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# Estimating Carbon Tetrachloride and Total Volatile Organic Compound Mass Remaining in Subsurface Disposal Area Pits

*A. Jeffrey Sondrup*
*Eric C. Miller*
*Edward H. Seabury*
*Nick Josten*

Idaho Completion Project

Bechtel BWXT Idaho, LLC

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A. Jeffrey Sondrup
Eric C. Miller
Edward H. Seabury
Nick Josten

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Idaho Completion Project
Idaho Falls, Idaho 83415

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# ABSTRACT

The purpose of this study was to provide an estimate of the mass fraction of carbon tetrachloride and volatile organic compounds remaining in the waste disposal pits at the Subsurface Disposal Area. Both Operable Unit 7-08 and Operable Unit 7-13/14 could use this information for estimating risk and making remediation decisions. The estimate initially was based on a comparison of the mass of volatile organic compounds originally buried at select locations in the Subsurface Disposal Area to the mass that currently remains at the same location, which is based on neutron-gamma logging of probeholes. However, a defensible estimate was not possible because of the inability to quantify uncertainty around the original chlorine mass per probehole estimate and the inadequacy of the neutron-gamma logging tool calibration function. A revised strategy also was unsuccessful because of heterogeneity of waste and inability to develop a tool response function capable of predicting all observed neutron-gamma data. Finally, for subsurface modeling purposes, an alternative and simpler approach was used to develop a plausible approximation for the mass fraction of volatile organic compounds remaining that did not rely on nuclear logging data. Although the uncertainty of the results is not known, there was sufficient basis to make a recommendation that 50% volatile organic compound mass remaining be used as a starting point for the modeling and 75% be considered an upper bound. It is recommended, however, that the sensitivity of any modeling result to these estimates be evaluated. Since more precise estimates will almost certainly involve nuclear logging data, any further attempts to estimate the fraction of remaining mass should in all probability involve redesigning the neutron-gamma tool and/or performing a comprehensive calibration to conditions and materials that are more likely to be encountered in the waste pits. Alternatively, a model-based tool response could be developed for more realistic conditions.

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# ACRONYMS

| | |
|---|---|
| $CCl_4$ | carbon tetrachloride |
| INEEL | Idaho National Engineering and Environmental Laboratory |
| MCNP | Monte Carlo N-Particle |
| OU | operable unit |
| RFP | Rocky Flats Plant |
| SDA | Subsurface Disposal Area |
| VOC | volatile organic compound |
| VVE | vapor vacuum extraction |

# Estimating Carbon Tetrachloride and Total Volatile Organic Compound Mass Remaining in Subsurface Disposal Area Pits

## 1. INTRODUCTION

### 1.1 Background

The Radioactive Waste Management Complex is located in the southwest portion of the Idaho National Engineering and Environmental Laboratory (INEEL) and was established in 1952 as a disposal site for solid low-level radioactive waste generated by the INEEL and other U.S. Department of Energy operations. It encompasses approximately 716,294 $m^2$ (177 acres) and consists of three main areas: (1) the Subsurface Disposal Area (SDA), (2) the Transuranic Storage Area, and (3) an administrative area. The SDA comprises individual pits, trenches, soil vaults, and an aboveground pad (see Figure 1).

From 1952 to 1970, hazardous, radioactive, and mixed waste from a variety of sources was buried in shallow pits and trenches at the SDA, including waste containing volatile organic compounds (VOCs). Historical records indicate that the vast majority of all waste containing VOCs at the SDA was associated with organic sludge generated at the U.S. Department of Energy Rocky Flats Plant[a] (RFP) Building 774 in Colorado (Vigil 1990). This organic sludge was later coded at the INEEL as Content Code 3 organic waste to distinguish it from other types of waste from RFP Building 774 and subsequently referred to as Series 743 waste.

Series 743 waste primarily consisted of used oils and degreasing agents such as carbon tetrachloride ($CCl_4$), 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene (Clements 1982). At RFP, the oils and degreasing agents were mixed with calcium silicate to reduce free liquids and form a very thick greaselike material, which was typically double bagged and placed into drums before shipment.

From October 1966 through November 1970, approximately 9,691 drums of Series 743 waste were buried in the SDA (Miller and Varvel 2001). Miller and Varvel (2001) reported that in the early 1970s, 1,015 Series 743 waste drums were retrieved from SDA Pits 11 and 12, leaving 8,676 buried waste drums. Their report estimated that these 8,676 drums contained 1.1E+6 kg of VOCs, 8.2E+5 kg of which was $CCl_4$.

The VOCs from Series 743 waste have been released from the pits in which they were buried and have migrated into the surrounding environment. Some VOCs were likely released in the short term following failure of waste packaging associated with drum dumping and compaction procedures. Since that time, other drums have corroded, and VOCs are slowly diffusing through the plastic bagging (Liekhus and Peterson 1995). Monitoring data show that VOCs are present in soil, soil gas, and perched water, and low but significant levels have been detected in the underlying Snake River Plain Aquifer, approximately 183 m (600 ft) below land surface (Koeppen et al. 2004). Although it is widely accepted that VOCs have migrated into the surrounding environment, no quantitative estimates have been made concerning the mass of VOCs that remain in source pits in which they were buried. Estimating the mass of $CCl_4$ and other VOCs remaining in source pits is important in supporting a variety of decisions relating to future SDA remediation.

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a. The RFP is located 26 km (16 mi) northwest of Denver Colorado. In the mid-1990s, it was renamed the Rocky Flats Environmental Technology Site. In the late 1990s, it was again renamed to its present name, the RFP Closure Project.

