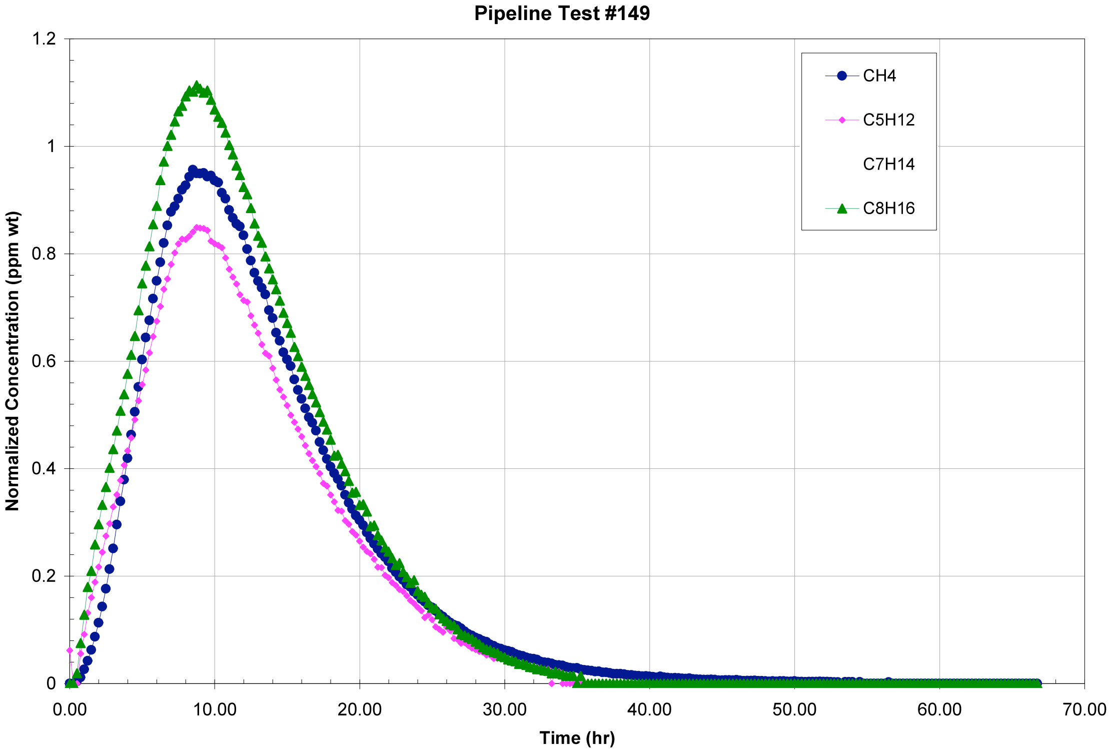


Figure 14. Results of Pipeline Test with a Slurry Contaminant of 800ppmv of CCl_4 and soil.

