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Origins of Volatile Organic Compounds Emerging from Tank 241-C-106 during Sluicing

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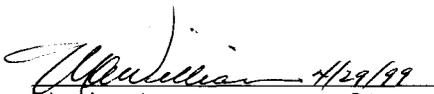
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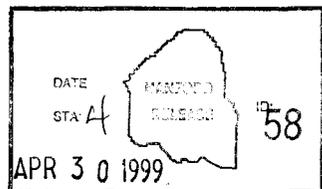
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Origins of Volatile Organic Compounds Emerging from Tank 241-C-106 during Sluicing

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EXECUTIVE SUMMARY

This report examines the origins of the volatile organic compounds released during sluicing operations of Tank 241-C-106. Characterization studies imply the organic material in this tank is located in the topmost sludge layer consisting of about 318 kL (84 kgal) of a mixture of low-level waste from B Plant and washed Plutonium Uranium Extraction (PUREX) process sludge from the AR vault. The organic-rich material in the tank originated from strontium removal operations in which glycolic and citric acid were used with bis(2-ethylhexyl)phosphoric acid and tributyl phosphate in a mixture of normal paraffin hydrocarbons. The best basis inventory indicates the tank contains 15,200 kilograms of total organic carbon. The oxalate ion content, which is apparently large, is not known with confidence. The organic constituents in the aqueous phase of the waste have not been investigated. However, an organic oil, which was separated from the sludge by centrifugation, was shown to contain principally sodium bis(2-ethylhexyl)phosphate with lesser quantities of butyl bis(2-ethylhexyl)phosphate and sodium butyl (2-ethylhexyl)-phosphate. The oil also contained small amounts of other phosphate esters and residual normal paraffin hydrocarbons. The amounts of the oil in grab samples of sludge collected in 1996 ranged from 0.5 to 3.0 percent by volume.

Hydrogen and other permanent gases evolve continuously from tank 241-C-106. In addition, approximately 45 organic compounds including alkanes, alkenes, alcohols, ethers, aldehydes, ketones, esters, and nitriles were present at concentrations greater than 5 ppb in the ventilation stack before sluicing operations began. About 50 percent of these compounds are water-soluble organic substances, that apparently are preferentially transported from the sludge to the dome space through the aqueous supernatant layer during quiescent periods.

The initiation of sluicing leads to large increases in the hydrogen and nitrous oxide release rates. In addition, more than 200 organic compounds representing 8 different organic structural groups appear in the ventilation stack during sluicing. Linear alkanes from propane to tetradecane are present, together with smaller amounts of some nonlinear hydrocarbons. Linear alkenes from propene to decene also are present with smaller amounts of linear alkadienes and alkynes. Cycloalkanes with three-, five-, and six-membered rings and certain decalins are present in low concentrations. Aromatic compounds including benzene, toluene, and the xylenes are much less abundant than the alkanes or alkenes. Several alcohols and ethers with structures topologically related to butanol and 2-ethylhexanol are found. Homologous series of linear aldehydes and ketones are present. One allylic nitrile and a homologous series of linear nitriles are observed. Inasmuch as the concentrations of these organic substances increase appreciably during sluicing, these substances must have been retained in the sludge in tank 241-C-106. A ninth group of compounds containing fluorine or chlorine atoms also was detected. However, it is not possible to determine whether they originate from the sludge. Tributyl phosphate was not detected in the ventilation stack.

The sludge apparently retains between 3 and 6 percent permanent gas in void spaces. Disturbance of the waste releases this gas, principally consisting of hydrogen, nitrous oxide, and nitrogen. The volatile organic compounds, which are distributed among the void spaces

and the aqueous and oil phases of the sludge, are released simultaneously. When sluicing begins, the concentrations of water-soluble volatile organic compounds in the ventilation stack increase, but the concentrations of the water-insoluble compounds increase even more.

Information about the structural characteristics of the volatile organic compounds, their volatility and their chemical and radiolytic conversion reactions provides a technical basis for relating the volatile organic compounds to the original process chemicals. In brief, the normal paraffin hydrocarbons are more volatile than the phosphate esters and their concentrations have been substantially depleted by evaporation during interim storage. Tributyl phosphate is partially water-soluble and it has largely been converted into dibutyl- and monobutylphosphate ions. Sodium bis(2-ethylhexylphosphate) is neither volatile, soluble in water, nor chemically reactive and it is now the most abundant organic compound found in tank 241-C-106, with the possible exception of sodium oxalate. The remaining original compounds and the molecules formed from them and retained in the waste undergo oxidative radiolytic reactions leading to the formation of hydrogen-deficient hydrocarbons and to alcohols, aldehydes, ketones, nitriles, and carboxylate ions. Hydrogen, nitrous oxide, nitrogen, and ammonia are simultaneously formed in the course of these reactions.

Some evolving alkanes, for example the linear paraffins and their monomethyl derivatives with more than nine carbon atoms, were original constituents of the normal paraffin hydrocarbon mixture. The alkanes with less than nine carbon atoms originate from the radiolytic reactions of the normal paraffin hydrocarbons and the phosphate esters.

The numerous alkenes in the mixture of volatile organic compounds also have predominantly linear structures. The heptenes, which are most prominent in this group, are formed by radiolysis of sodium bis(2-ethylhexyl)phosphate.

The cycloalkanes and certain decahydronaphthalenes are present in low absolute concentrations. Compounds of this structural class were known to be impurities in the original normal paraffin hydrocarbon mixture, but small amounts also may form during radiolysis.

The concentrations of benzene, toluene, and the xylenes are very low because these substances were removed from the normal paraffin hydrocarbon mixture during manufacture and their formation by radiolysis is disrupted by competitive oxidation reactions.

The relatively high abundance of 1-butanol is related to the hydrolysis and radiolysis of the mono-, di-, and tributylphosphates remaining in the waste. The concentration of 2-ethyl-1-hexanol is much smaller because the rates of hydrolysis and radiolysis of the corresponding ester are much slower. Methanol, ethanol, and propanol are formed as intermediates in the oxidation sequences leading to formate, acetate, and propionate ions. Most of the ethers have structures topologically related to the original phosphate esters.

The homologous series of linear aldehydes and ketones and nitriles result from radiolysis reactions of the hydrocarbons. In addition, abundant ketones with seven and eight carbon atoms are produced during radiolysis of the abundant sodium bis(2-ethylhexyl)phosphate.

In summary, the organic compounds emerging from the ventilation stack during sluicing are derived from the mixture of phosphate esters and normal paraffinic hydrocarbons originally used for strontium removal in B Plant. The composition of the original mixture has been altered by the evaporation of hydrocarbons, the hydrolysis of tributyl phosphate, and the radiochemical conversions of the hydrocarbons and phosphate esters. Sodium bis(2-ethylhexyl)phosphate, the least volatile and least reactive compound in the original mixture, has been selectively retained. Its slow decomposition is responsible for the relatively high abundance of compounds having seven and eight carbon atoms among the volatile organic compounds.

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LIST OF TERMS

°C	degrees Celcius
AR	process sludge
BL	B Plant low level waste
CWP	PUREX cladding waste
DBP	dibutylphosphate
EPA	Environmental Protection Agency
k/gal	kilogallons
<i>M</i>	moles
NIST	National Institute of Science and Technology
NPH	normal paraffin hydrocarbon
ppb	parts per billion
ppm	parts per million
PUREX	Plutonium-Uranium Extraction
SAS	Special Analytic Services
TBP	tributyl phosphate
TOC	total organic carbon
TST	triple sorbent tubes
UR	uranium recovery waste
VOC	volatile organic compound

1.0 INTRODUCTION

Unexpectedly high concentrations of inorganic gases and volatile organic compounds (VOC) were released from the ventilation stack of tank 241-C-106 during sluicing operations on November 18, 1998. Workers experienced serious discomfort. They reported an obnoxious acrid odor and the 450 ppm VOC in ventilation stack 296-C-006 exceeded the level approved in the air discharge permit. Consequently, the operation was terminated. Subsequent analyses of samples collected opportunistically from the stack indicated many organic compounds including heptenes, heptanones, and normal paraffin hydrocarbons (NPH) and their remnants were present. Subsequently, a process test designed to avoid unnecessary worker exposure and enable collection of analytical samples from the stack, the breathing area, and the receiver tank was conducted on December 16, 1998. The samples obtained during that operation, in which the maximum VOC content of the stack was approximately 35 ppm, have been analyzed by teams at Pacific Northwest National Laboratory and Special Analytic Services (SAS). This report examines the results of these investigations. Future revisions of the report will examine the analytical results obtained for samples collected during sluicing operations in March.

This report contains the available evidence about the source term for these emissions. Chapter 2 covers characterization work, including historical information about the layers of waste in the tank, the location of organic compounds in these layers, the total organic carbon (TOC) content and the speciation of organic compounds. Chapter 3 covers the data for the samples from the ventilation stack, which has the highest concentrations of organic compounds. Chapter 4 contains an interpretation of the information connecting the composition of the organic emissions with the composition of the original source term. Chapter 5 summarizes the characterization work, the sample data, and the interpretation of the results.

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2.0 CHARACTERIZATION

2.1 WASTE LAYERS

Schreiber (1996) and Reynolds (1997) discussed the origins of the waste in tank 241-C-106. Their conclusions, which are based on the review of historical operations records, the physical appearance of cores, and analytical work on grab samples, are summarized in Table 2-1.

Table 2-1. Waste Layers in Tank 241-C-106
(Schreiber 1996, Reynolds 1997)¹

Layer Height (in.)	Waste Type	Volume (k gal)
(5) Above 78	Aqueous liquid supernatant	
(4) 52 to 78	Sludge of unknown origin, but taken to be a mixture originating from B-Plant low-level waste (BL) and washed PUREX sludge from the AR vault (AR)	84
(3) 29 to 52	Washed PUREX sludge (AR)	64
(2) 17 to 29	PUREX cladding waste (CWP)	34
(1) Below 17	Uranium recovery waste (UR)	15

Note:

PUREX = Plutonium-Uranium Extraction (process)

¹Reynolds and Schreiber provide somewhat different estimates of waste heights, but the differences are insignificant for identifying the source term.

The composition of the lower three layers is based on historical information and observations of the 1986 core (Weiss and Schull 1988, Schreiber 1996, Reynolds 1997, Bailey 1999). The conclusion that these layers originated from washed Plutonium-Uranium Extraction (PUREX) process sludge (AR), PUREX cladding waste (CWP), and uranium recovery waste (UR) is relatively secure. Reynolds describes Agnew's contributions. He points out that these three waste types have negligible concentrations of organic compounds and notes the AR sludge contains very high concentrations of strontium (Agnew 1995, 1996; Agnew et al. 1995, 1997; Reynolds, 1997,1999).