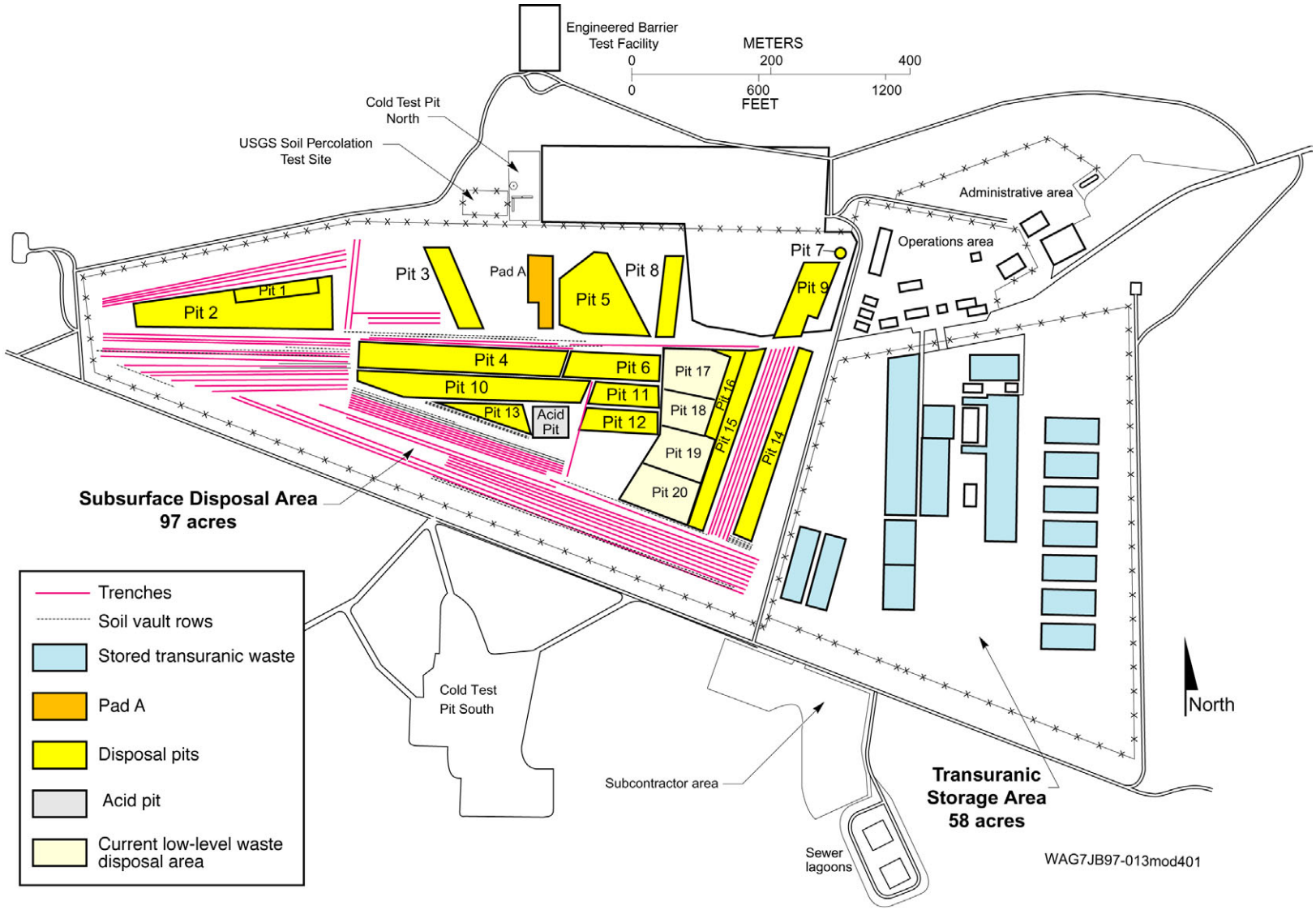


Figure 1. Map of the Radioactive Waste Management Complex showing the location of the Subsurface Disposal Area.

## 1.2 Purpose and Scope

The purpose of this study was to provide an estimate of the mass of $CCl_4$ and total VOCs remaining in the waste disposal pits at the SDA. Both Operable Unit (OU) 7-08 and OU 7-13/14 could use the results of this study for making remediation decisions. Specific uses for the estimate were to:

- Provide data to support computer modeling to determine preliminary remediation goals and the remediation timeframe for Organic Contamination in the Vadose Zone (OU 7-08)
- Provide data to support computer modeling to assess baseline and residual risks for the SDA waste pits and trenches (OU 7-13/14)
- Determine if in situ pretreatment is indicated for grouting; retrieval or capping; and, if necessary, the type of pretreatment (e.g., thermally enhanced vapor vacuum extraction [VVE], shallow VVE, or disruption of waste with VVE)
- Evaluate safety-significant equipment associated with VOC-bearing waste for all assembled alternatives (with or without pretreatment)
- Prioritize waste retrieval efforts and support development of design requirements (engineering measures and personal protective equipment)
- Develop preliminary remediation goals for OU 7-13/14 source-term control relevant to VOCs in conjunction with other contaminants of concern
- Identify preliminary cap design characteristics (e.g., permeability, venting, and gas collection layer).

Another purpose of this study was to provide general recommendations for future activities that may be considered to more rigorously estimate the $CCl_4$ and total VOC mass remaining in SDA pits.

Although the various purposes can tolerate differing levels of uncertainty, the original goal was to get the best estimate possible (i.e., least amount of uncertainty) given the available data and resources.

# 2. VOLATILE ORGANIC COMPOUND MASS REMAINING IN SUBSURFACE DISPOSAL AREA PITS

## 2.1 Qualitative Indicators of Volatile Organic Compound Mass Using Nuclear Logging Data

Before this effort, there had been no formal attempt to estimate of the amount of VOCs remaining in the SDA source pits. However, Magnuson and Sondrup (1998) demonstrated with a computer model and a reasonable parameter set that, before VVE operations, the subsurface $CCl_4$ plume could have been created by releasing only about one-fourth of the $CCl_4$ inventory estimated by Miller and Varvel (2001). The model even included a substantial loss of gas-phase $CCl_4$ to the atmosphere. This suggests that a large portion of the original inventory may remain in the pits. This is discussed in more detail in Section 4. Other sources of evidence indicate that a substantial amount of VOCs remains in the source and continues to be released. The evidence includes but is not limited to:

- The inability of the VVE system[b] to reduce vapor concentrations near VOC source areas (Sondrup, McMurtrey, and Harvego 2003)

- The VVE system has removed approximately the amount of VOCs estimated to be in the vadose zone before operations began, yet significant VOC contamination remains in the vadose zone

- Concentrations of VOCs in vapor samples collected from Type B vapor probes installed in the waste pits indicate the presence of liquid-phase VOCs (Myers et al. 2004)

- Observations of intact plastic bags containing "fresh-looking" sludge during excavation of waste in Pit 9 as part of the Glovebox Excavator Method Project.

Although each point of evidence is a strong indication that VOCs remain in the source area, they do not provide information to help quantify the amount remaining.

## 2.2 Preliminary Quantitative Estimates of Volatile Organic Compound Mass Remaining in Subsurface Disposal Area Pits

### 2.2.1 Type A Probe Installation and Neutron-Gamma Probe Logging

In 2000 and 2001, more than 100 Type A probes were installed through the waste in Pits 4, 5, 9, and 10 at the SDA. Type A probes are sections of steel pipe fitted with a drive point, installed through the waste zone down to the first basalt layer at approximately 6–8 m (20–25 ft) below land surface. Nuclear logging instruments are lowered into the Type A probes to obtain nuclear data from the subsurface. The Type A probe data, generated by the nuclear logging instruments, were used to select locations for other types of probes.

Another purpose of Type A logging was to gather data to estimate the amount of chlorine and, thus, chlorinated solvents remaining in the waste pits. A neutron activation instrument for detecting prompt gamma rays from chlorine-35, an indicator for chlorinated hydrocarbons, was used to take readings in several Type A probes located in the Series 743 sludge focus area, a region of Pit 4 known to contain a significant amount of Series 743 waste (see Figure 2). The ability of neutron-gamma logging to provide in situ information regarding distribution and relative amounts of chlorine had been demonstrated, but it had not been used in a quantitative sense to estimate mass.

Figure 3 shows the 1,165-keV chlorine capture gamma count rate results from neutron-gamma logging performed along a transect of Type A probes shown in Figure 2. (Lengths of the vertical lines in Figure 3 indicate probe depths.) Readings were taken at 15.2-cm (6-in.) intervals for the total depth of each probe. Results show a band of high-chlorine content that agrees with the disposal locations shown in Figure 2.

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b. The VVE system employed at the SDA is operated by OU 7-08 to remediate the VOC contamination currently in the vadose zone (outside the pits) and to prevent further migration of VOCs toward the aquifer.