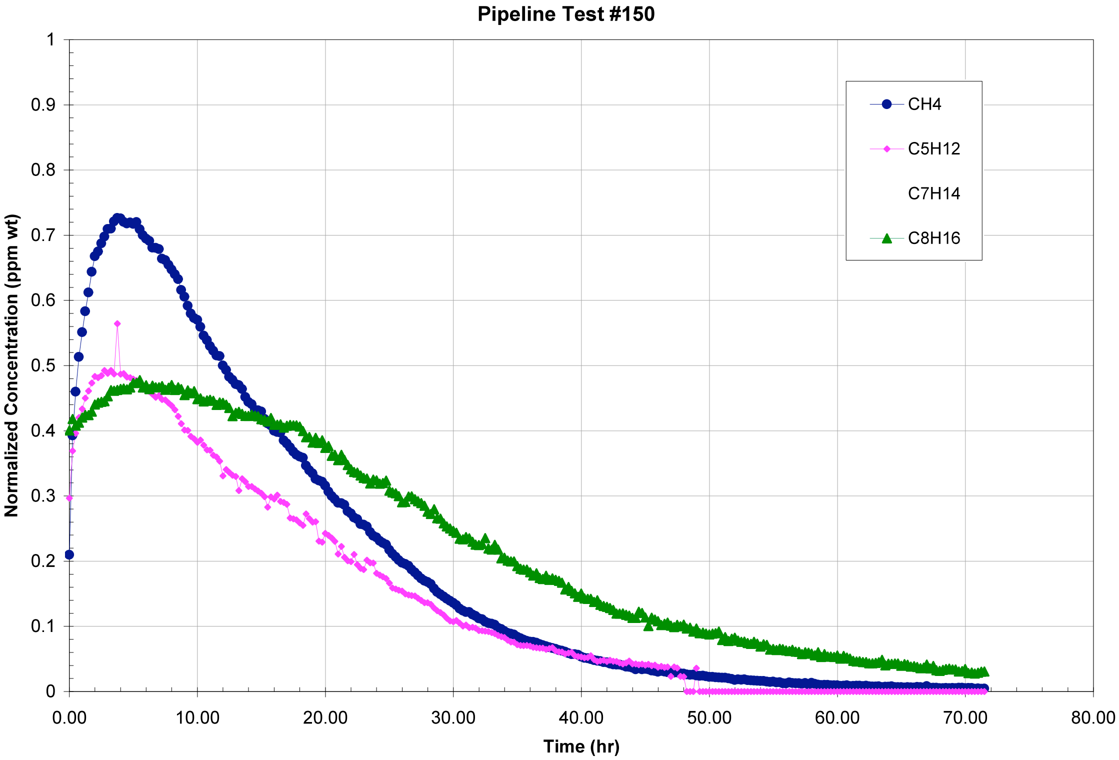


Figure 15. Results of Pipeline Test using CCl_4 and Soil as the Contaminant.

6.7. Tracer Development Studies for Mercury

The tracer studies focused on selecting a tracer for detecting and quantifying heavy metals. Initial testing was conducted with Methyl Mercaptan (CH_3SH), which acts as reactive tracer with the heavy metal of interest, in this case mercury. This reaction is characterized by the consumption of the tracer when in the presence of mercury. By measuring the change in the concentration of the reactive tracer in the pipeline, the presence of the contaminant can be detected.

6.7.1. Chamber Tests

A series of chamber and pipeline tests were conducted to evaluate various reactive tracers for detection of mercury contamination. The chambers were constructed of 2 inch PVC or copper pipe, were seven inches long, and capped at each end. The chambers were flooded with a gaseous mixture of a conservative tracer and the reactive tracer. A vapor sample was removed from the chamber every thirty minutes and analyzed on a gas chromatograph for the concentrations of the conservative and reactive tracer. The ratio of the reactive tracer to the conservative tracer was used to determine the rate of the reaction. Table 12 presents a summary of the tests conducted.

The PVC chamber tests showed extremely small decreases in the ratio of reactive to conservative tracer. This indicated a slow or weak reaction between CH_3SH and the Hg contaminant. The test that indicated the strongest reaction was the copper chamber with no Hg contaminant. After further testing with the copper and CH_3SH, it was determined that CH_3SH had a stronger reaction with the copper chamber than the Hg contaminant. This information forced us to expand our search for a reactive tracer with both a stronger reaction with Hg and a smaller reaction with copper, a common pipeline material.

Two additional tracers were selected for testing. Testing similar to the chamber tests was conducted with the two new tracers. These tests were conducted in 40 ml glass vials. A small amount of Hg (1 to 2 grams) was added to the vial and the airspace flushed with a gaseous sample of each tracer. Samples were again taken every 30 minutes and the concentration of the reactive tracer was used to determine the rate of reaction. Figure 16 shows the results of the Hg vial test with the two additional tracers. Tracer B, Butyl Mercaptan, ($C_4H_{10}S$) reacts quickly with the Hg and the concentration of Tracer B is about zero within 30 minutes of being exposed to the Hg. Tracer C, Ethyl Mercaptan, (C_2H_6S) has a much slower reaction rate with the concentration of Tracer C still detectable after 2 hours of being exposed to the Hg. Additionally, similar tests were conducted placing pieces of copper in the vial to determine the rate of reaction with the copper. For these tests the normalized concentrations were steady indicating minimal to no reaction.

Table 12 – Summary of Testing for Reactive tracer development for Mercury.