Unfortunately, the composition of the topmost sludge layer, which is identified as Layer 4 in Table 2-1, cannot be established from the available records. As discussed by Schreiber (1996) and Reynolds (1997), neither the historical records nor the analytical data obtained by the work on the 1986 core or the 1996 grab samples are adequate to establish the relative amounts of material originating from B Plant low-level waste (BL) and washed PUREX sludge from the AR vault (AR). Consequently, the fourth layer is conservatively described as an 84k-gal

mixture of AR and BL waste. Reynolds cites Agnew's work implying organic compounds are present exclusively in BL waste (Agnew 1995, 1996, Agnew et al. 1995, 1997; and Reynolds 1997, 1999).

2.2 ORIGINAL ORGANIC SOURCE TERM

B Plant waste contained mixtures of phosphate esters and NPH solvent (Agnew 1995, 1996; Agnew et al. 1995, 1997; Scheele et al. 1995; Cowley and Meacham 1998). The composition of the process chemicals is shown in Table 2-2.

Table 2-2. B Plant Process Chemicals (Cowley and Meacham 1998, Scheele et al. 1996)

Organic Complexants
Citric acid and glycolic acid
Organic Solvents
Bis(2-ethylhexyl)phosphoric acid, 1 part by weight (CH ₃ CH ₂ CH ₂ CH ₂ CH(CH ₃ CH ₂)CH ₂ O) ₂ PO(OH)
Tributyl phosphate (TBP), 6.5 parts by weight (CH ₃ CH ₂ CH ₂ CH ₂ O) ₃ PO
TBP contained dibutyl butylphosphonate (CH ₃ CH ₂ CH ₂ CH ₂ O) ₂ (CH ₃ CH ₂ CH ₂ CH ₂)PO
Normal paraffin hydrocarbon (NPH), 10 parts by weight
A mixture of alkanes rich in linear C12 molecules, but also Containing linear C11, C13, and C14, as well as branched Compounds and cycloalkanes

The NPH solvent was prepared by distilling to maximize the concentration of dodecane and passing through molecular sieves to minimize the concentrations of undesirable branched paraffins and aromatic molecules. The solvents supplied by different manufacturers had different compositions, but in general they were rich in linear, i.e., normal, dodecane. However, they also contained linear undecane, tridecane, and tetradecane, together with lesser amounts of branched paraffinic hydrocarbons, especially mono-, di- and trimethyl derivatives. Some substituted cycloalkanes codistilling in the same temperature range were retained in the NPH, but the aromatic hydrocarbon content was low.

2.3 TOC CONTENT

Attempts to establish the total organic content of the individual layers of waste in tank 241-C-106 have not been successful. The analytical work on the 1986 core composite was accomplished without serious complications. Unfortunately, the analytical work on 1996 grab samples from Layers 3 and 4 did not proceed smoothly. Schreiber's assessment of the work (1996) indicates the grab samples were withdrawn from locations that were probably disturbed during sample collection and that the samples heights may have been misidentified. In addition, both sets of 1996 grab samples were taken from locations that had been previously disturbed. The region below Riser 1 had been used for the collection of the 1986 core, and Riser 7 had been occupied by a thermocouple tree (Bailey 1999). Inasmuch as the viscosity of the waste layers differs, mobile material from an upper layer may have flowed into the regions from which the core and thermocouple equipment had been removed. The grab samples from these locations are unlikely to be representative of the waste at the location from which they were withdrawn.

The supernatant liquid drained from the 1986 composite core sample contained 2,500 micrograms of TOC/mL (Schreiber 1996). The results obtained for the grab samples in 1996, which were all taken above the 29-in. level, suggested the supernate contained about 2,900 micrograms of TOC/mL. The values for the solid sludge are much different. The analytical work on the 1986 core implies an organic carbon content of 6,600 microgram/mL for the entire tank, and the analytical work for the 1996 grab samples implies 20,000 micrograms/mL for the solid sludge above the 29-in. level.

The oxalate ion content was not reported for the 1986 core. The oxalate ion content of the grab samples from 1996 varied significantly (Appendix A).

The TOC implied by the characterization work has been entered into the best basis inventory as 15,200 kg. When the oxalate ion content is calculated in the same manner as was used to determine the best basis TOC content, the total amount of carbon in oxalate ion exceeds the measured total amount of organic carbon. Examination of the data set shown in Appendix A indicates this result is a consequence of one especially high measurement.

Notwithstanding the array of difficulties, the results indicate the sludge layer that lies between 52 and 78 in. contains between 13,000 and 30,000 micrograms of TOC/mL. The amount of carbon in the form of oxalate ion, while certainly appreciable, is uncertain.

2.4 OIL LAYER

When first examined, the grab samples collected from Layers 3 and 4 appeared to contain only solid sludge and an aqueous liquid. However, in response to a request to remove excess water from the sludge, the samples were centrifuged and a third phase, an organic oil, formed on top

of the water layer in four grab samples. The amount of the oil ranged from 0.5 to 3.0 percent by volume of sludge (Schreiber 1996).

The oil separated from samples thought to be withdrawn from Layer 4 in accord with the layering described in Table 2-1. However, the oil also separated from samples thought to be withdrawn from Layer 3, a result that is not in accord with the layering described in Table 2-1. This discrepancy cannot now be definitely resolved. However, the appearance of the oil in samples thought to be collected about 30 in. from the bottom of the tank in Layer 3 may be an artifact of the manner in which the samples were collected or of the manner in which the waste filled the cavities created when the 1986 core and the thermocouple were removed.

The observations are most consistent with the view that the oil is present only in Layer 4 and that Layer 4 contains between 0.5 to 3.0 percent oil by volume. The amount of carbon in the oil was calculated on the following basis.

$$84 \text{ (kgal waste)} \times 0.005 \text{ (kgal oil/kgal waste)} \times 3.8 \text{ (kL oil/kgal oil)} = 1.6 \text{ kL of oil}$$

$$84 \text{ (kgal waste)} \times 0.030 \text{ (kgal oil/kgal waste)} \times 3.8 \text{ (kL oil/kgal oil)} = 9.6 \text{ kL of oil}$$

adopting the density as 1.0 g oil/mL:

$$1.6 \text{ kL of oil} \times 1000 \text{ (L oil/kL oil)} \times 1000 \text{ (g oil/L oil)} = 1,600 \text{ kg of oil}$$

$$9.6 \text{ kL of oil} \times 1000 \text{ (L oil/kL oil)} \times 1000 \text{ (g oil/L oil)} = 9,600 \text{ kg of oil}$$

As discussed later, the oil is principally sodium bis(2-ethylhexyl)phosphate (BEHP). The TOC content can be estimated to be

$$1,600 \text{ (kg sodium BEHP)} \times 192/344 \text{ (kg carbon/kg BEHP)} = 900 \text{ kg TOC}$$

$$9,600 \text{ (kg sodium BEHP)} \times 192/344 \text{ (kg carbon/kg BEHP)} = 5,400 \text{ kg TOC}$$

This approach suggests the oil contains between 900 and 5,400 kg TOC.

These values can be contrasted with the best basis inventory value of 15,200 kg TOC, which presumably includes the carbon in the oil, in aqueous solution and in the sludge.

2.5 SPECIATION OF THE OIL

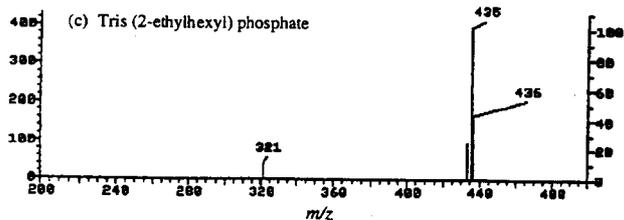
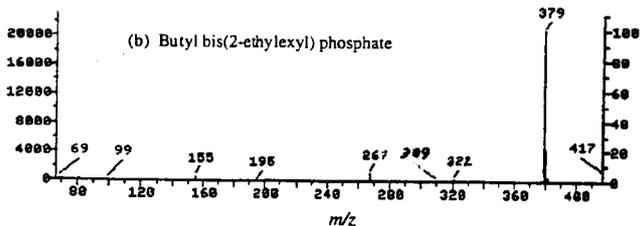
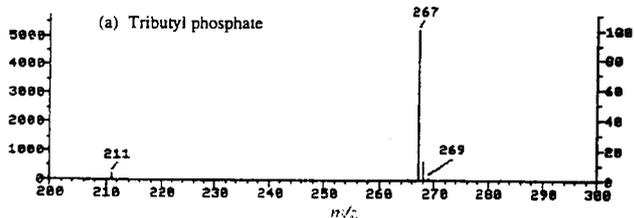
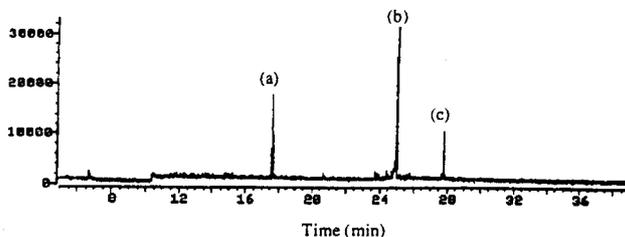
Campbell and coworkers have studied the organic phosphates and normal paraffinic hydrocarbons in several C farm tanks (Campbell et al. 1994, 1995a, 1995b, 1996a, 1996b, 1997; Mong and Campbell 1999). They investigated two different samples of the oil from tank 241-C-106, one from Riser 1 and one from Riser 7, and made the following observations.

- Although sodium bis(2-ethylhexyl)phosphate is a salt, it floats on aqueous solutions of sodium hydroxide.

- Infrared analyses suggested that the principal component in the oil was sodium bis(2-ethylhexyl)phosphate.
- The monoalkyl- and dialkylphosphates in the sample were converted to their volatile methyl esters with diazomethane. The chromatograms obtained by electron impact ionization and chemical ionization mass spectrometry after derivatization with diazomethane are shown in Figure 2-1.