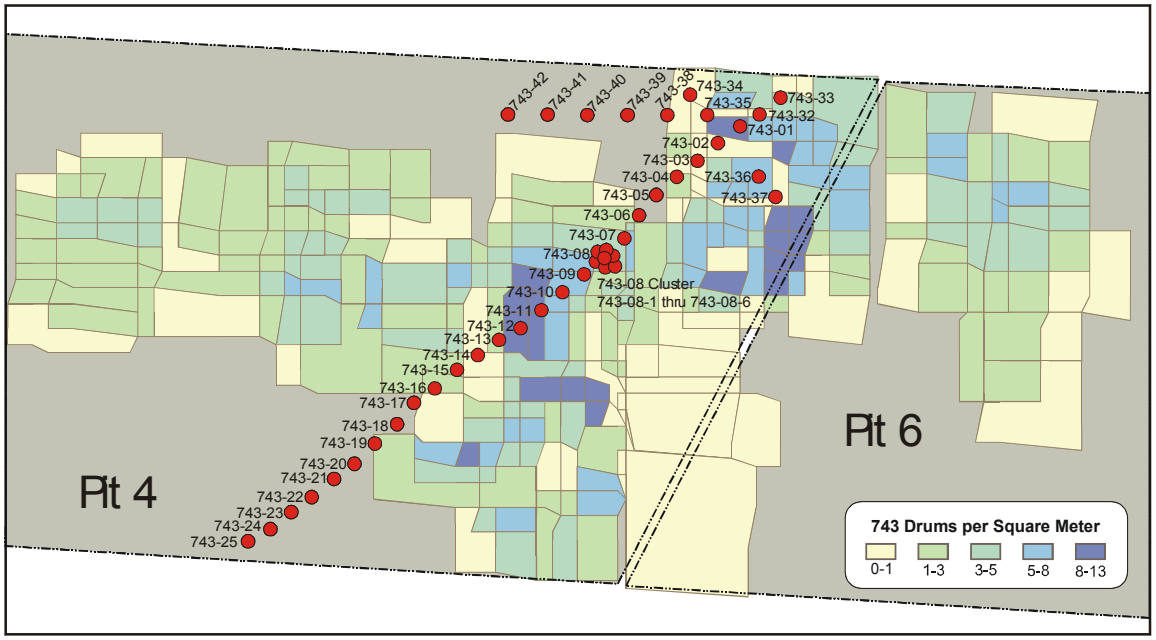


Figure 2. Series 743 drum burial density and Type A probe locations in the Series 743 sludge focus area of the Subsurface Disposal Area.

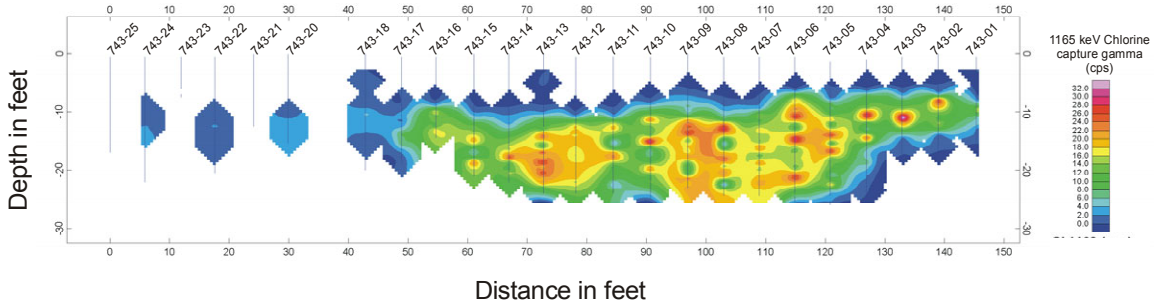


Figure 3. Cross section of 1,165-keV chlorine capture gamma count rate data along the Type A probe transect in the Series 743 sludge focus area.

### 2.2.2 Preliminary Estimate of Remaining Volatile Organic Compound Mass Using Historical and Neutron-Gamma Logging Data

In March 2003, a draft report was written to provide a quantitative estimate of the mass of $CCl_4$ and total VOCs remaining in SDA pits. Although this draft report provided estimates of $CCl_4$ and VOC mass remaining in the SDA, enough technical uncertainty existed in the estimates that the report was not finalized. The methodology used in the draft report was based on understanding both the historical mass of $CCl_4$ and VOCs buried in the SDA and the current estimates based on neutron-gamma logging of Type A probes in the Series 743 sludge focus area (Josten 2002, Appendix A). An average original chlorine mass per probehole based on historical data was compared to an average "current" chlorine mass per probehole based on neutron-gamma logging to yield the fraction of chlorine remaining in the subsurface. Since it was assumed the total mass of chlorine originally buried (i.e., unaltered sludge) was known, it was possible (making certain assumptions) to estimate the absolute mass of $CCl_4$ and total VOC mass that remain buried in the SDA.

***2.2.2.1 Estimate of Volatile Organic Compound Mass in Unaltered Sludge.*** Estimating the $CCl_4$ and VOC mass per probehole originally buried required an estimation of both the average original chlorine mass per drum buried in the region of interest and the burial density (i.e., volume of Series 743 waste per unit volume). Historical records were available to estimate the number of Series 743 drums buried, the total weight of Series 743 drums buried, and their burial densities within the region of interest. In addition, previous work (Miller and Varvel 2001) established a defensible methodology by which drum weights and volumes could be used to estimate chlorine mass fractions within Series 743 waste. With this information, a reasonable estimate of the average chlorine mass per probehole within the region of interest was calculated.

***2.2.2.2 Estimate of Volatile Organic Compound Mass from Neutron-Gamma Logging.*** Estimates of the remaining $CCl_4$ and VOC mass per probehole were calculated from the neutron-gamma logging data by assuming that chlorine was homogeneously dispersed throughout the volume surrounding the probehole. The neutron-gamma 1,165-keV chlorine data, measured in counts/second, were converted to chlorine concentrations in weight percent by means of a tool calibration function (see Figure 4). This calibration function was developed by GTS Duratek (the logging subcontractor) based on measurements in a brine solution containing up to 25 wt% chlorine. The effective volume of investigation for each logging measurement was assumed to correspond with a 15.2-cm-thick (6-in.-thick) annulus extending outward 30 cm (1 ft) from the center of the probe casing. Each 6-in.-thick annulus describes a subcylinder (see Figure 5). The chlorine weight percent of each subcylinder was estimated from the count rate measurement for the subcylinder and the calibration function. The chlorine mass for each subcylinder was calculated by multiplying the chlorine weight percent by the subcylinder density (assumed soil and/or waste density of 1.7 g/cm$^3$) and volume. The total chlorine mass for each probehole was then obtained by summing the chlorine mass for all subcylinders (see Figure 5). (In Figure 5, the depth of the probehole was 5.5 m [18 ft], and measurements were taken every 15.2 cm [6 in.].)

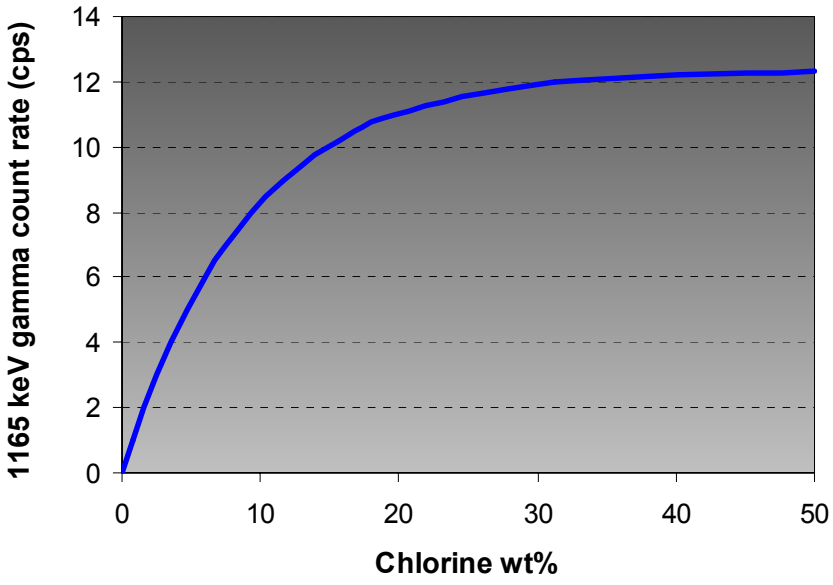


Figure 4. GTS Duratek neutron-gamma tool calibration function for the 1,165-keV chlorine capture gamma.