Test #	Pipe	Tracer	Contaminant	Method	Notes
235A	7.5" copper pipe	CH3SH	None	Flood with Tracer flow with N2.	Detected both methane and mercaptan. Peaked and decreased within about 2 hours.
235B	7.5" copper pipe	CH3SH	1.5g Hg	Flood with Tracer flow with N2.	Detected methane which peaked and decreased in about 4 hours. No Mercaptan peaks.
235C	7.5" copper pipe	None	10g Hg	Flow with N2	No methane or mercaptan peaks detected.
236	Short copper pipeline	CH3SH	96.8g Hg	Slug with tracer and flow with N2	Detected Methane. Did not detect MM. 91% CH4 recovery.
237	Short copper pipeline	CH3SH	None	Slug with tracer and flow with N2	Detected both CH4 and MM. 105% recovery of CH4, 71% recovery MM
238	Short PVC pipeline	CH3SH	55.1g Hg	Placed HG in center portion of pipeline. Flooded center and last section of pipeline with Tracer B. Sealed for an hour and then began N2 flow from end.	Leaky Pipeline due to poor seal. Unusually high normalized curves.
239	Short PVC pipeline	CH3SH	55.1g Hg in SS cup	Slug with tracer and flow with N2.	Detected both CH4 and MM. 48% recovery for CH4 and 5% recovery for MM.
240	Short PVC pipeline	CH3SH	55.9 g Hg in 2 SS holders	Slug with tracer and flow with N2.	
241		CH3SH	None	Slug with tracer and flow with N2.	
245	50 ft PVC pipeline	CH3SH	50.9 g Hg	Flooded entire pipeline with tracer,.	Place HG at 14ft from exit end of pipeline. Sealed for 1 hour. Started flow at 120-130 ml/min.
246	50 ft PVC pipeline	CH3SH	50.3 g Hg	Slowly injected Diluted Tracer E in to exit end of pipeline.	Place HG at 14 ft from exit end of pipeline. Sealed for about 4 hours. Ran advective flow at 100 ml/min, for 13 hours.
247	50 ft PVC pipeline	C4H10S	32.1g Hg split between two trays placed in same secion of pipe about 4 inches apart.	Flood Method from the pipe head.	Injected tracers and sealed pipeline and let rest over night. Start advective flow at 50ml/min for the test.

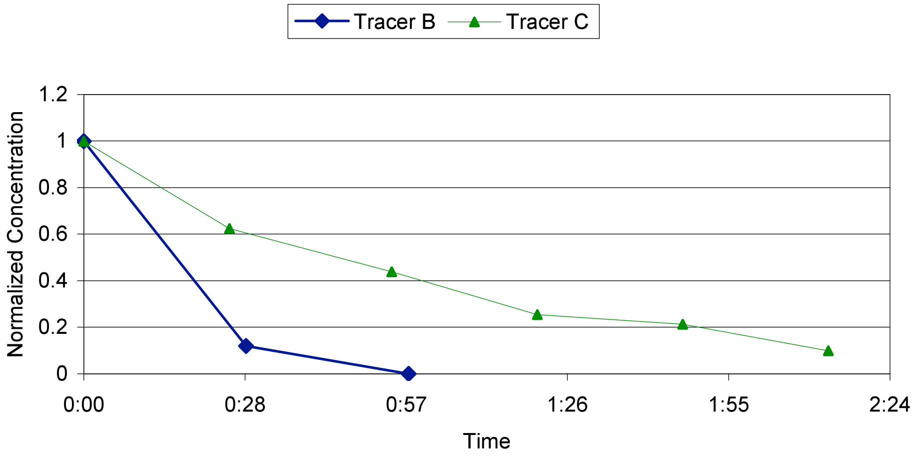


Figure 16. Results of Vial Tests with Tracers B ($C_4H_{10}S$) and C (C_2H_6S) with Mercury.

6.7.2. Pipeline Test

A pipeline test was conducted to demonstrate the ability of the reactive tracer to detect the presence of Hg in a pipeline. $C_4H_{10}S$ was selected for the test because of its fast reaction rate with the contaminant, mercury. A 35.7 ft PVC pipeline was constructed, and 32.1g of Hg contaminant was placed in the pipeline 16.2 feet from the inlet of the pipe. See Figure 17. A gaseous mixture of $C_4H_{10}S$ and a conservative tracer (CH_4) were injected into the inlet of the pipeline. A slow, constant flow of nitrogen was used to flow the tracer mixture through the pipe, over the contaminant, and to the GC for analysis. The conservative tracer is not influenced by the contaminant and indicates how a tracer will react when there is no contaminant within the pipe. The reactive tracer, on the other hand, is influenced by the contaminant and any behavior different then the conservative tracer indicates the presence of contaminant.

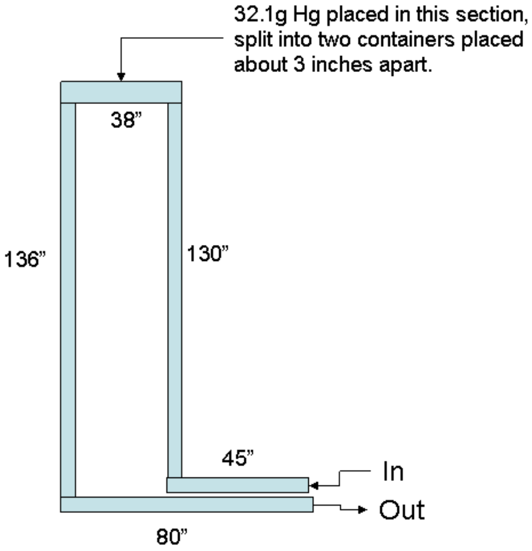


Figure 17. Configuration of Pipeline for the Heavy Metal Tracer Testing.