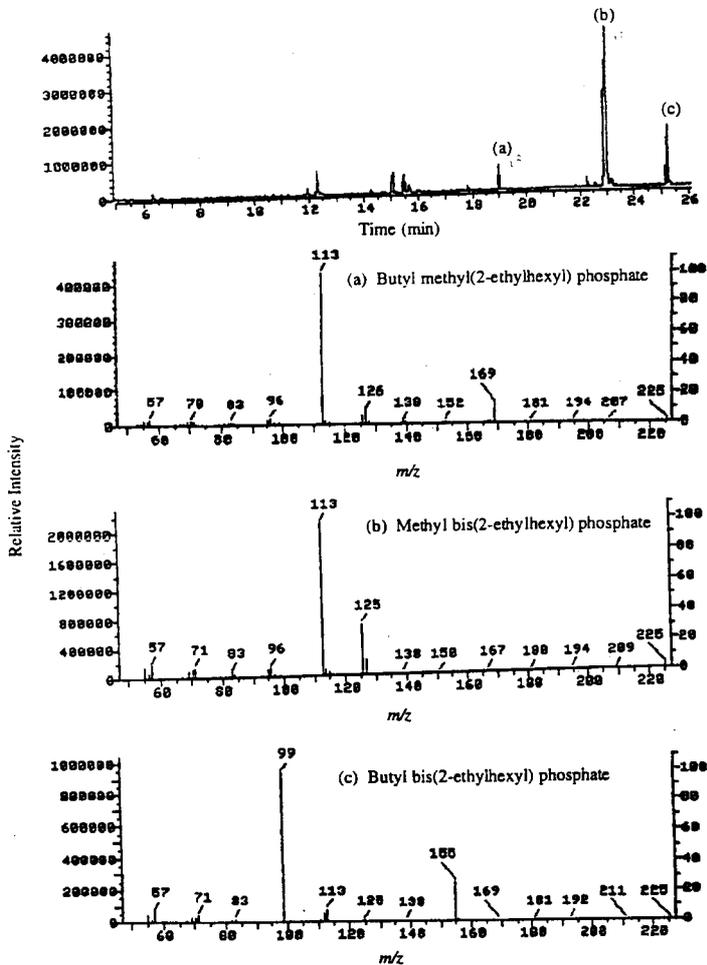
Figure 2-1a. Gas Chromatography-Mass Spectrometry of the Phosphate Esters Obtained from the Oil from Tank 241-C-106. Panel A displays the results obtained when the oil was treated with hydrochloric acid and the esters were methylated in ether before gas chromatography-mass spectrometry analysis by electron impact ionization.

(Campbell et al. 1996) (2 sheets)



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Figure 2-1b. Gas Chromatography-Mass Spectrometry of the Phosphate Esters Obtained from the Oil from Tank 241-C-106. Panel B displays the results obtained when the oil was extracted with methylene chloride and the extract was analyzed by gas chromatography-mass spectrometry by chemical ionization. (Campbell et al. 1996) (2 sheets)



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Residual paraffinic hydrocarbons are apparent at short retention times in Panel A. The chromatographic observations and the mass spectra displayed in Panels A and B indicate the oil is composed principally of sodium bis(2-ethylhexyl)phosphate, butyl bis(2-ethylhexyl)phosphate, and sodium butyl(2-ethylhexyl)phosphate with lesser amounts of other phosphates. More quantitatively, the results presented by Campbell and coworkers (Campbell et al. 1996a, 1996b and Campbell and Mong 1999) imply the oil contains about 45 percent sodium bis(2-ethylhexyl)phosphate, 17 percent butyl bis(2-ethylhexyl)phosphate, 13 percent sodium butyl(2-ethylhexyl)phosphate, 8 percent tributyl phosphate (TBP), 4 percent tris(2-ethylhexyl)phosphate, and 13 percent NPH.

The investigation revealed that the oil contains the original process chemicals, BEHP, TBP, and NPH, together with other phosphates formed from BEHP and TBP during B Plant operations.

2.6 HYDROGEN RELEASE

Ongoing monitoring activities indicate approximately 370 L of hydrogen per day are released from tank 241-C-106. The rate of hydrogen generation, 1.6×10^{-5} mol/kg of waste per day, ranks second among all tanks, whether single or double shell (Hu 1999a). Neither nitrous oxide nor ammonia releases from this tank are regularly monitored. However, the concentrations of these gases and several other gases were measured in the ventilation stack during sluicing operations (Huckaby et al. 1999 and Bonfoey et al. 1999a). The quantities of oxygen, nitrogen, and argon were unexceptional before and during sluicing. The amount of carbon dioxide in the stack was depleted because of contact with the alkaline supernatant. Methane was below the detection limit, 20 ppm, before and during sluicing. The concentration of ammonia, which increased to about 7 ppm during sluicing, cannot be interpreted easily because some of this gas was removed by the water scrubber.

Notably, the concentrations of hydrogen and nitrous oxide increased significantly during sluicing. Before sluicing there was about 12 ppm hydrogen in the stack, but during sluicing the concentration ranged from 22 to 32 ppm (Huckaby et al. 1999). The concentration of nitrous oxide, which was less than 20 ppm before sluicing began, ranged from 80 to 100 ppm in the ventilation stack during sluicing (Huckaby et al. 1999). The increases in hydrogen and nitrous oxide are consistent with earlier observations suggesting tank 241-C-106 retains 3 to 6 percent gas (Stewart and Chen 1998), but the apparently larger increase for the nitrous oxide is puzzling.

Hydrogen is produced from water by radiolysis and as a byproduct of the thermal and radiolytic oxidation of organic compounds in the waste; nitrous oxide is formed from nitrite ion predominantly during thermal and radiolytic oxidation reactions of the organic molecules (Stock and Pederson 1998). Hu (1999a, 1999b) concludes radiolysis of the sludge is the dominant pathway for hydrogen formation in tank 241-C-106. The high rate of hydrogen formation per kilogram of waste and the observed releases of nitrous oxide during sluicing are

consistent with the formation and evolution of numerous oxidized organic molecules as described in Chapters 3 and 4.

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3.0 ORGANIC CONSTITUENTS IN VENTILATION STACK OF TANK 241-C-106

Five opportunistic samples were collected from the ventilation stack of tank 241-C-106 during sluicing operations on November 18, 1998. These samples were analyzed by Huckaby and Evans (1999).

Approximately 50 samples were collected before and during sluicing operations on December 16, 1998. These samples were obtained from the breathing areas near tank 241-C-106, the ventilation stack of tank 241-C-106, and the dome space of tank 241-AY-102. The volatile organic compounds were collected in SUMMA¹ canisters and triple sorbent tubes (TST).

In brief, Huckaby and coworkers (1999) and Bonfoey and coworkers (1999a) found about the same amounts of organic compounds were present in the TST and the SUMMATM canisters that were collected at the same time at the same location for the test on December 16, 1998. However, the results for the SUMMATM canisters provided additional information about the more volatile organic compounds. This discussion will center the contents of the SUMMATM canisters.

The concentrations of the compounds in the breathing area before and during sluicing, although considerably attenuated by dilution in air, correlated with the observations for the substances in the ventilation stack of tank 241-C-106 (Bartley et al. 1999). Similarly, the lower concentrations of the volatile organic compounds collected in the SUMMATM canisters in the dome space of the receiver tank correlated with their concentrations in the stack. Consequently, this report will focus on results obtained by analyzing samples from the SUMMATM canisters obtained from the ventilation stack of tank 241-C-106 during peak operations, about 1.5 to 2.5 hours after the start of the booster pump on December 16, 1998.

The analytical teams report data for "target compounds" and "tentatively identified compounds". The substances selected by the customer for quantitative analyses following the protocols of the U.S. Environmental Protection Agency (EPA) and the National Institute of Science and Technology (NIST) are designated target compounds. The concentrations of these substances are determined by using pure compounds. The other substances found in the sample are designated tentatively identified compounds. The identification is customarily made by comparing the mass spectrum of the compound with the mass spectra of compounds assembled in a large, commercially available library originally prepared by the National Institutes of Health.

¹ SUMMA is a trademark of Moletrics, Inc., Cleveland, Ohio.

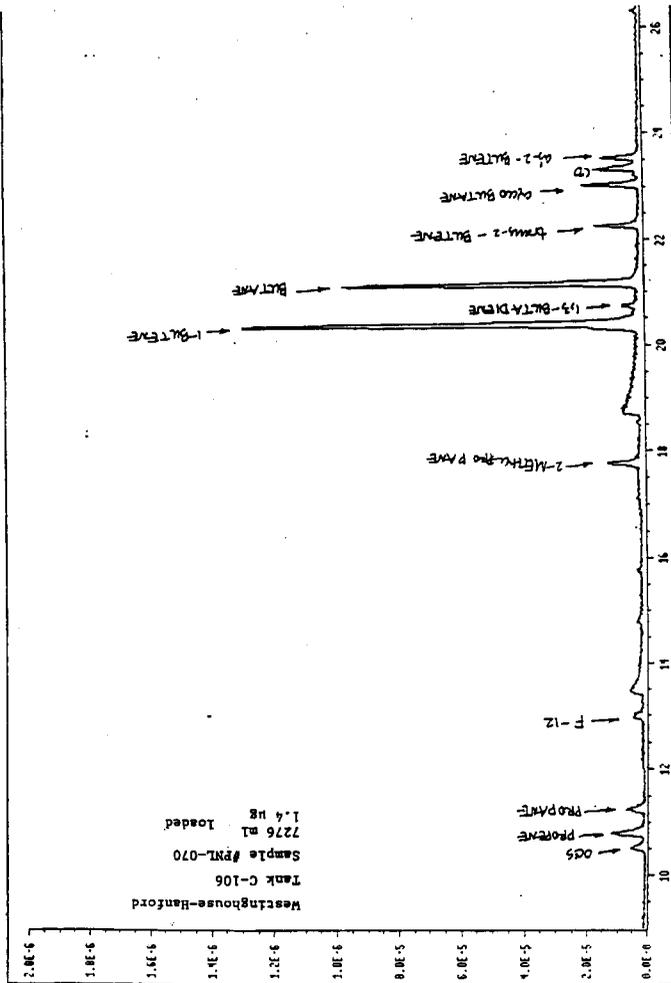
3.1 ORGANIC CONSTITUENTS IN VENTILATION STACK BEFORE SLUICING

Samples of the vapor from the dome space of quiescent tank 241-C-106 had been collected and analyzed in 1994 by Rasmussen (1994) and Jenkins and coworkers (Jenkins et al. 1995 and Ma et al. 1997). The gas chromatogram recorded by Rasmussen is shown in Figure 3-1.

The investigators established the VOC content in the dome space was quite low, only a few parts per million. Their analytical work revealed that there were many different alkanes, alkenes, aldehydes and ketones, alcohols, and nitriles together with some other substances. Acetone, butanol, the heptenes and the heptanones were more abundant than the other organic compounds.