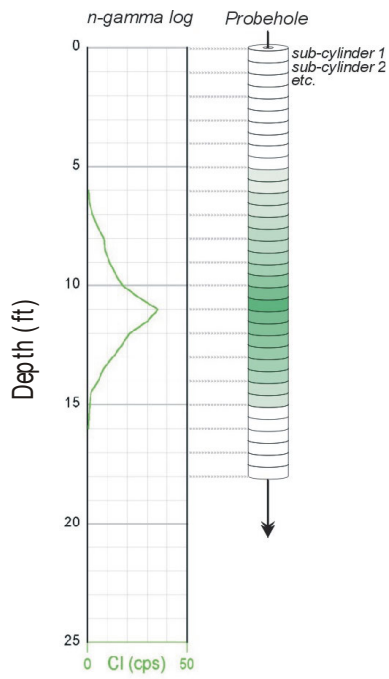


Figure 5. The 1,165-keV chlorine capture gamma count rates for Probehole 743-03.

### 2.2.3 Conclusions from Preliminary Mass Estimates

A comparison of the original chlorine mass estimate based on historical data and the current mass estimate based on neutron-gamma logging indicated that approximately 50% of the original $CCl_4$ and VOC remains in the SDA pits. However, attempts to apply rigorous statistical confidence intervals to this number were unsuccessful because of uncertainties for both the historical estimates as well as for current estimates using neutron-gamma logging results. Estimating rigorous confidence intervals around the average historical chlorine mass per probehole was precluded by the inability to adequately quantify both spatial variability of drum burial and possible distribution of drum densities around their respective mean values. The only conclusion was that probehole data associated with smaller burial volumes were likely better data points that those associated with large burial volumes.

Estimating rigorous confidence intervals around the average neutron-gamma logging results was not addressed, given the inability of the calibration-based tool response function (see Figure 4) to adequately explain the observed data. Figure 6 reveals that a significant number of the observed count rates exceeded the theoretical maximum count rate predicted by the calibration-based function. (In Figure 6, more than 800 measurements were nondetects [not shown], most of them in the overburden or in probeholes where it is believed no Series 743 sludge was buried.) Based on both the lack of rigorously quantified uncertainty around the original chlorine mass per probehole estimate and the inadequacy of the neutron-gamma logging tool calibration function, a quantitative estimate of remaining $CCl_4$ and VOC mass was not defensible.

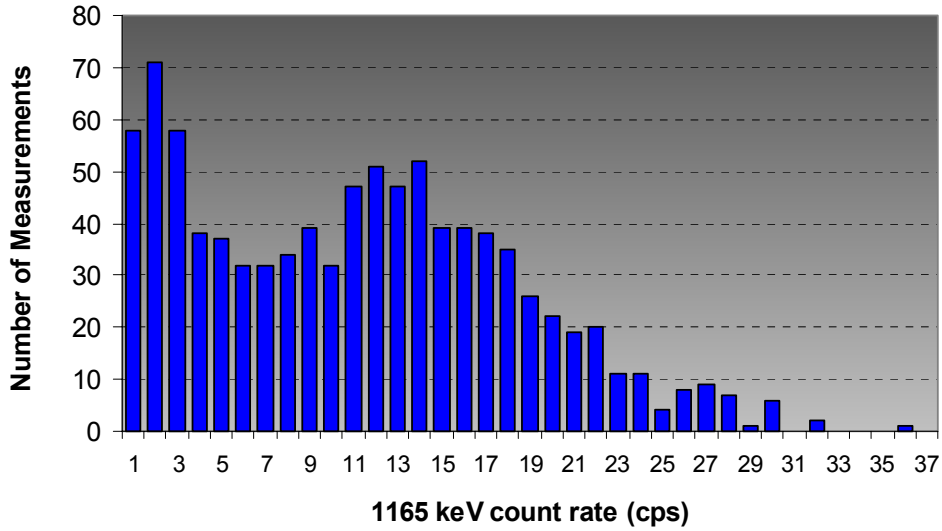


Figure 6. Histogram of observed 1,165-keV chlorine capture gamma count rates for logging measurements made at the Series 743 sludge focus area.

## 2.3 Revised Strategy for Quantifying Volatile Organic Compound Mass Remaining

As previously noted, two significant technical challenges in defensibly quantifying VOC mass remaining in the SDA became apparent. These challenges were the lack of quantifiable uncertainty around the historical chlorine mass per probehole estimate and the inadequacy of the neutron-gamma logging tool calibration function.

In an effort to address the lack of quantifiable uncertainty around the historical VOC mass estimate, both the spatial variability of drum disposal locations and the drum density distribution within those locations were evaluated. It was concluded that these constraints would be difficult to address, and no clear strategy was apparent to overcome them. Therefore, rather than relying upon spatial variability and drum density, the estimate of remaining VOC mass could be made by determining whether an individual neutron-gamma measurement was taken within Series 743 sludge versus another medium (e.g., soil or debris). If it could be determined that a measurement was made in sludge, the chlorine concentration of that measurement could be compared to the average chlorine concentration of unaltered sludge.

### 2.3.1 Distinguishing Measurements Made within Sludge from Another Media

Various strategies were established to distinguish measurements of sludge from nonsludge. The most promising strategy was based on the relatively high concentration of calcium contained within the Series 743 waste form. Because the neutron-gamma probe was not specifically calibrated for calcium, a strategy to evaluate calcium-to-silicone ratios was used essentially to normalize calcium counts to a common element (i.e., silicon) known to exist in both sludge and nonsludge (e.g., soil). In typical soil, the ratio of silicon to calcium is approximately 3. The ratio of silicon to calcium in Series 743 sludge has been estimated to be approximately 0.3. This order-of-magnitude difference was used as an initial basis to determine whether any given observation was sludge or nonsludge; however, in practice, such a clear distinction was not observed. This has been conjectured to be a function of the very high gamma signal

emitted in a sludge observation, which is thought to dominate any other signal (e.g., silicon and calcium). Other identified strategies (e.g., evaluating aluminum counts) to distinguish sludge from other media likewise proved ineffective. As a result, it was assumed that any measurable chlorine would represent Series 743 sludge.

### 2.3.2 Development of a Model-Based Tool Response Function within Series 743 Sludge

As previously noted, the calibration-based tool response function was not able to explain all experimental observations (specifically those above a count rate of approximately 12 cps). As a result, a quantitative estimate of VOC and $CCl_4$ mass remaining in SDA pits using the calibration-based tool response function was not possible. Several strategies were evaluated in order to develop a more robust and appropriate tool response function that could reinterpret and fully explain all observed data. The two most promising strategies considered were (1) recalibration of the neutron-gamma tool within simulated Series 743 waste (rather than a brine solution) and (2) development of a tool response function based on computer simulations of material representing Series 743 waste. Before investing the resources required to recalibrate the neutron-gamma tool, it was decided that computer modeling would be a more efficient means of developing a new tool response function. This strategy required quantitative estimates of the elemental composition of Series 743 waste over a reasonable range of sludge conditions defined by varying the extent of VOC loss, the mass of water present, and the degree of waste compaction. Such compositional information would be the basis for modeling that could potentially produce a tool response function (or a family of tool response functions) that could predict all observed data including those above a count rate of 12 cps. In addition, modeling over this possible range of conditions would enable the uncertainty of the model-based tool response function to be quantified.