Figure 18 shows the normalized concentrations of the conservative and reactive tracers as they exit the pipeline over time. Both profiles have similar behavior in that they both start at zero concentration, increase as the slug is pushed through the pipe, and then decrease to zero again as the tracer slug exits the pipeline. What is different between the two, though, is the peak concentration of each tracer. The normalized concentration of the conservative tracer as it exits the pipeline is close to its original concentration producing a normalized concentration of around one. This is as expected because the conservative tracer will not be influenced by the contaminant. The peak-normalized concentration of $C_4H_{10}S$ as is exits the pipeline is much smaller than the original concentration since much of the tracer has reacted with the mercury in the pipeline. This too is expected due to its interaction with the contaminant.

This test shows that $C_4H_{10}S$ acts as a reactive tracer and can be used to detect Hg contamination in pipelines.

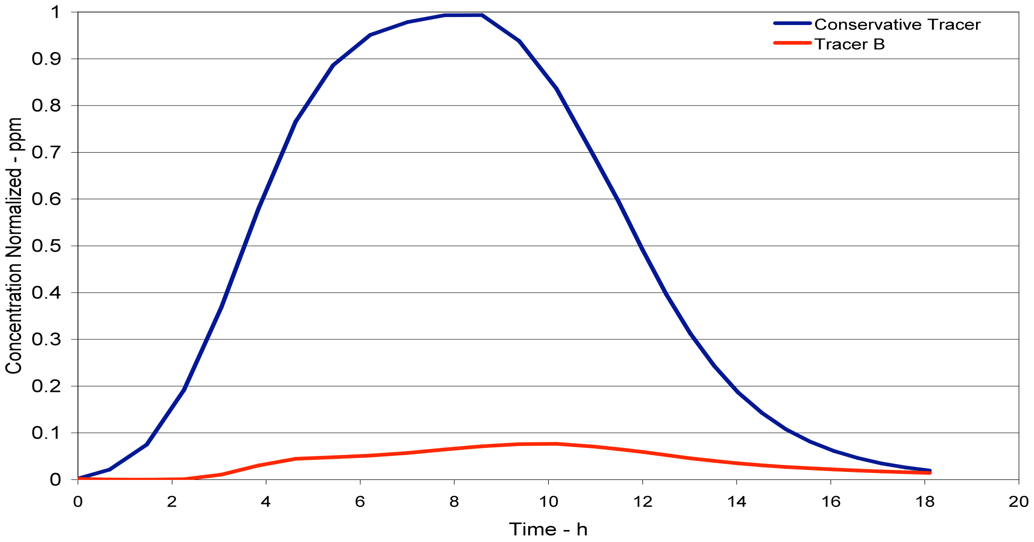
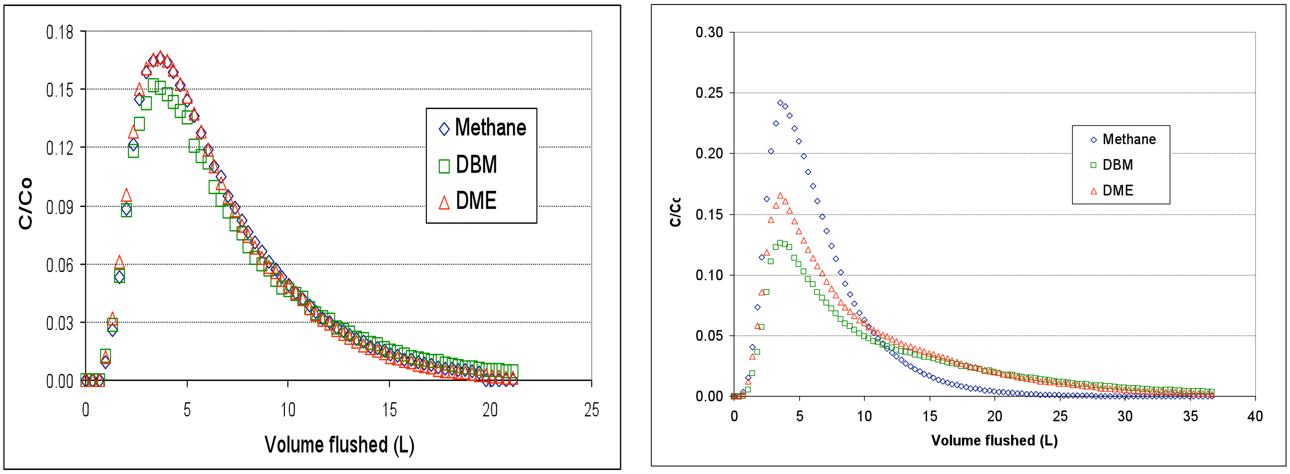