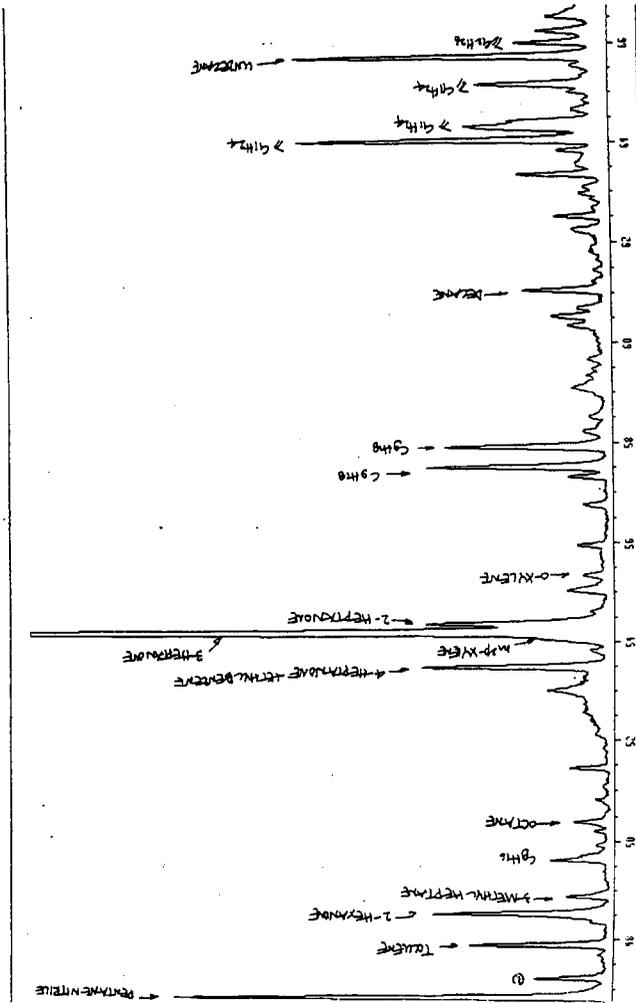
The samples that were opportunistically collected from the ventilation stack on November 18, 1998 during sluicing operations, contained 450 ppm VOC. The analytical work showed the same families of compounds were present and that the heptenes and heptanones were again prominent constituents.

Figure 3-1. Annotated Gas Chromatogram of the Organic Compounds in The Dome Space of Tank 241-C-106 in 1994 (Rasmussen 1994) (4 sheets)



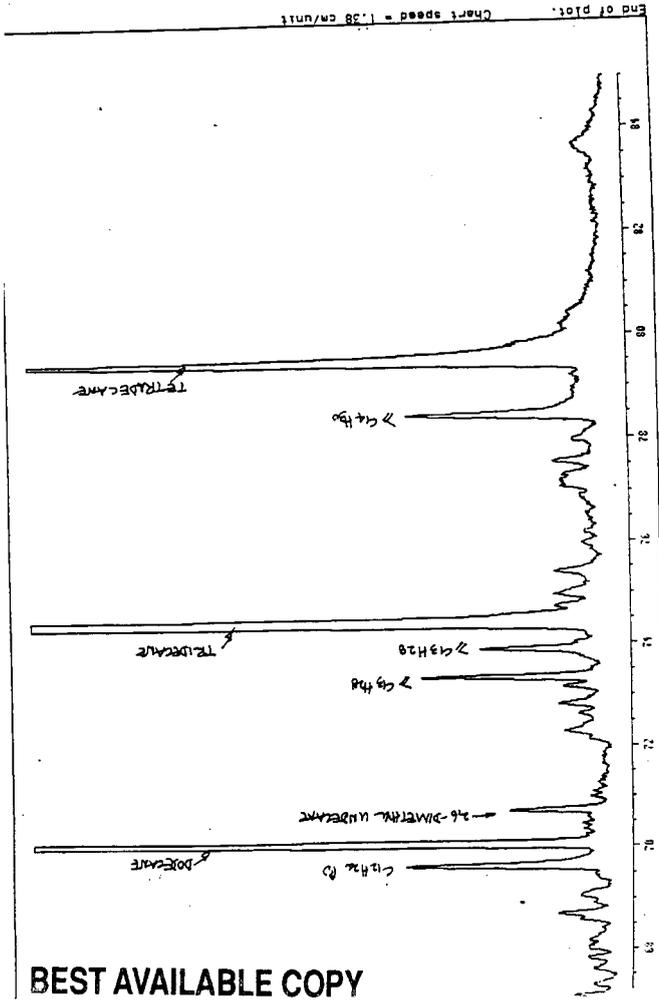
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Figure 3-1. Annotated Gas Chromatogram of the Organic Compounds in The Dome Space of Tank 241-C-106 in 1994 (Rasmussen 1994) (4 sheets)



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Figure 3-1. Annotated Gas Chromatogram of the Organic Compounds in The Dome Space of Tank 241-C-106 in 1994 (Rasmussen 1994) (4 sheets)



However, as noted in the introduction, this report will discuss the analytical work on the target compounds and tentatively identified compounds in the SUMMA™ canisters collected in the ventilation stack on December 16, 1998.

The concentrations of the compounds present in the stack of tank 241-C-106 at concentrations greater than 5 ppb before sluicing began are summarized in Table 3-1. In the table, the compounds are grouped by chemical structure. Rather than listing the concentration reported by each laboratory for each compound, the authors chose to use ranges from 5 to 10 ppb, 10 to 100 ppb, and 100 to 1000 ppb for the compounds in the stack before sluicing. The concentrations of the tentatively identified compounds are more accurately portrayed by this coarser treatment. In the table, the letter P means that the compound was observed by Pacific Northwest National Laboratory in the designated concentration range; the letter S means that the compound was observed by SAS in the designated concentration range. The combination PS means that the compound was observed by both laboratories at the designated concentration. Sometimes one laboratory observed more of a compound than the other laboratory, but inspection of the table shows there is broad agreement between the independently obtained results.

Table 3-1. Organic Compounds in the Stack of Tank 241-C-106 Before Sluicing.
(Huckaby et al. 1999; Bonfoey et al. 1999a) (2 sheets)

Compound	CAS Number	Stack Before		
		5-10 ppb	10 to 100 ppb	100 to 1000 ppb
Alkanes				
Propane	74-98-6		P	
Butane	106-97-8		PS	
Pentane	109-66-0		PS	
Hexane	110-54-3	PS		
Heptane	142-82-5	PS		
Decane	124-18-5		P	
Undecane	1120-21-4		PS	
2-Methyldecane	6975-98-0	P		
3-Methyldecane	13151-34-3	S		
5-Methyldecane	13151-35-4	S		
Dodecane	112-40-3		PS	
Tridecane	629-50-5		PS	
Cycloalkanes				
Cyclopropane	75-19-4		P	
Ethylcyclopropane	1191-96-4	P		
Alkenes				
Propene	115-07-1		P	
2-Methylpropene			P	
2-Methyl-1-propene	115-11-7		P	
1-Butene	106-98-9		S	

Table 3-1. Organic Compounds in the Stack of Tank 241-C-106 Before Sluicing.
(Huckaby et al. 1999; Bonfoey et al. 1999a) (2 sheets)

Compound	CAS Number	Stack Before		
		5-10 ppb	10 to 100 ppb	100 to 1000 ppb
1-Pentene	109-67-1	S		
E-2-Heptene	592-77-8	P	S	
Z-2-Heptene	592-77-8	P	S	
E-3-Heptene	592-78-8	P		
Z-3-Heptene	592-78-9	S		
Alcohols and Ethers				
Methanol	67-56-1		P	
Ethanol	64-17-5			PS
1-Propanol	71-23-8		PS	
1-Butanol	71-36-3		PS	
3-Heptanol	589-82-2	P		
Tetrahydrofuran	109-99-9	S		
1,3-Dioxane	505-22-6		P	
2-Methyl-1,3-dioxane	626-68-6		P	
2-Methyl-1,3-dioxalane	497-26-7		PS	
1,3-Diethyl-1,4-epoxybutane		P		
Aldehydes and Ketones				
Acetaldehyde	75-07-0		PS	
Butanal	123-72-8		PS	
Acetone	67-64-1		PS	
2-Butanone	78-93-3		PS	
2-Heptanone	110-43-3	S	P	
3-Heptanone	106-35-4		PS	
4-Heptanone	123-19-3		S	
Nitriles				
Acetonitrile	75-05-8		S	
Propanenitrile	107-12-0	PS		
Butanenitrile	109-74-0	P		
Miscellaneous Compounds				
Carbon disulfide				
Methyl formate	107-31-3	P		
Methyl nitrite	624-91-9	P		

Notes:

P = Pacific Northwest National Laboratory

S = Special Analytical Services

The observations presented in Table 3-1 closely agree with the observations of earlier investigations of the composition of the organic compounds in the dome space (Rasmussen 1994, Jenkins et al. 1995, and Ma et al. 1997).

The more recent work indicates the ventilation stack contains about 45 compounds at concentrations greater than 5 ppb. This group includes 12 alkanes, 2 cycloalkanes, 9 alkenes, 10 alcohols and ethers, 7 aldehydes and ketones, 3 nitriles, and 2 esters. More than 20 of the 45 compounds contain oxygen and are significantly soluble in water. Ten hydrocarbons have fewer than 6 carbon atoms and normal boiling points below 50 °C. The remaining compounds include 4 heptenes and 9 paraffinic hydrocarbons. As discussed more fully in Chapter 4, the water-soluble compounds are more efficiently transported from the sludge to the dome space than the water-insoluble hydrocarbons during quiescent intervals. Not surprisingly, only the more volatile or more abundant hydrocarbons among the many compounds now known to be present in the sludge are present at more than 5 ppb in the ventilation stack before sluicing begins.

3.2 ORGANIC CONSTITUENTS IN VENTILATION STACK AFTER SLUICING

The analytical results of the SAS team for the target compounds are assembled in Table 3-2. The samples were obtained in the tank 241-C-106 ventilation stack after about 2 hours of operation on December 16, 1998.