### 2.3.3 Quantitative Estimates of the Elemental Composition of Series 743 Waste

Miller and Varvel (2001) characterized the chemical composition of Series 743 sludge buried in the SDA. From this characterization, elemental mass fractions within the sludge were calculated for unaltered sludge. In the case of chlorine, the average elemental mass fraction for unaltered sludge was estimated to be 52 wt%. Following release of VOCs, void space is created within the waste form. Two models have been postulated to describe the change in physical (e.g., density) and chemical conditions (e.g., elemental mass fractions) within the sludge, as VOCs are lost. In the compaction model, overburden pressure closes the void space as VOCs escape, causing bulk density to increase slightly while hydrogen content decreases. In the noncompaction model, void space remains open, but water may infiltrate to partially or fully fill the void space. According to this model, bulk density will decrease as VOCs escape, and the amount of hydrogen may increase or decrease depending on the amount of water infiltration. Using unaltered sludge conditions as a starting point, the reasonable range of possible sludge densities and elemental compositions was calculated based on these two conceptual models and simple concepts of mass conservation.

## 3. DEVELOPMENT OF A MODEL-BASED TOOL RESPONSE FUNCTION USING THE MONTE CARLO N-PARTICLE MODEL

A modeling study was conducted using the Monte Carlo N-Particle (MCNP) computer code to determine the behavior of the neutron-gamma tool over the possible range of sludge conditions. Initial model runs were conducted on homogeneous sludge (i.e., no soil or debris) over the range of possible sludge conditions. Limited model runs were subsequently performed for heterogeneous conditions (i.e., sludge and soil).

## 3.1 Homogeneous Medium Results

The large number of variations in probe and VOC container geometry would make a comprehensive modeling study of a heterogeneous environment surrounding the neutron-gamma probe unfeasible. It was determined therefore to examine the behavior of the probe in a homogeneous (i.e., sludge only) environment with varying amounts of VOC loss, compaction, and moisture. The geometry of the simulations and computational grid is shown in Figure 7 (The distance between the source and the detector is 40 cm [15.7 in.]).

Results of the simulations are shown in Figure 8. (In Figure 8, the shaded region is the envelope of results for the noncompaction cases.) Results show the 1,165-keV chlorine gamma-ray count rate versus chlorine weight percent. As can be seen in the figure, the results depict a model-based tool response curve very similar in both shape and magnitude to the calibration-based tool response curve. This finding was troubling for two reasons. First, as in the case of the calibration-based response curve, it failed to predict the observed high chlorine count rate data. Second, it may imply that the tool itself may be sensitive only for low values of chlorine weight percent.

## 3.2 Monte Carlo N-Particle Model Validation against the Original Calibration-Based Tool Response Function

Because of the inability of homogeneous modeling to predict the observed high chlorine rate count data, accuracy of the MCNP model was brought into question. A variety of possible sources of model error was considered. Ultimately, to have confidence in the results of MCNP modeling, simulations of the neutron-gamma tool calibration would be performed and checked against results of comparable simulations performed previously by GTS Duratek (Josten 2002).

Calibration measurements of the neutron-gamma tool were made by GTS Duratek using a brine (saltwater) tank. Different salinities were used in the measurements, varying from 0 to 25 wt% salts. The MCNP calculations performed by both INEEL and GTS Duratek agreed within statistical uncertainties and provided normalization between the models and measurements.

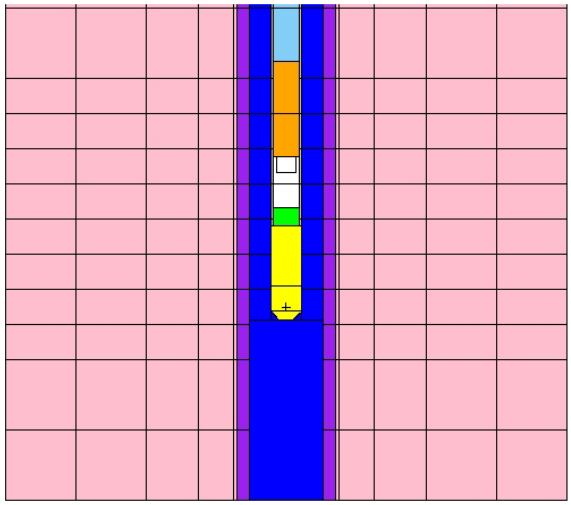

Figure 7. Monte Carlo N-Particle simulation geometry for the homogeneous model.

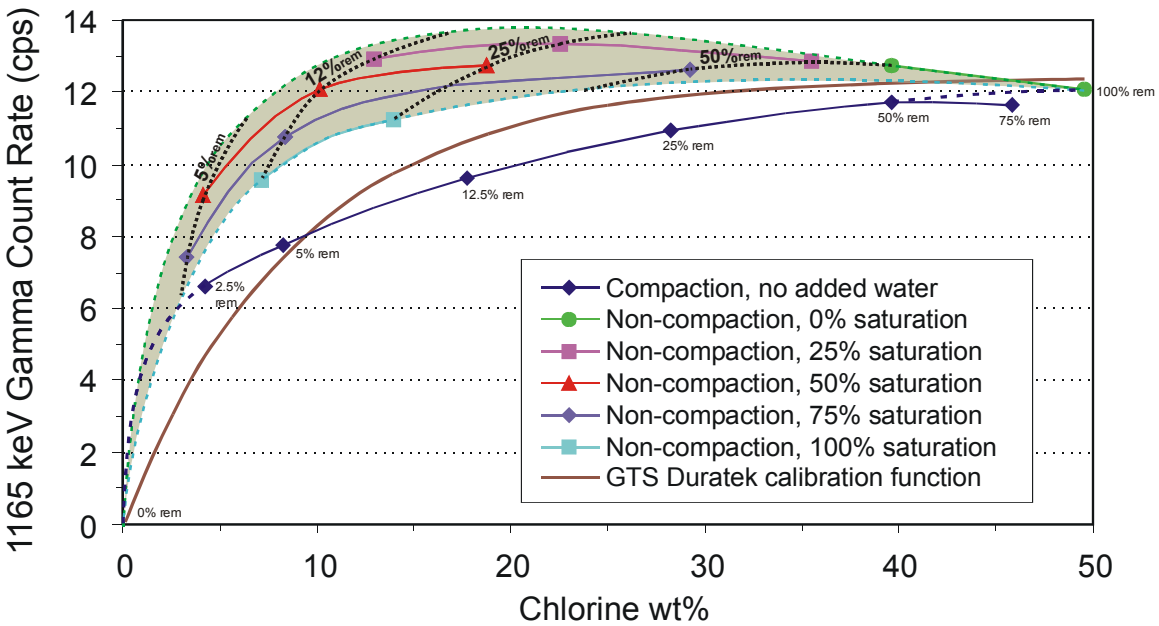


Figure 8. The 1,165-keV gamma count rate for homogeneous compaction and noncompaction cases with infiltration.

An additional simulation was performed at the INEEL to determine the absolute gamma-ray efficiency of the neutron-gamma probe. Results of this simulation agreed with the measurements within 30%. A deviation of this magnitude between the calculated and the measured efficiency is to be expected, as many features of the detector crystal, such as dead layers and coaxial cavities, were not incorporated into the model.

Based on the results of these benchmarking model runs, it was determined that the MCNP model was operating as expected, and the inability to predict observed high chlorine count rate data was likely from heterogeneities and complexities not previously simulated in the waste form itself.

## 3.3 Heterogeneous Medium Results

In order to help understand the impact of heterogeneous conditions on count rate and to see if the high count rates observed in the data could be produced using the model, two additional simulations were performed. Both of these simulations involved cases where the medium surrounding the probe was not homogeneous but instead consisted of soil with an isolated region containing VOC sludge (chlorine). The two different geometries are shown in Figures 9 and 10. As shown in Figure 9, one case consisted of a 15-cm-thick (6-in.-thick) layer of VOC sludge surrounding the borehole axis. (The source and detector are 40 cm [15.7 in.] apart. The chlorine-bearing zone is 15 cm [6 in.] thick.) In Figure 10, we see the second case, where a 15-cm-thick (6-in.-thick) zone of VOC sludge is next to the borehole axis. (The source and detector are 40 cm [15.7 in.] apart. The chlorine-bearing zone is 15 cm [6 in.] thick.) In both cases, the gamma count rates are calculated at different detector positions along the axis of the borehole. The results of these simulations are shown in Figure 11.