Figure 18. Results of the Pipeline Test Showing the Concentration of the Conservative and Reactive Tracer.

6.8. Tests for Tritium in Contaminated Pipes

In cooperation with Pacific Northwest National laboratory (PNNL), Vista has been working on developing an implementation approach to use the PCUT technology for pipelines contaminated with tritium. The approach developed consists of using both conservative and partioning tracers to accurately determine the liquid volume of water within the pipeline. A portion of the gaseous flow through the pipe that is used to advect the tracers is split off and condensed to determine the tritium concentration of the moisture vapor. The tritium concentration from the moisture vapor is then multiplied by the volume of water in the pipe (determined from the PCUT method) to calculate the total amount of tritium in the pipeline. A series of three pipeline tests were conducted and the results all indicated that water concentrations could be determined quite accurately (within about 5%) and the tritium concentrations can also be accurately assessed at around 15%. The percent error on the total tritium volume for all three tests was approximately 10% on average. Figure 19 presents the tracer elution curves for one of these tests.



A B

Figure 19. Elution Tracer Curves for Tritium Pipeline Tracer Test. A = Normalized Effluent Tracer Concentration for a Clean Pipeline Test; B = Normalized Effluent Tracer Concentration for a Contaminated Pipeline Test.

6.9. Test Duration

Most of the demonstration tests have been conducted at slow advection flow rates and therefore slow advection velocities. To demonstrate that PCUT can be implemented in a useful operational period, the advection flow rate was increased by a factor of a little less than 20 over most of the previous tests conducted. Figure 8, shown on page 20, illustrates the results of advecting a conservative tracer along a 116-ft, 2-in.-diameter PVC pipe at 175 ml/min. The time of arrival of the tracer was less than 4 h. By comparison, it took over 60 h to fully recover the conservative tracer when the test was conducted at the flow rate of most previous demonstration tests (i.e., ~10 ml/min.) The accuracy of the measurement was determined by estimating the length of the pipe from the time of arrival of the tracer. The length of the 116-ft pipe was estimated to be 119 ft (i.e., a 2.5% error). It is clear from these tests that the advection velocity could be further increased.

7. *Numerical Modeling*

Numerical modeling was utilized on the project to develop a tool that could be used to design longer and more complex experiments than could be practically set up in the laboratory. In addition the numerical modeling could be used to simulate field cases and evaluate different response signatures to interrupt results and also better design experiments. To perform the modeling a Finite Element Groundwater flow code, FEFLOW, was selected. As a groundwater flow code, FEFLOW already has the advective transport equation, dispersion effects and chemical sorption on the soil particles which is numerically the same as partitioning. The numerical models of the short pipe have been assembled and results of the conservative tracer time histories match well with those obtained during the Phase I testing. Figure 20 presents the comparison between the numerical model results and the actual measured conservative tracer time history from the Phase I demonstration test under the same flow field. Once the appropriate coefficient of conductivity was obtained using the conservative tracer, then a sorption term was added to represent the partitioning behavior. The coefficient of sorption was adjusted until the two curves matched. The resulting comparison of the partitioning behavior of C_7F_{14} with contamination present is presented in Figure 21. The fit is not as strong as that obtained for the conservative tracer due to some unique characteristics of the model. Due to the relative percentage of the pipe length that the initial tracer flood incorporates, a portion of the tracer slug arrives at the pipe exit (analytical instrument) very quickly without having experienced sufficient time to partition into the contaminant.

In the numerical model, the sorption characteristics occur instantaneously and therefore capture some of the tracer and delay the peak as shown in Figure 21. This is different from what occurs in the real pipe, since the leading edge of the tracer slug reaches the contamination and is then swept to the exit without sufficient partitioning time. This causes the tracer to arrive quicker for the actual test tests than the numerical. As was shown for the long pipe, this same characteristic does not occur since the tracer slug is moving at a slow fixed speed before any contaminant is reached and therefore has uniform exposure time over the contaminated region.