Table 3-2. Target Compounds in the Ventilation Stack of Tank 241-C-106 After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a) (2 sheets)

C-106 Target Analyte Concentrations for SUMMA™ Analyses			Sample Designation		
			VS006-051-2078		
Target Analyte Name	Mol Wt	CAS Number	Ppbv	mg/m ³	Flag
Freon 12	121	75-71-8	5.0	0.025	M
Methyl chloride	50.5	74-87-3	5.0	0.010	M
N-Butane	58	106-97-8	590	1.4	D
Ethyl Chloride	64.5	75-00-3	5.0	0.013	M
Freon 11	137.5	75-69-4	5.0	0.028	Q
N-Pentane	72	109-66-0	173	0.51	
Dichloromethane	85	75-09-2	5.0	0.017	M
2-Methyl-Pentane	86	107-83-5	18	0.063	
1-Hexene	84	592-41-6	310	1.1	D
N-Hexane	86	110-54-3	130	0.46	
Chloroform	119.5	67-66-3	5.0	0.024	M
Benzene	78	71-43-2	7.0	0.022	
Carbon Tetrachloride	154	56-23-5	5.0	0.031	M
3-Methyl-Hexane	100	589-34-4	5.8	0.024	

Table 3-2. Target Compounds in the Ventilation Stack of Tank 241-C-106 After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a) (2 sheets)

C-106 Target Analyte Concentrations for SUMMA™ Analyses			Sample Designation		
			VS006-051-2078		
Target Analyte Name	Mol Wt	CAS Number	Ppbv	mg/m ³	Flag
N-Heptane	100	142-82-5	230	0.92	
Toluene	92	108-88-3	33	0.13	
N-Octane	114	111-65-9	65	0.30	
Tetrachloroethylene	166	127-18-4	5.0	0.034	M
Chlorobenzene	112.5	108-90-7	5.0	0.023	M
Ethylbenzene	106	100-41-4	5.0	0.022	M
m,p-Xylene	106	108-38-3 106-42-3	5.0	0.022	
Styrene	104	100-42-5	5.0	0.021	M
N-Nonane	126	111-84-2	77	0.40	
1,1,2,2-Tetrachloroethane	168	79-34-5	5.0	0.034	M
o-Xylene	106	95-47-6	5.0	0.022	M
N-Decane	142	124-18-5	120	0.67	
1,2,4-Trimethylbenzene	120	95-63-6	5.0	0.025	M
Ethanol	46	64-17-5	500	0.94	D
Acetonitrile	41	75-05-8	79	0.13	
Acetone	58	67-64-1	240	0.57	
Furan	68	110-00-9	5.0	0.014	M
2-Propanol	60	67-63-0	5.0	0.012	Q
1-Propanol	60	71-23-8	20	0.049	
Propanenitrile	55	107-12-0	68	0.15	
Butanal	72	123-72-8	5.0	0.015	M
2-Butanone	72	78-93-3	62	0.18	
Tetrahydrofuran	72	109-99-9	8.2	0.024	
1-Butanol	74	71-36-3	186	0.56	B
Butanenitrile	69	109-74-0	5.0	0.014	M
2-Pentanone	86	107-87-9	24	0.083	
1,4-Dioxane	88	123-91-1	5.0	0.018	M
4-Methyl-2-Pentanone	100	108-10-1	5.0	0.020	Q
2-Hexanone	100	591-78-6	118	0.48	
3-Heptanone	114	106-35-4	2037	9.5	D
2-Heptanone	114	110-43-3	382	1.8	D
Cyclohexanone	98	108-94-1	5.0	0.020	M
2-Octanone	128	111-13-7	13	0.069	

Notes:

D = Target analyte reported is the result of a secondary dilution.

M = Target analyte was absent (not detected) in sample.

Q = Target analyte was detected, but at concentrations less than VPRQL.

¹ mg/m³ calculated at 25°C and 101.3 kPa (1 atmosphere)

The analytical results of the SAS team for the tentatively identified compounds are assembled in Table 3-3. The samples were obtained in the tank 241-C-106 ventilation stack after about 2 hours of operation on December 16, 1998. This much larger group of organic substances was elaborated on the basis of substances' retention times, their mass spectra, comparison with related results provided by the Oak Ridge National Laboratory and the Oregon Graduate Institute, and chemical inferences based on the original source term.

Table 3-3. Tentatively Identified Compounds in Ventilation Stack of Tank 241-C-106 After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a)
Extended List of Tentatively Identified Compounds in Sample VS006-051-S078.¹
(5 sheets)

Tentative ID	CAS#	Mol Wgt	Concentration (mg/m ³)	Concentration (ppbv)
Propene	115-07-1	42	1.48	860
Propane	74-98-6	44	0.71	395
1-Propyne	74-99-7	40	0.09	57
Methyl nitrite	624-91-9	61	0.10	39
Cyclopropane	75-19-4	42	0.18	103
Isobutane	75-28-5	58	0.14	60
Acetaldehyde	75-07-0	44	0.14	79
1-Butene	106-98-9	56	4.75	2075
E-2-Butene	624-64-6	56	0.41	180
Z-2-Butene	590-18-1	56	0.37	162
1-Propene, 2-methyl-	115-11-7	56	0.84	365
Unknown		74	0.08	27
C4-diene/yne		54	0.07	31
1,1-Dimethylcyclopropane	1630-94-0	70	0.10	33
Butane, 2-methyl-	78-78-4	72	0.20	69
1-Pentene	109-67-1	70	1.30	454
1-butene, 2-methyl	563-46-2	70	0.35	122
2-Pentene, E	627-20-3	70	0.37	127
2-Pentene, Z	627-20-3	70	0.14	49
Ethylcyclopropane	1191-96-4	70	0.28	97
1,2-dimethyl cyclopropane	930-18-7	70	0.08	30
C5 cycloalkane/alkene		70	0.06	20
1,3-pentadiene		68	0.04	13
Unknown		78	0.05	15
Unknown		78	0.02	5
C5 diene/cycloalkane		68	0.02	6
Unknown		76	0.13	42
C5 diene/ cycloalkane		68	0.02	7
1-Pentene, 4-methyl-	691-37-2	84	0.26	76
Cyclopentane	287-92-3	84	0.04	11
Pentane, 2-methyl-	107-83-5	86	0.32	90
C6 alkene/cycloalkane		84	0.03	10
Silanol, trimethyl-	1066-40-6	90	0.08	22

Table 3-3. Tentatively Identified Compounds in Ventilation Stack of Tank 241-C-106 After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a)
 Extended List of Tentatively Identified Compounds in Sample VS006-051-S078.¹
 (5 sheets)

Tentative ID	CAS#	Mol Wgt	Concentration (mg/m ³)	Concentration (ppbv)
Propanenitrile	107-12-0	55	0.26	114
1,5-Hexadiene	592-42-7	82	0.06	17
C6 aliphatic compound		86	0.10	27
Unknown		86	0.05	13
Pentane, 3-methylene-	760-21-4	84	0.04	11
3-Hexene, E	13269-52-8	84	0.12	34
2-Hexene, E	4050-45-7	84	0.24	69
C6 Cycloalkane/alkene		84	0.04	12
C6 Cyclic alkene		82	0.03	8
3-Hexene, Z	7642-09-3	84	0.27	79
Cyclopropane, propyl-	2415-72-7	84	0.08	24
1-Hexyne	693-02-7	82	0.18	53
C6 alkene/cycloalkane		84	0.07	19
Unknown		91	0.21	56
Unknown		82	0.06	18
3-Hexene, -methyl, isomer	692-24-0	98	0.06	15
Cyclopentene, methyl, isomer		82	0.06	17
1-Hexene, 5-methyl-		98	0.05	13
3-Hexene, 2-methyl-, E	692-24-0	98	0.11	29
Hexane, 2-methyl-	591-76-4	100	0.10	25
2-Hexene, 5-methyl-, E	7385-82-2	98	0.16	39
3-Heptene, E	14686-14-7	98	0.34	84
2-Hexyne		82	0.12	36
2-hexene, 5-methyl, Z		98	0.10	26
Cyclohexene		82	0.04	12
1-Hexene, 2-methyl-	6094-02-6	98	0.13	34
1-Heptene	592-76-7	98	1.77	440
Butanenitrile, 2-methylene-	1647-11-6	81	0.69	208
3-Heptene, E	592-78-9	98	4.38	1093
2-Heptene, E	14686-13-6	98	6.61	1649
2-Heptene, Z	592-77-8	98	5.35	1334
2,4-hexadiene, 4-methyl-		96	0.03	9
Cyclopropane, butyl-	930-57-4	98	1.28	319
Methylcyclohexane		98	0.12	31
Hexane, 2,4-dimethyl-	589-43-5	114	0.05	10
Cyclopentane, ethyl-	1640-89-7	98	0.13	32
Heptadiene, isomer	2454-31-1	96	0.10	25
Unknown C8 alkene/cycloalkane	5685-46-1	112	0.13	29
1-Heptene, 3-methyl-	4810-09-7	112	0.11	23
Unknown, mz 112		112	0.05	11
C7cycloalkene/diene		96	2.25	572

Table 3-3. Tentatively Identified Compounds in Ventilation Stack of Tank 241-C-106 After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a)
 Extended List of Tentatively Identified Compounds in Sample VS006-051-S078.¹
 (5 sheets)

Tentative ID	CAS#	Mol Wgt	Concentration (mg/m ³)	Concentration (ppbv)
Heptane, 3-methyl-	589-81-1	114	3.24	696
2-Octene, isomer		112	0.62	136
2-Heptyne	1119-65-9	96	1.85	471
3-Hexanone	589-38-8	100	0.09	22
Heptane, 3-methylene-	1632-16-2	112	3.88	848
3-heptene, 5-methyl-,	50422-80-5	112	0.40	87
4-Octene, isomer	14850-23-8	112	0.24	53
C8 alkene/cycloalkane		112	2.55	557
2-Octene, isomer	7642-04-8	112	0.27	60
2-Heptene, 3-methyl-	3404-75-9	112	0.78	171
2-Octene, isomer	38851-70-6	112	0.30	65
Octene, isomer		112	0.11	24
3-Hexanone, 5-methyl-	623-56-3	114	0.17	35
Cyclohexane, ethyl-	1678-91-7	112	0.08	18
Cyclohexane, 1,1,3-trimethyl-	3073-66-3	126	0.10	19
C8 aliphatic hydrocarbon		126	0.11	20
Unknown		113	0.26	56
4-Heptanone	123-19-3	114	3.62	776
Hexanenitrile	628-73-9	97	0.20	51
n-Butyl ether	142-96-1	130	0.48	91
3-Heptanol	589-82-2	116	0.71	150
Unknown		126	0.09	17
Unknown		126	0.06	11
Unknown		124	0.10	20
C9 cycloalkane/alkene		126	0.09	18
Unknown		128	0.78	149
4-Heptanone, 3-methyl-	15726-15-5	128	0.16	31
Unknown		128	1.85	353
1,3-Diethyl-1,4-epoxybutane		128	2.12	406
C7 alkene/cycloalkane		128	1.98	379
Unknown		126	2.28	443
C10 aliphatic hydrocarbon-		142	0.12	20
4-Octanone	589-63-9	128	0.41	79
Heptanenitrile	629-08-3	111	0.45	99
3-Octanone	106-68-3	128	0.14	27
2-Octanone	111-13-7	140	0.25	43
Cyclohexane, 1-methyl-3-propyl-	4291-80-9	140	0.15	27
Unknown		140	0.07	13
Unknown		140	1.83	320
Decane, 4-methyl-	2847-72-5	156	0.34	54
1-Hexanol, 2-ethyl-	104-76-7	130	0.68	129

Table 3-3. Tentatively Identified Compounds in Ventilation Stack of Tank 241-C-106 After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a)
 Extended List of Tentatively Identified Compounds in Sample VS006-051-S078.¹
 (5 sheets)