As can be seen in Figure 11, the gamma count rate increases as the detector approaches the chlorine-bearing zone, with the maximum count rate occurring when the detector is in the plane of the zone. This occurs for both cases. In Case 1 where the chlorine-bearing zone surrounds the borehole, the chlorine appears to be measurable nearly 80 cm (2.6 ft) from the detector. In Case 2, the chlorine is

measurable approximately 30 cm (1 ft) from the detector. This indicates that each real measurement is then a result of the superposition of the effects of chlorine within a zone of at least 30 cm (1 ft) and possibly 80 cm (2.6 ft) above and below the measurement point (detector). This violates our assumption that any measurable chlorine count rate would signify that the detector is next to Series 743 sludge (see Section 2.3.1).

The heterogeneous model simulation results demonstrate that count rates can be considerably affected both by the matrix composition and the distribution of a chlorine-containing material around the neutron-gamma tool. Consequently, without an independent means to quantify both the matrix composition and the distribution of chlorine-containing material around the neutron-gamma tool, it is difficult to defensibly estimate the mass of VOCs remaining in SDA pits using this approach.

## 3.4 Monte Carlo N-Particle Modeling Summary

Results from both the homogeneous and heterogeneous model cases indicate that the count rate of the 1,165-keV gamma ray alone is insufficient to determine the amount of chlorine present near the probe. In the homogeneous scenario, differing chlorine concentrations can lead to the same gamma count rate depending on the amount of moisture present. Also, the gamma count rate appears to reach a plateau, where changing the chlorine concentration does not appreciably change the count rate. In the heterogeneous situation, a moderate gamma count rate may occur by either being close to a particular chlorine concentration or by being a greater distance from a higher chlorine concentration.

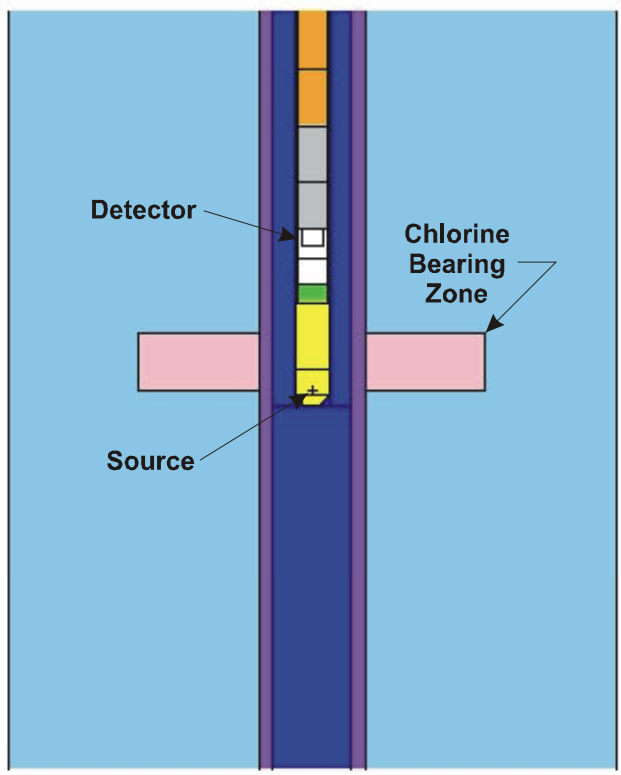


Figure 9. Heterogeneous model geometry with a thin chlorine-bearing zone surrounding the borehole.

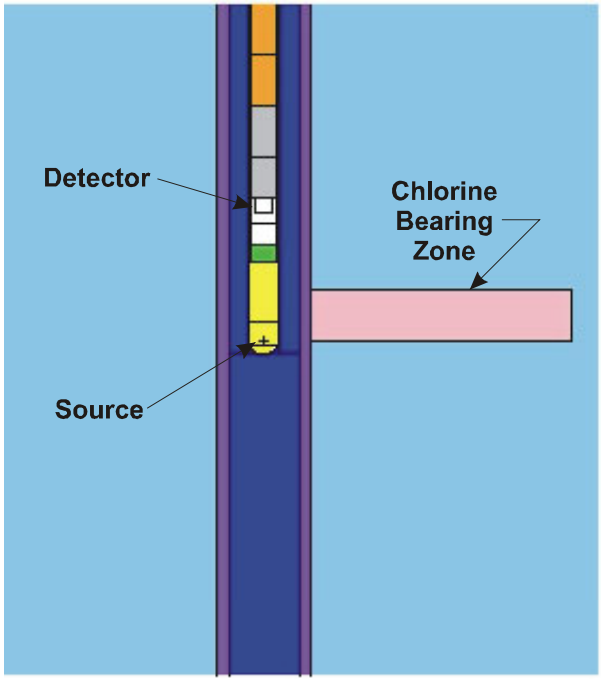


Figure 10. Heterogeneous model geometry with a thin chlorine-bearing zone next to the borehole.

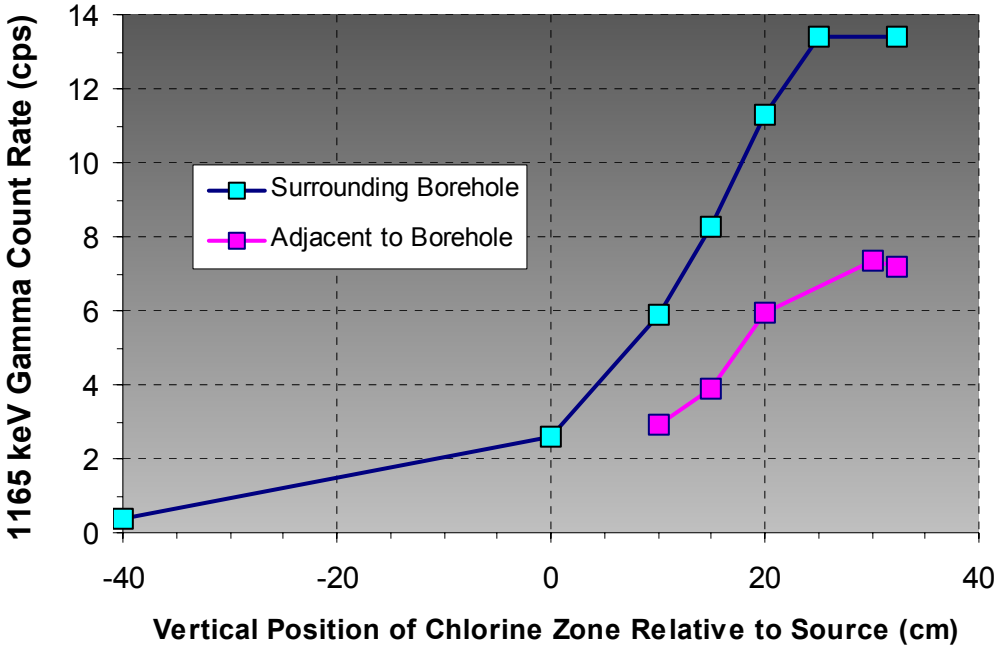


Figure 11. The 1,165-keV gamma count rates for the two heterogeneous geometry cases.