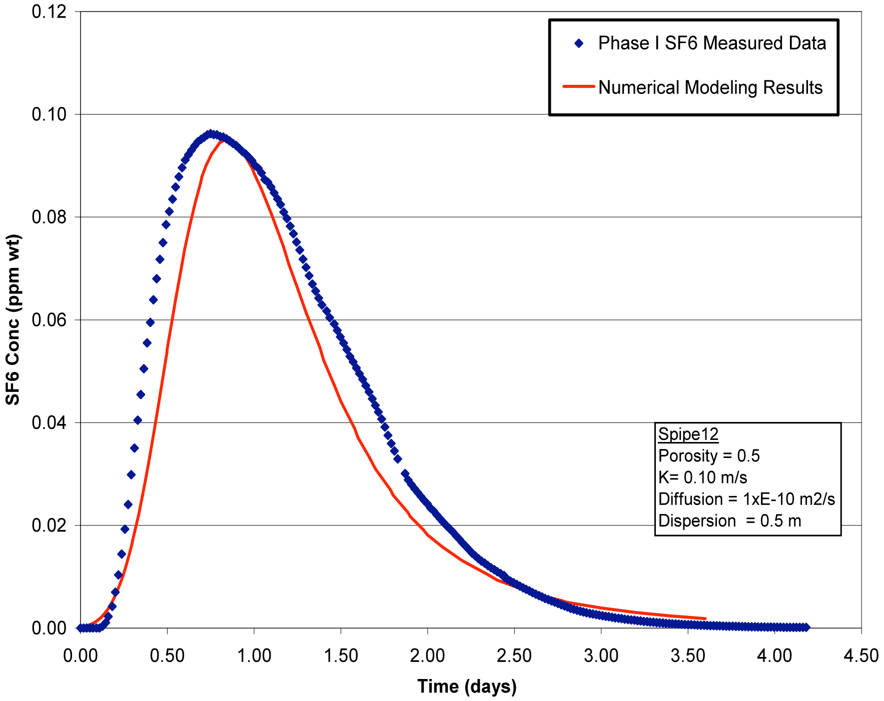


Figure 20. Comparison of the numerical modeling results and actual Phase I results for the short pipe from Phase I for the Conservative Tracer.

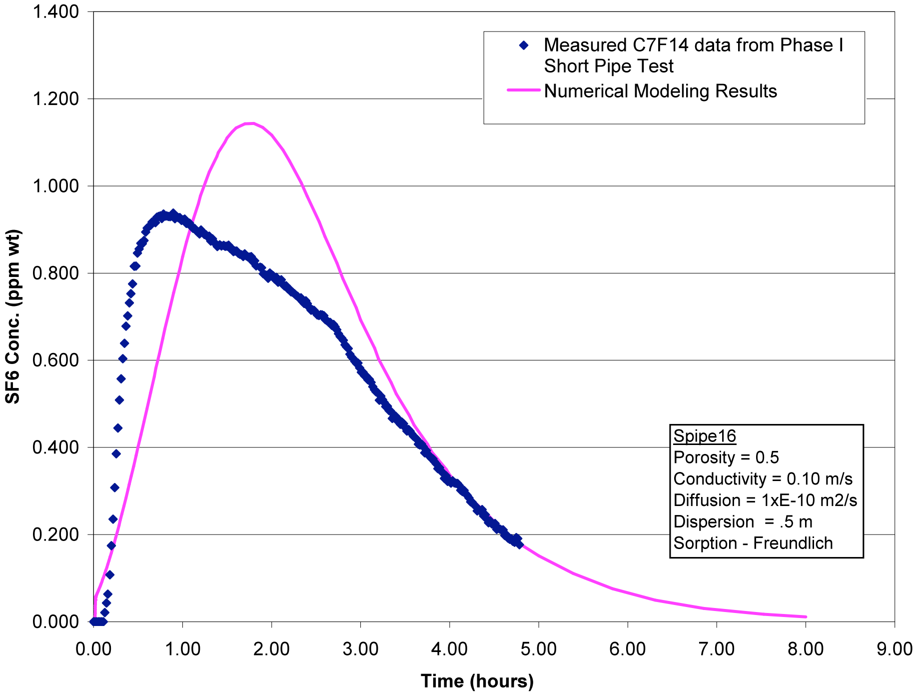


Figure 21. Comparison of the numerical modeling results and actual Phase I results for the short pipe from Phase I for the Partitioning Tracer (C_7F_{14}).