Tentative ID	CAS#	Mol Wgt	Concentration (mg/m ³)	Concentration (ppbv)
Cyclohexane, (2-methylpropyl)-	1678-98-4	140	0.10	17
Unknown		154	0.06	10
Decane, 3-methyl-	13151-34-3	156	0.05	9
Octanenitrile	124-12-9	125	0.33	64
3-Undecene, isomer	821-97-6	154	0.14	22
Undecane	1120-21-4	156	1.41	221
Unknown		154	0.09	14
Unknown		154	0.27	42
Naphthalene, decahydro-2-methyl-	2958-76-1	152	0.12	19
Unknown		139	0.14	24
trans-Decalin, 2-methyl-	1000152-47-	152	0.15	24
Cyclohexane, C5 substituted		154	0.15	24
Undecane, 6-methyl-	17302-33-9	170	0.07	10
Naphthalene, decahydro, methyl isomer		152	0.16	26
Undecane, 2-methyl-	7045-71-8	170	0.13	19
Undecane, 3-methyl-	1002-43-3	170	0.05	7
Dodecene, isomer		168	0.11	16
Naphthalene, decahydro-dimethyl-, isomer		166	0.03	5
Dodecane	112-40-3	170	2.60	373
Naphthalene, decahydro dimethyl-, isomer		166	0.04	6
Dodecane, 6-methyl-	6044-71-9	184	0.40	53
Cyclohexane, 2-butyl-1,1,3-trimethyl-	54676-39-0	182	0.07	9
Cyclohexane, (4-methylpentyl)-	61142-20-9	168	0.07	10
Undecane, 2,10-dimethyl-	17301-27-8	184	0.07	9
Decane, 2,6,7-trimethyl-	62108-25-2	184	0.44	59
Tridecene, isomer		182	0.17	23

Table 3-3. Tentatively Identified Compounds in Ventilation Stack of Tank 241-C-106 After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a) Extended List of Tentatively Identified Compounds in Sample VS006-051-S078.¹
(5 sheets)

Tentative ID	CAS#	Mol Wgt	Concentration (mg/m ³)	Concentration (ppbv)
Tridecane	629-50-5	184	3.48	462
Tridecane, 6-methyl-	13287-21-3	198	0.05	6
Dodecane, trimethyl-, isomer		212	0.12	13
Tetradecane	629-59-4	198	0.90	111

Notes:

¹Quatitation is based on the chlorobenzene-d₆ internal standard. The extended TIC list reports nontarget compounds at estimated concentrations of 5 ppbv or higher. Analyzed by GC-MS with Cryotrapping.

Table 3-4 presents the analytical results reported by Pacific Norwest National Laboratory and SAS for the compounds present the tank-241-C-106 ventilation stack before sluicing began and about 2 hours later, during the operation, on December 16, 1998. This table is formatted in the same way as Table 3-1, except it includes an additional concentration range, greater than 1,000 ppb (1 ppm). No concentrations exceeded 10,000 ppb (10 ppm) in the December operation.

Table 3-4. Chemical Families of Target and Tentatively Identified Compounds in the Ventilation Stack Before Sluicing and After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a; Huckaby et al. 1999). (6 sheets)

Compound	Stack Before Sluicing Operation				Stack After ~ 2 hrs			
	CAS Number	5-10 ppb	10-100 ppb	100-1,000 ppb	5-10 ppb	10-100 ppb	100-1,000 ppb	1000-10,000 ppb
Alkanes								
Propane	74-98-6		P				PS	
Butane	106-97-8		PS				PS	
2-Methylpropane	75-28-5					S	P	
Pentane	109-66-0		PS				PS	
2-Methylbutane	78-78-4					S		
Hexane	110-54-3	PS					PS	
2-Methylpentane	107-83-5					PS		
Neopentane								
3-Methylpentane	96-14-0				P			
Heptane	142-82-5	PS					PS	
2-Methylhexane	591-76-4					S		
3-Methylhexane	589-34-4				PS			
2,4-Dimethylpentane	108-08-7							
Octane	111-65-9					PS		
3-Methylheptane	589-81-1						PS	
2,4-Dimethylhexane	589-43-5				S			
Nonane	111-84-2					PS		
Decane	124-18-5		P				PS	
Undecane	1120-21-4		PS				PS	

Table 3-4. Chemical Families of Target and Tentatively Identified Compounds in the Ventilation Stack Before Sluicing and After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a; Huckaby et al. 1999), (6 sheets)

Compound	Stack Before Sluicing Operation				Stack After ~ 2 hrs			
	CAS Number	5-10 ppb	>10-100 ppb	>100-1,000 ppb	5-10 ppb	>10-100 ppb	>100-1,000 ppb	>1000-10,000 ppb
2-Methyldecane	6975-98-0	P				P		
3-Methyldecane	13151-34-3	S			S	P		
4-Methyldecane	2847-72-5					PS		
5-Methyldecane	13151-35-4	S				P		
Dodecane	112-40-3		PS				PS	
2-Methylundecane	7045-71-8				P	S		
3-Methylundecane	1002-43-3				PS			
5-Methylundecane					P			
6-Methylundecane	17302-33-9				S			
2,9-Dimethyldecane	1002-17-1					P		
Tridecane	629-50-5		PS				S	P
6-Methyldodecane	6044-71-9					S		
2,6-Dimethylundecane	17301-23-4					P		
2,10-Dimethylundecane					S			
2,6,7-Trimethyldecane						S		
Tetradecane	629-59-4						PS	
6-Methyltridecane	13287-21-3				S			
7-Methyltridecane	26730-14-3					P		
2,6,10-Trimethyldodecane						S		
Cycloalkanes								
Cyclopropane	75-19-4		P			P	S	
Ethyl-	1191-96-4	P				S		
Propyl-	2415-72-7					S		
Butyl-	930-57-4						S	
1-Methyl-2-pentyl-	41977-37-1					P		
cis-1-Butyl-2-methyl								
trans-1-Butyl-2-methyl								
1,1-Dimethyl	1630-94-0					S		
1,2-Dimethyl	930-18-7					S		
Cyclopentane	287-92-3					S		
Methyl-	96-37-7				P			
Ethyl-	1640-89-7					S	P	
cis-1,2-Dimethyl-	1192-18-3						P	
1,2-Dibutyl-								
Cyclohexane,	110-82-7				P	S		
Methyl-	108-87-2					S		
Ethyl-						S		
1,1,3-trimethyl-	3073-66-3					S		
1-Methyl-3-propyl-	4291-80-9					PS		
2-(Methylpropyl)-	1678-98-4					PS		
Pentyl-	4292-92-6					P		
(4-methylpentyl)-	61142-20-9				S			
1-Ethyl-2,2,6-trimethyl-						P		
2-Butyl-1,1,3-trimethyl-	54676-39-0				S	P		

Table 3-4. Chemical Families of Target and Tentatively Identified Compounds in the Ventilation Stack Before Sluicing and After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a; Huckaby et al. 1999). (6 sheets)

Compound	Stack Before Sluicing Operation				Stack After ~ 2 hrs			
	CAS Number	5-10 ppb	>10-100 ppb	>100-1,000 ppb	5-10 ppb	>10-100 ppb	>100-1,000 ppb	>1000-10,000 ppb
1,1,2,3-tetramethyl-1R,2T,4T,5C-Tetramethyl-	19899-39-9					P		
Naphthalene, decahydro	493-02-7					P		
2-Methyl-Methyl, isomer	1000152-47					PS		
1,5- or 2,3-Dimethyl-2,6-Dimethyl-	1008-80-6				PS	S		
	1618-22-0				PS			
Spiropentane								
Aromatic Compounds								
Benzene	71-43-2				PS			
Toluene	108-88-3					PS		
Ethylbenzene	100-41-4							
o-Xylene	95-47-6							
p/m-Xylene	106-42-3							
1-Ethyl-2-Methyl-Benzene	611-14-3							
1,2,4-Trimethylbenzene	95-63-6							
1,3,5-Trimethylbenzene	108-67-8							
Styrene	100-42-5							
Alkenes								
Propene	115-07-1		P				PS	
2-Methylpropene			P				P	
2-Methyl-1-propene	115-11-7		P				PS	
1-Butene	106-98-9		S			P		S
E-2-Butene	624-64-6						PS	
Z-2-Butene	590-18-1						S	
2-Methyl-1-butene	563-46-2					P	S	
1-Pentene	109-67-1	S					S	
E-2-Pentene	646-048-8					P	S	
Z-2-Pentene	627-20-3					P		
2-Methyl-1-pentene	763-29-1					P		
4-Methyl-1-pentene	691-37-2					PS		
3-Methylenepentane	760-21-4					S		
1-Hexene	592-41-6						PS	
2-Methyl-1-hexene					P	S		
Methyl-3-hexene, isomer	692-24-0					S		
5-Methyl-1-hexene						S		
E-2-Hexene	4050-45-7					PS		
Z-2-Hexene	592-43-8					P		
E-3-Hexene	13269-52-8					S		
3-Ethyl-2-Hexene								

Table 3-4. Chemical Families of Target and Tentatively Identified Compounds in the Ventilation Stack Before Sluicing and After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a; Huckaby et al. 1999). (6 sheets)

Compound	Stack Before Sluicing Operation				Stack After ~ 2 hrs			
	CAS Number	5-10 ppb	>10-100 ppb	>100-1,000 ppb	5-10 ppb	>10-100 ppb	>100-1,000 ppb	>1000-10,000 ppb
E-5-Methyl-2-hexene	7385-82-2					S		
Z-5-Methyl-2-hexene						S		
Z-3-Hexene	7642-09-3					S		
E-2-Methyl-3-hexene	692-24-0					PS		
Z-2-Methyl-3-hexene	15840-60-5							
3-Ethyl-3-hexene	16789-51-8					P		
1-Heptene	592-76-7						S	P
3-Methyl-1-heptene						S		
E-2-Heptene	592-77-8	P	S					PS
Z-2-Heptene	592-77-8	P	S					PS
3-Methyl-2-heptene	3404-75-9					P	S	
E-3-Heptene	592-78-8	P					S	P
Z-3-Heptene	592-78-9	S						PS
3-Methyl-3-heptene	7300-03-0						P	
5-Methyl-3-heptene, isomer	50422-80-5					S		
3-Methyleneheptane	1632-16-2						PS	
E-2-Octene	13389-42-9					P	S	
Z-2-Octene	7642-04-8					PS		
4-Octene, isomer	14850-23-8					S		
Octene, isomer						S		
Z-3-Undecene	821-97-6					S		
Dodecene, isomer						S		
6-Dodecene, (E)-	7206-17-9							
Tridecene, isomer						S		
1,2-Dimethyl-3-methylene-cyclopropane					P			
Methylcyclopentene, isomer						S		
Cyclohexene					S			
Alkadienes and Alkynes								
1,3-Pentadiene						S		
3-Methyl-1,4-pentadiene	1115-08-8					P		
1,4-Hexadiene					P			
1,5-Hexadiene	592-42-7					S		
Heptadiene, isomer	2454-31-1					S		
1,4-Heptadiene	5675-22-9							
1,5-Heptadiene, (Z)-	7736-34-7							
4-Methyl-2,4-hexadiene					S			
1-Propyne	74-99-7					S		
3-Methyl-1-butyne	589-23-2					P		
1-Hexyne	693-02-7					S		
2-Hexyne						S		
2-Heptyne	1119-65-9						PS	