# 4. AN ALTERNATIVE APPROACH FOR APPROXIMATING THE REMAINING VOLATILE ORGANIC COMPOUND MASS FOR MODELING PURPOSES

Sections 2 and 3 of this report contain a description of the methods and efforts applied in trying to estimate the remaining VOC mass using nuclear logging data. Even though a credible quantitative estimate could not be established using the logging data, the needs for an estimate as outlined in Section 1.2 remain, especially the need to assess baseline risks and determine preliminary remediation goals for both OU 7-08 and OU 7-13/14. The primary tool for assessing risk and determining preliminary remediation goals is computer modeling of subsurface VOC transport. The mass of VOCs remaining in the pits is a key input to the numerical modeling. In order for modeling to proceed, an alternative and simpler approach was used to develop a plausible approximation for the amount of remaining VOC mass.

The general methodology for the alternative approach is to estimate the total amount of VOC mass that has been released and subtract it from the original VOC inventory to arrive at the amount remaining. The original inventory is undoubtedly the better known of these two factors. The more difficult number to estimate accurately is the amount released from the waste form since burial. The latter number was approximated through use of numerical modeling, while key modeling findings were corroborated with information from scientific literature. Since the total VOC inventory is predominately $CCl_4$, $CCl_4$ data were used to simplify the analysis, and the conclusions are assumed to apply to all VOCs.

In 1998, Magnuson and Sondrup (1998) modeled the fate and transport of VOCs released from Series 743 sludge. At the time, the best-estimate $CCl_4$ inventory was approximately 1.13E+5 kg (LMITCO 1995). Initial attempts to calibrate the model, a process of matching model results to field data, were largely unsuccessful because the inventory was insufficient even if all of it was released. A decision was made to double the inventory to 2.26E+5 kg in hopes of improving the calibration. This produced a good match between model results and field observations.

Even with a larger inventory, it was necessary to release 2.13E+5 kg, or 94% of the 2.26E+5 kg, by 1995, the end of the calibration period, in order to achieve an adequate calibration. In addition, it was necessary to use a rather uncharacteristically large value of tortuosity for the surficial sediment to keep too much contamination from diffusing to the surface where it is lost to the atmosphere. Tortuosity accounts for the increased distance contaminant molecules must travel in a porous medium. The tortuosity of the surficial sediment in the model was assigned a value of 20. Even at that value, nearly 80% (1.68E+5 kg) of the released mass migrated to the soil surface, while only 20% (4.53E+4 kg) remained in the vadose zone. The amount in the aquifer is considered negligible. Since that modeling effort, an investigation by Varvel and Sondrup (2001) reported SDA sediment tortuosity values ranging from 2.8 to 4.6. Although these were measured during relatively dry conditions, it is highly unlikely that a long-term average value would approach 20. If a value closer to the measured values had been used in the modeling, it likely would have required an even larger inventory than double the original amount to calibrate the model. Therefore, assuming the modeling is a reasonable representation of actual conditions, the amount released by Magnuson and Sondrup, 2.13E+5 kg, can be considered the minimum that would have to have been released in order to create the observed vadose zone plume.

The modeling results of Magnuson and Sondrup (1998) and other questions regarding the inventory prompted a thorough and comprehensive investigation into the $CCl_4$ inventory. This investigation resulted in the current and much larger estimate of 8.2E+5 kg (Miller and Varvel 2001), a 7.25-fold increase over the earlier 1.13E+5-kg estimate (LMITCO 1995). If, as modeling suggests, it is necessary to release a minimum of 2.13E+5 kg, or 26% of the 8.2E+5-kg inventory, in order to create the amount of

contamination in the vadose zone, the remaining 74% of the original inventory, or 6.1E+5 kg, should be considered an upper-bound estimate of the percent remaining in the source-zone sludge.

Given that a more appropriate value for the tortuosity of the surficial sediment is likely 10 or less, as opposed to 20, it's also likely that more than 26% of the VOC mass would have to be released in order to produce the observed vadose zone contamination. To estimate how much more, we considered a simple analysis of diffusion-dominated transport from the waste pits. Diffusional transport is proportional to the concentration gradient of the contaminant in the medium. Figure 12 represents a simplified schematic of the upper vadose zone at the SDA. The maximum $CCl_4$ gas concentration measured in the waste pits was 6.2E+4 ppmv at a depth of 4.3 m (14 ft) in Probe 743-08-VP2 in Pit 4 in 1992. This is nearly equal to the pure component equilibrium vapor concentration of $CCl_4$. The maximum concentration measured in the vadose zone is approximately 5.0E+3 ppmv at a depth of 21.3 m (70 ft) measured in several wells near Probe 743-08-VP2. If we consider the vapor concentration in the air at ground surface above the waste pit to be zero or very small and the vapor concentration in the pit to be uniform, we can estimate vertical concentration gradients above and below the pit. In this case, the gradient above the pit is 1.0E+4 ppmv/ft, and the gradient below the pit is 1.1E+3 ppmv/ft. The ratio of upper to lower gradients is approximately 9:1, which in broad terms can be thought of this way: for every 10 molecules of $CCl_4$ released from the sludge in the pit, nine will go up and one will go down. This ratio is slightly higher than the modeling result of 8:2. If we apply the 9:1 result to the revised larger inventory (8.2E+5 kg) and maintain that there was approximately 4.53E+4 kg of $CCl_4$ in the vadose zone in 1995 as stated beforehand, then the amount released would have to have been 10 times 4.53E+4 kg, which is nearly 55% of the revised inventory. The current estimate would then have to be less than this since VOCs are still being released.

When considering the mass escaping to the atmospheres, scientific studies indicate that numbers of 80% or higher are not uncommon, especially for shallow contamination. A study by Baehr (1987) of gasoline transport from a shallow residual source with a shallow water table showed that after 5.5 years, over 80% of the initial mass was lost to the atmosphere, and the percentage was still increasing albeit slowly. The infiltration rate in this case was more than 10 times the annual average infiltration rate at the SDA. Given that infiltration will tend to drag more contamination downward, it is not difficult to imagine that the amount migrating to the atmosphere could be even larger than predicted by Baehr if the infiltration rate had been smaller. This suggests that a 90% loss of mass to the atmosphere is not unrealistic. Baehr also states that halogenated hydrocarbons, like $CCl_4$, will be transported in a similar manner to the gasoline-range hydrocarbons because they exhibit comparable vapor pressures.

It should be noted that the estimate of percent mass remaining is highly sensitive to the ratio of mass lost to the atmosphere versus mass remaining in the vadose zone if the mass in the vadose zone is to remain constant (4.53E+4 kg in this case). For example, using the revised larger inventory and an 8:2 ratio, the mass remaining is 72%, while for a ratio of 9.3:0.7, the mass remaining would be approximately 22%. To expect ratios above this is improbable because of other mechanisms such as density and infiltration, which transport contaminants downward.

Based on the foregoing information, it is reasonable to assume in approximate terms that there is at least 25% of the original mass remaining and perhaps as much as 75%. Based on this range, a median value of 50% VOC mass remaining is recommended as a starting point for future modeling efforts and 75% to be considered an upper bound. It is purely coincidental that the value of 50% remaining agrees with the result from the preliminary work described in Section 2.2.