Using the baseline information developed from the short pipe modeling, the same model parameters were used to model the results from Pipe Test # 7 which used a long pipe. The same coefficients worked nicely producing a good fit between the model results and the experimental results. The long pipe was a challenge to model due to the long and thin nature of the configuration. The finite element code was able to handle the configuration and produce correct results with a reasonable time step.

The comparison between the model and experimental results for the long pipe configuration is presented in Figure 22 and Figure 23. Both fits are quite strong and demonstrate the ability to model the tracer movement in pipes. This allows the numerical models to be used as planning tools for future deployments of the technology. Other pipeline models can be easily created to evaluate how the tracers might react under various different flow conditions and pipe configurations. With the modeling capability an operational design capability exists.

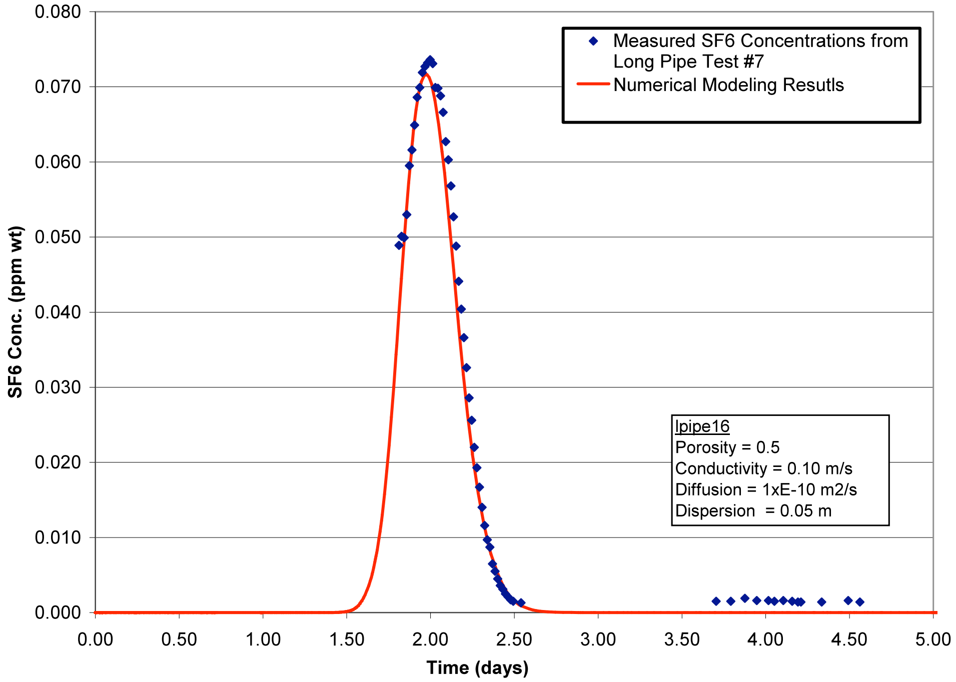


Figure 22. Comparison of the numerical modeling results and actual SF_6 *results for a long pipe test (Pipe Text #7).*