Table 3-4. Chemical Families of Target and Tentatively Identified Compounds in the Ventilation Stack Before Sluicing and After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a; Huckaby et al. 1999). (6 sheets)

Compound	Stack Before Sluicing Operation				Stack After ~ 2 hrs			
	CAS Number	5-10 ppb	>10-100 ppb	>100-1,000 ppb	5-10 ppb	>10-100 ppb	>100-1,000 ppb	>1000-10,000 ppb
Alcohols and Ethers								
Methanol	67-56-1		P				P	
Ethanol	64-17-5			PS			PS	
2-Butoxy-Ethanol	111-76-2							
1-Propanol	71-23-8		PS			PS		
2-Propanol	67-63-0				P			
1-Butanol	71-36-3		PS				PS	
2-Heptanol	6033-23-4					P		
3-Heptanol	589-82-2	P					PS	
2-Ethylhexanol	104-76-7						PS	
Dibutyl ether	142-96-1					S		
Furan	110-00-9							
Tetrahydrofuran	109-99-9	S			PS			
1,3-Dioxane	505-22-6		P					
1,4-Dioxane	123-91-1							
2-Methyl-1,3-dioxane	626-68-6		P					
2-Methyl-1,3-dioxalane	497-26-7		PS					
1,2-Diethyl-1,4-epoxybutane							PS	
1,3-Diethyl-1,4-epoxybutane		P					PS	
2,2,5,5-Tetramethyltetrahydrofuran	15045-43-9					P		
Aldehydes and Ketones								
Acetaldehyde	75-07-0		PS			PS		
Butanal	123-72-8		PS			P		
2-Ethenyl-2-butanal	20521-42-0							P
Hexanal					P			
Z-4-Hepteneal	6728-31-0					P		
Acetone	67-64-1		PS				PS	
2-Butanone	78-93-3		PS			PS		
2-Pentanone	107-87-9					PS		
4-Methyl-2-pentanone	108-10-1				P			
4-Methyl-3-pentanone					P			
2-Hexanone	591-78-6						PS	
3-Hexanone	589-38-8					S		
Cyclohexanone	108-10-1						P	
2-Heptanone	110-43-3	S	P				PS	
3-Heptanone	106-35-4		PS					PS
4-Heptanone	123-19-3		S				PS	
3-Methyl-4-heptanone	15726-15-5					S		
5-Methyl-3-hexanone	623-56-3					PS		

Table 3-4. Chemical Families of Target and Tentatively Identified Compounds in the Ventilation Stack Before Sluicing and After Sluicing for Approximately 2 Hours on December 16, 1998 (Bonfoey et al. 1999a; Huckaby et al. 1999). (6 sheets)

Compound	Stack Before Sluicing Operation				Stack After ~ 2 hrs			
	CAS Number	5-10 ppb	>10-100 ppb	>100-1,000 ppb	5-10 ppb	>10-100 ppb	>100-1,000 ppb	>1000-10,000 ppb
Miscellaneous Compounds								
Carbon disulfide						S		
Methyl formate	107-31-3	P						
Methyl nitrite	624-91-9	P				PS		
Trimethylsilanol	1066-40-6					PS		
Pyridine	110-86-1					P		
Methyl nitrate						S		
Ethyl nitrate						S		
Nitrous acid, butyl ester	544-16-1							
Formic acid, butyl ester	592-84-7							
Carbon Dioxide								
Nitrous Oxide								
Ammonia	7664-41-7							
NOX (Direct Read)								
NO								
NO ₂								

Notes:

- P = Pacific Northwest National Laboratory
- S = Special Analytical Services

The two laboratories provide consistent, complementary information about the organic composition of the vapor and, by inference, about the composition of the organic material remaining in the condensed phases.

As already mentioned, the identities and concentrations of 40 target compounds have been established by comparing the samples with authentic materials, the identities of 100 other compounds have been tentatively established by other means. The relative concentrations of these substances do not change appreciably even though the absolute concentrations vary significantly during sluicing, depending on the nozzle orientation and other factors. This variation in VOC concentration has been exploited to control the rate at which the VOCs are released during sluicing.

Rasmussen (1994) and the Oak Ridge team (Jenkins et al 1994, Ma et al. 1997) provided information about the organic components in the dome space under quiescent conditions. The more numerous observations from Pacific Northwest National Laboratory and SAS are consistent with the earlier findings. Before sluicing begins, about 45 compounds are present in the ventilation stack with concentrations greater than 5 ppb. About 50 percent of these compounds contain oxygen and are completely or partially soluble in water. Ethanol is the only compound at greater than 100 ppb in the stack before sluicing. About 25 percent of the compounds are low-molecular-weight hydrocarbons, several of which have boiling points lower than the temperature of the sludge. Four heptenes and nine paraffinic hydrocarbons constitute the remainder of this group.

When sluicing begins, the VOC concentration in the stack increases greatly. The concentrations of some compounds already present at the 5 ppb level, including acetonitrile, acetaldehyde, butanal, 2-butanone, and several dioxanes, show modest change, but the concentrations of most compounds, including the heptenes and heptanones, increase significantly, and many other substances, which were undetectable before sluicing, appear at measurable concentrations. These observations show a distinct pattern: sluicing causes larger increases in the relative concentrations of water-insoluble organic components. The concentrations of water-soluble organic compounds also increase, but to a smaller degree. These observations imply that water-soluble organic compounds generated in the sludge are transported to the dome space more efficiently than water-insoluble compounds by transport through aqueous phases under quiescent conditions. The insoluble organic compounds are selectively retained in the sludge.

The same substances evolved from the waste during operations in November and December. The absolute concentrations differ in each operation, but the relative concentrations are not substantially different.

The observations summarized in Tables 2, 3, and 4 indicate about 55 alkenes, alkadienes, and alkynes, 35 alkanes, 25 cycloalkanes, 2 aromatic compounds, 20 alcohols and ethers, 25 aldehydes and ketones, 10 nitriles, and 10 miscellaneous compounds were present at more than 5 ppb. About 50 of these substances were present in concentrations between 100 and 1000 ppb. The concentrations of tridecane, 1-butene, 1-heptene, E-2-heptene, E-3-heptene,

Z-3- heptene, 3-methyl-2-heptene, 3-heptanone and 2-ethenylbutanal were between 1,000 and 10,000 ppb in the stack. No organic compounds were present at concentrations exceeding 10,000 ppb during this test.

The 200 compounds can be assembled into eight different structural categories for convenient discussion.

Alkanes. Alkane hydrocarbons, ranging from propane to tetradecane and including lesser amounts of branched chain hydrocarbons, principally methylalkanes, emerge from the sludge. The appearance of undecane, dodecane, tridecane, and tetradecane and their methyl derivatives coupled with the virtual absence of highly branched compounds indicate these alkanes originate from unchanged NPH remaining in the sludge. The lower molecular weight alkanes arise from radiolytic reactions of the original NPH and the phosphate esters, as discussed later.

Alkenes. A large family of alkene hydrocarbons is observed. The alkene hydrocarbons range from propene to decene and include small amounts of some alkadienes and alkynes. These compounds have predominantly linear structures. Many of these substances originate from chemical transformations of the NPH, but the higher relative abundance of the heptenes indicates they arise from BEHP, which is now the most abundant constituent in the oil. As discussed in the next section, the alkanes in the waste, whether originally present in the NPH or formed from it during storage, and the phosphate esters undergo radiolysis to produce lower molecular weight alkenes.

Hydrogen is the most abundant byproduct of the radiolytic conversion of alkanes into alkenes (Spinks and Woods 1990).

Cycloalkanes. Cycloalkanes with three-, five-, and six-membered rings and certain decalins with joined six-membered rings are present in low concentrations. The compounds with 10 or more carbon atoms could have been present as impurities in the original NPH. Alternatively, these substances and the other lower molecular weight compounds may be products of radiolytically induced cyclization reactions.

Benzene, Toluene, Xylenes, and Other Aromatic Hydrocarbons . The concentrations of benzene, toluene, and the xylenes and other aromatic hydrocarbons are very low. This observation is compatible with the information that aromatic compounds were removed from the NPH during manufacture. In addition, the formation of aromatic compounds from alkanes by radiolysis requires the formation of several reactive intermediate compounds that can be intercepted by oxidizing agents present in the waste.

Alcohols and Ethers. Several alcohols and ethers are present in relatively high concentration. Only two substances, 1-butanol and 2-ethyl-1-hexanol, form by simple hydrolysis reactions. Methanol, ethanol, and propanol are intermediates in reaction sequences leading to aldehydes and carboxylate ions. The topological structures of the ethers indicate they arise predominantly from butyl or 2-ethylhexyl groups.

As discussed more fully in Chapter 4, the alcohols, ethers, aldehydes, ketones and nitriles are produced in rather long organic reaction sequences that begin with the formation of C-hydroxy, C-nitroso, C-nitro, and O-nitro compounds.

Nitrite ion is reduced to nitrous oxide, nitrogen, and ammonia in the reaction sequences leading to the oxygen-containing compounds and nitriles.

Aldehydes and Ketones. Homologous series of aldehydes and ketones are evident. As a result of their greater reactivity, the concentrations of the aldehydes are significantly smaller than the concentrations of the corresponding ketones. The more abundant ketones with seven and eight carbon are formed during radiolysis of BEHP.

Nitriles. Homologous series of linear nitriles also are constituents of the emerging VOCs. Linear nitriles are often observed in dome spaces of the tanks, but a new toxicologically active allylic nitrile, 2-methylenebutanenitrile, also is present in significant amount in tank 241-C-106. Relatively high concentrations of this toxicologically active (Bartley et al. 1999) compound were reported independently by Pacific Northwest National Laboratory and SAS. While no commercial sample of this nitrile is available to confirm its identification, the retention time and the mass spectrum provide substantial support for the tentative structural assignment. The nitriles are volatile and evolve from the waste, but they also hydrolyze to provide carboxylate ions that are retained in the alkaline supernatant layer.

Halogens. Ten halogen compounds were included among the target analytes. According to the SAS report, only one of these compounds was present in detectable concentrations. It was present before and after the operation of the pump at less than 5 ppb. Sluicing does not appear to be responsible for the appearance of these compounds.

Tributyl Phosphate. TBP, which is present at relatively low concentration in the oil and has a low vapor pressure was not detected as a constituent of the vapor by SAS or Pacific Northwest National Laboratory in SUMMA™ or TST samples.