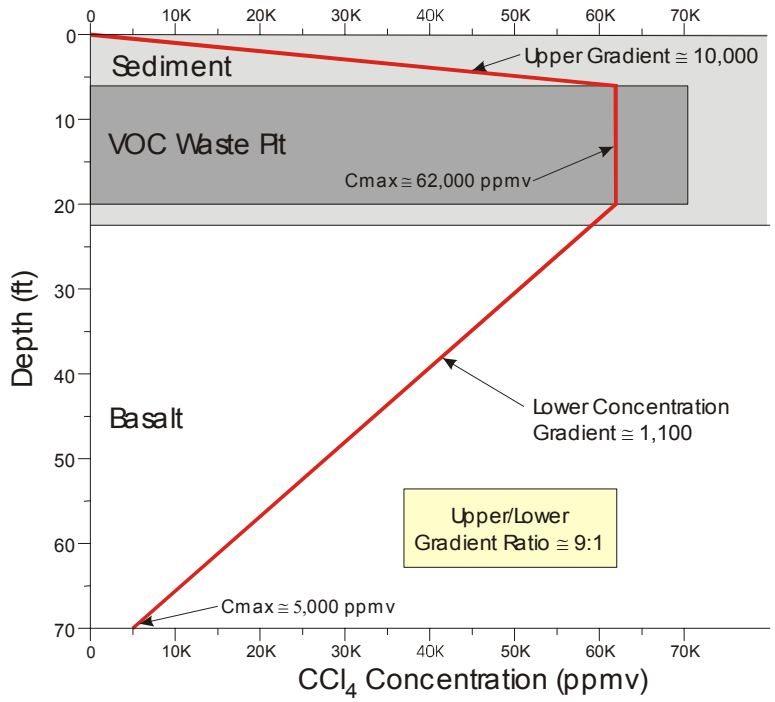


Figure 12. Simplified schematic of the upper vadose zone at the Subsurface Disposal Area showing a rudimentary vertical profile of carbon tetrachloride soil gas concentrations.

Although no quantitative uncertainty evaluation was conducted to arrive at these estimates, they do have some basis. In addition, it is believed that long-term contaminant transport modeling used for risk assessments and preliminary remediation goal determinations can tolerate a reasonably high level of uncertainty (e.g., ± 25%). Variation within this range is not expected to change the modeling predictions substantially, because the modeling predictions are constrained by spatial and temporal observations of contaminant levels, and the abundance of available data forces a smaller range of possible model outcomes. This assumption can and should be evaluated as part of any modeling effort using this data. It should be noted that while the variability within the range of 25–75% will have a marginal effect on some study objectives (e.g., long-term modeling), it could have a significant impact on other study objectives (e.g., groutability of the waste) and should almost certainly not be used for such without careful consideration of the implications.

# 5. CONCLUSIONS AND RECOMMENDATIONS

Preliminary attempts to quantify VOC mass remaining in SDA pits were largely unsuccessful based on the lack of quantifiable uncertainty around the original chlorine mass per probehole estimate and the inadequacy of the neutron-gamma logging tool calibration function. A revised strategy that also relied on neutron-gamma logging data was also unsuccessful because of (1) the inability to distinguish Series 743 sludge from other media (e.g., soil and debris) and (2) the inability to develop a tool response function capable of predicting all observed neutron-gamma data. In addition, even if an adequate tool response function were developed, it would remain difficult to defensibly estimate the mass of VOC remaining in SDA pits without the ability to independently characterize both the matrix composition and the distribution of the chlorine-containing material around the neutron-gamma tool.

An alternative, simpler approach was used to approximate the amount of VOC mass remaining without any attempt to quantify the uncertainty. Based on the approach, an estimate of 50% VOC mass

remaining is recommended as a starting point for numerical modeling to predict risks and remediation goals for OU 7-08 and OU 7-13/14. An estimate of 75% mass remaining is recommended as an upper bound. The lack of uncertainty surrounding these estimates should be carefully considered in interpreting any results derived from their use.

Before any further work commences that involves neutron-gamma logging, a broad-based technically defensible strategy should be developed to logically ensure the objectives of the project as stated in Section 1.2 could be achieved. This strategy would likely involve redesigning the neutron-gamma tool such that it interrogates a volume of material that more closely approximates homogeneous conditions, and sensitivity of the tool is maximized in the region of interest to the project (50 wt % in this case). It also should include a recalibration of the tool to constituents other than chlorine that are unique to Series 743 waste or be able by some other means to distinguish between Series 743 sludge and other media. In addition, the tool also will require a thorough calibration to conditions and materials that are more likely to be encountered in the waste pits or alternatively a model-based tool response developed for the same conditions and materials.

# 6. REFERENCES


Baehr, A., 1987, "Selective Transport of Hydrocarbons in the Unsaturated Zone Due to Aqueous and Vapor Phase Partitioning," *Water Resources Research*, Vol. 23, No. 10, October 1987, pp. 1926–1938.

Clements, Thomas L., 1982, *Content Code Assessments for INEL Contact-Handled Stored Transuranic Wastes*, WM-F1-82-021, U.S. Department of Energy Idaho Operations Office.

Josten, Nicholas E., 2002, *Type A Nuclear Logging Data Acquisition and Processing for Operable Units 7-13/14 and 7-10*, INEEL/EXT-02-00558, Rev. 1, Idaho National Engineering and Environmental Laboratory.

Koeppen, L. Don, Alva M. Parsons, A. Jeffrey Sondrup, Paul D. Ritter, and Gail L. Olson, 2004, *Fiscal Year 2003 Environmental Monitoring Report for the Radioactive Waste Management Complex*, ICP/EXT-04-00259, Rev. 1, Idaho Completion Project.

Liekhus, K. J. and E. S. Peterson, 1995, *Measurement of VOC Permeability of Polymer Bags and VOC Solubility in Polyethylene Drum Liner*, INEL-95/0164, Idaho National Engineering and Environmental Laboratory.

LMITCO, 1995, *A Comprehensive Inventory of Radiological and Nonradiological Contaminants in Waste Buried in the Subsurface Disposal Area of the INEL RWMC During the Years 1952–1983*, INEL-95/0310, Rev. 1, Idaho National Engineering and Environmental Laboratory.

Magnuson, S. O. and A. J. Sondrup, 1998, *Development, Calibration, and Predictive Results of a Simulator for Subsurface Pathway Fate and Transport of Aqueous- and Gaseous-Phase Contaminants in the Subsurface Disposal Area at the Idaho National Engineering and Environmental Laboratory*, INEEL/EXT-97-00609, Idaho National Engineering and Environmental Laboratory.

Miller, Eric C. and Mark D. Varvel, 2001, *Reconstructing the Past Disposal of 743-Series Waste in the Subsurface Disposal Area for Operable Unit 7-08, Organic Contamination in the Vadose Zone*, INEEL/EXT-01-00034, Rev. 0, Idaho National Engineering and Environmental Laboratory.

Myers, Dennis R., Joel M. Hubbell, Nicholas Josten, L. Don Koeppen, Paul D. Ritter, Hopi Salomon, A. Jeffrey Sondrup, Deborah L. Mc Elroy, and Carolyn W. Bishop, 2004, *Fiscal Year 2003 Summary Report for the OU 7-13/14 Probing Project*, ICP/EXT-04-00189, Rev. 0, Idaho Completion Project.

Sondrup, A. Jeffrey, Ryan D. McMurtrey, and Lisa A. Harvego, 2003, *Interim Remedial Action Report for the OU 7-08 Organic Contamination in the Vadose Zone Project*, INEEL/EXT-02-00862, Rev. 0, Idaho National Engineering and Environmental Laboratory.

Varvel, M. D. and A. J. Sondrup, 2001, *Operable Unit 7-08 Estimate of Tortuosity Factor for Gas Diffusion in Overburden Soil in the Subsurface Disposal Area*, INEEL/EXT-01-01534, Rev. 0, Idaho National Engineering and Environmental Laboratory.

Vigil, M. J., 1990, *Subsurface Disposal Area (SDA) Waste Identification (1952–1970 Emphasis)*, EGG-WM-8727, Rev. 2, Idaho National Engineering and Environmental Laboratory.