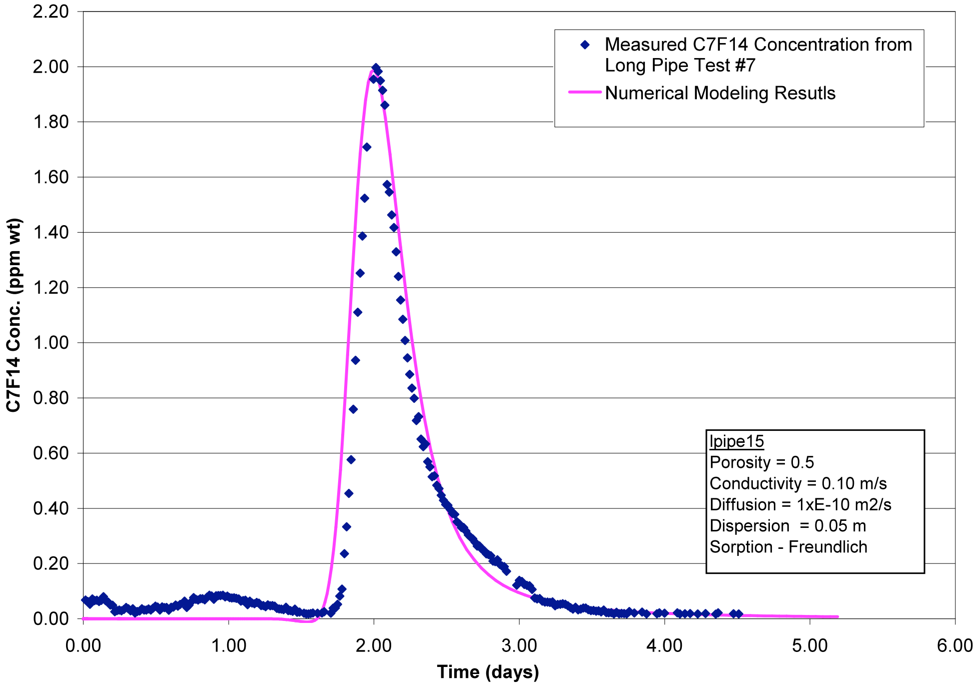


Figure 23. Comparison of the numerical modeling results and actual C_7F_{14} *results for a long pipe test (Pipe Test #7).*

8. Summary and Conclusions

VISTA ENGINEERING TECHNOLOGIES, L.L.C., has developed a new, minimally invasive technology called PCUT (Pipeline Characterization Using Tracers) for detection, location and quantification of residual contamination in pipes and ducts using gaseous tracers. PCUT can be used in support of deactivation and decommissioning (D&D) of piping and ducts that may have been contaminated with hazardous chemicals, such as chlorinated solvents, petroleum products, heavy metals, or radioactive materials. The same technology can be used to detect, locate, or quantify mold in building ductwork, explosives and other dangerous or hazardous materials in ductwork, storage containers or enclosures, and residual contamination on mechanical parts or process systems in support of industrial cleaning.

PCUT typically uses varying combinations of two types of tracers for detection, location, and quantification: conservative and interactive tracers. The *conservative* tracer does not interact with the contaminant, is fully recovered, and is used as a reference, while the *interactive* tracer uniquely changes concentration in the presence of a contaminant. There are two categories of interactive tracers. The *partitioning interactive* tracer interacts with the contaminant by partitioning into and then out of the contaminant. The *reactive interactive* tracer reacts with the contaminant and permanently changes concentration after coming in contact with the contaminant.

The pipe or duct is first inundated with both the conservative and interactive tracers and then an inert gas, such as nitrogen, is used to advect the tracers to the extraction point at a known flow velocity where the concentration curves are measured with an on-line gas chromatograph or other analytical instrument. Detection, location, and quantification of the contamination are accomplished from the amplitude or time of arrival of the concentration curves.

The advantages of PCUT are that:

- It is a minimally invasive, remote method for inspection of potentially contaminated pipes and ducts.
- Tracer movement is not impacted by pipe diameter or configuration.
- There are no moving parts or equipment that must be introduced into or may get stuck in the pipe.
- There is no sparking potential or ignition source with gaseous tracers.
- There are no decontamination requirements for the inspection equipment.

The laboratory experiments conducted to date have been extremely successful and clearly show that PCUT can readily detect the presence of liquids and semi-solid contaminants of very different natures in terms of vapor pressures. The volumes detected have ranged from 1.5 liter in a 23-foot pipeline to 300 ml in a 116-foot pipeline. This shows that the PCUT approach is very sensitive, even with dried substances and low vapor pressure substances (e.g., the dried glue). The PCUT approach can also accurately quantify the volume of the contaminant (within 10%). The same PCUT technique can also be utilized to accurately estimate the location of the contamination within the pipeline (within 10%). Demonstration tests indicate that PCUT should be able to be implemented operationally over a period of several hours and can detect and locate more than one region of contamination in the pipe.

It is equally clear from the results of the demonstration tests that if appropriate tracers are available or can be developed for the contaminants of interest, this remote sensing technique will work and will be very accurate. Currently, the PCUT approach is ready for demonstration in pipes contaminated with petroleum products, chlorinated solvents such as TCE, PCE and CCl_4, some heavy metals such as mercury, and tritium. PCUT is also ready for demonstration in other applications like ducts, containers, and enclosures. Additional tracers are under development for other heavy metals and radionuclides of interest. If appropriate tracers are available, the PCUT approach should be able to address any pipeline characterization need and has application in other man-made environments.

It is the intention of Vista Engineering Technologies to commercialize PCUT for use in D&D activities at DOE and other industrial sites after the Phase II effort based upon the success of the Phase I effort. In general discussions with personnel from the Hanford and SRS sites, we have received sufficient interest concerning the technique that we believe there are important real world market for this technique. Dr. Maresca, as Vice President of Vista Research, and now as President of Vista Engineering Technologies, has successfully commercialized many detection and measurement technologies for use in pipelines as described in Section 4.4 and 4.7. It is anticipated that a service-based product will be derived out of the Phase II effort.

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