4.0 ORIGINS OF VOLATILE ORGANIC COMPOUNDS

4.1 INTRODUCTION

Although uncertainties exist about the TOC and oxalate ion contents of the sludge in Layers 3 and 4 and about the total amount of oil in the waste, the analytical work on the oil and the volatile components in the ventilation stack during sluicing uniquely establishes that the volatile compounds originate from B Plant process chemicals. The original mixture had 10 parts by weight NPH, 6.5 parts tributyl phosphate, and 1 part sodium bis(2-ethylhexyl)phosphate. The oil isolated from the waste is predominantly sodium bis(2-ethylhexyl)phosphate with lesser amounts of butyl bis(2-ethylhexyl)phosphate and sodium butyl (2-ethylhexyl)phosphate, other phosphate esters, and residual NPH. The chemical changes that occurred in the composition of this material are considered in this section as prelude to completing the discussion of the origins of the VOCs in the ventilation stack. Some chemical changes occurred during the process, but most changes have taken place during interim storage. The following sections describe how ongoing physical processes, principally evaporation, and chemical processes such as ester hydrolysis and radiolytic transformations are continuously altering the organic composition.

4.2 HYDROCARBON TRANSFORMATIONS

4.2.1 Hydrocarbon Vaporization

This pathway for hydrocarbon loss has been discussed in tank characterization reports, the organic solvent topical report (Cowley and Meacham 1998), and in an engineering assessment of the waste transfer from tank 241-C-103 (Bartley et al. 1995). Bartley and coworkers (1995) have summarized the available information and developed an engineering model to describe the rates at which organic constituents evolve from waste. Hydrocarbon evaporation is the most important factor in changing the NPH/phosphate ester ratio. The characterization work on the oil from tank 241-C-106, Figure 2-1, implies that the originally abundant NPHs are now minor constituents of the oil. Nevertheless, readily detectable concentrations of the original NPHs emerge during the sluicing operation.

4.2.2 Hydrocarbon Chemistry

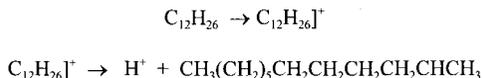
Hydrocarbons do not undergo ionic reactions in the sludge in tank 241-C-106. The hydrogen generation model advanced by Hu (1999a, 1999b) which implies thermally-initiated reactions are much less important than the radiolytically-initiated reactions, is in accord with this viewpoint. Only the radiolytic reactions will be discussed in this report.

4.2.3 Hydrocarbon Radiolysis

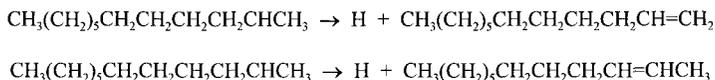
The radiolytic reactions of the water-insoluble hydrocarbons take place in the oil. It is necessary to distinguish between direct and indirect radiolytic reactions. In radiolytic reactions, the radiation damage occurs directly between the emanation and a target molecule; in indirect radiolytic reactions, the radiation damage occurs as a consequence of an initial reaction between the emanation and water, then the radicals resulting from that interaction react with an organic molecule. Radiolysis of the organic molecules in the Hanford Site waste is most effective in aqueous solution where the radiolytic emanations of soluble cesium and strontium ions take place. Both direct reactions and indirect reactions occur in water. The indirect reactions occur in aqueous solution between soluble organic compounds and the hydroxyl radical and its anion, nitric oxide, and nitrogen dioxide (Meisel et al. 1993, Camaioni et al. 1998). The rates of radiolysis of the organic compounds in the oil are slower because the concentrations of water and cesium, strontium, nitrite, and nitrate ions are very low. Moreover, the reagents, i.e., hydroxyl radical, nitric oxide, and nitrogen dioxide, produced in the aqueous phase are not effectively transported to the oil phase because they are consumed in competitive reactions in water. In this situation, the compounds in the oil decompose more slowly.

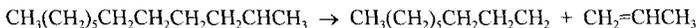
Nevertheless, radiolysis has changed the composition of the NPH during the operation of the PUREX process and during storage. Specific transformations occurring during the PUREX process have been discussed by Davis (1984) and the general character of the chemical transformations of hydrocarbons have been outlined by Spinks and Woods (1990).

Hydrocarbon radiolysis is a complex process; this discussion is intended to highlight the reactions leading to the principal VOCs rather than exhaustively describe the formation of all the products. The formation of the initial radical cation of dodecane is sketched in the first equation. Proton loss occurs to form intermediate free radicals; the example shows one of six possible radicals.

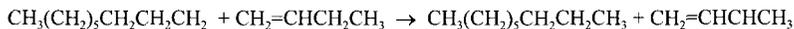


Free alkyl radicals decompose by several reaction pathways including beta scission to form an alkene and a hydrogen atom or another alkyl free radical and an alkene. The reactions of the family of alkanes in the waste form methyl, ethyl, 1-propyl, 1-butyl, 1-pentyl, and other radicals and ethene, 1-butene, 1-pentene, 1-hexene, and the other alkenes in homologous series.



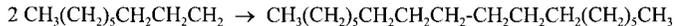


Reactive alkyl radicals, such as 1-nonyl radical, abstract hydrogen atoms from other hydrogen donors including the original NPH and reactive products of radiolytic reactions, such as alcohols and alkenes, to produce lower molecular weight alkanes and another radical.

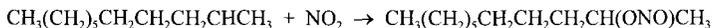
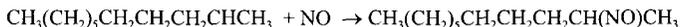


Hydrogen loss from the allylic radical provides 1,3-butadiene, one of the family of alkadienes observed in the ventilation stack.

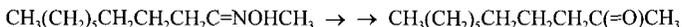
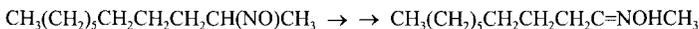
Recombination reactions between two alkyl radicals can produce a higher molecular weight product. Compounds of this type are frequently observed as products of the radiolysis of neat hydrocarbons, but such substances have not been found in detectable amounts in the Hanford Site waste.



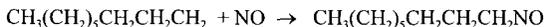
Although slower in oil than in water, competing recombination reactions with OH, NO, and NO₂ produce other families of intermediate compounds as sketched for the nonan-2-yl radical.



The C-nitroso, C-nitro and O-nitro compounds formed in these reactions are susceptible to ionic organic reactions. The C-nitroso and C-nitro compounds are converted into 2-dodecanone and the O-nitro compound is converted into the same alcohol formed in the recombination reaction with the hydroxyl radical shown in the first step. The two arrows indicate several steps are required for the conversion.



When the same reactions take place with 1- radicals, the products are aldehydes and the intermediate C-nitroso compound also produces nitriles.





The alkenes, alcohols, aldehydes and ketones, and nitriles formed in these reactions also undergo radiolysis. The alcohols, which are more reactive than the hydrocarbons, are oxidized to produce aldehydes or ketones.

The general features of the chemistry are outlined in Table 4-1.

Table 4-1. Principal Radiolytic Pathways for NPH Oxidation

Fragmentation Chemistry of Initial Radicals		
Reaction Pathway	Intermediate	Product
Hydrogen atom loss	None	Linear alkene
Alkyl radical loss	Smaller alkyl radical	Smaller linear alkane
	Smaller alkene	Smaller linear alkene
Recombination Chemistry of Initial Radicals		
Reagent	Intermediate	Product
OH	Alcohol	Alcohol
NO ₂	O-Nitro compound	Alcohol
NO ₂	C-Nitro compound	Aldehyde or ketone
NO	C-Nitroso compound	Aldehyde, ketone or nitrile
Ensuing Chemistry of Products of Recombination Reactions		
Initial Product	Intermediate	Product
Alcohol	Hydroxyalkyl radical	Aldehyde or ketone
Aldehyde	Formyl radical	Carboxylate ion
Nitrile	Tetrahedral intermediates	Carboxylate ion

The net result is that the original NPH are partially fragmented into lower molecular weight alkanes and alkenes and partially oxidized into alcohols, aldehydes and ketones, nitriles, and carboxylate ions. Studies of the radiolysis of alkanes have established that methane, ethane, propane, and butane, ethene, propene, and butene, ethyne, propyne, and butyne, and cyclopropane are formed during the radiolytic reactions. As the molecular dimensions are reduced, the molecules simultaneously become more volatile and more soluble.

The decomposition reactions of the NPH account for many compounds including homologous series of linear alkanes, alkenes, aldehydes, ketones, and nitriles observed in the dome space above the undisturbed waste, Figure 2-1, in the ventilation stack before sluicing begins, Table 3-1, and in the ventilation stack during sluicing, Tables 4 through 6.

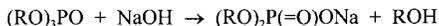
4.3 PHOSPHATE ESTER TRANSFORMATIONS

4.3.1 Phosphate Ester Vaporization

The large reduction in the NPH/TBP ratio for the oil layer in tank 241-C-103 has been attributed to the selective evaporation of NPH. Bartley and coworkers (1995) have summarized the available information concerning the rate at which NPH and TBP evolve from two component liquid mixtures and the rate at which TBP hydrolyzes. They developed an engineering model describing the dependence of the evaporation and hydrolysis rates of these materials on the ventilation rate, temperature, and related factors. The model indicates only small amounts of TBP evaporating with the NPH to continuously enrich the TBP content of the remaining organic liquid. Although the evaporation rate of BEHP has not been specifically addressed, that the vapor pressure of the salt is negligible and no evaporative loss can be anticipated. Extrapolating these concepts to the oil in tank 241-C-106 implies that insignificant quantities of the phosphate esters have been lost by evaporation.

4.3.2 Phosphate Ester Hydrolysis

Trialkyl, dialkyl, and monoalkyl phosphates hydrolyze to liberate an alcohol and a less alkylated phosphate, as shown in the following equations, where R represents the alkyl group.



TBP forms 1-butanol and dibutylphosphate ion (DBP), DPB forms 1-butanol and monobutylphosphate ion (MBP), and MBP forms 1-butanol and phosphate ion, BEHP forms 2-ethylhexanol and (2-ethylhexyl)phosphate ion, and (2-ethylhexyl)phosphate ion forms 2-ethylhexanol and phosphate ion. The rate constants for these reactions differ greatly. Solubility differences play an equally important role in determining the reaction rate. TBP is sufficiently soluble in the aqueous solution to enable the reaction with hydroxide ion, but BEHP is essentially insoluble in the aqueous solution and the rate constant for the hydrolysis reaction is very small.

The rate constants for hydrolysis of the triesters are much larger than the rate constants for hydrolysis of the diesters. A similar difference occurs between the rates of hydrolysis of the dialkyl phosphates and the monoalkyl phosphates (Cox and Ramsay 1964). The rate constants for hydrolysis of dialkyl esters are several orders of magnitude smaller than the rate constants for the hydrolysis of the corresponding trialkyl esters, and the rate constants for the hydrolysis of monoalkyl esters are several orders of magnitude smaller than the rate constants for the

dialkyl esters. The very slow rates of reaction of the dialkyl and monoalkyl phosphates have been confirmed in a recent investigation. Wolfenden and coworkers (1998) reported the rate constant for the reaction of water with dimethylphosphate ion was about 10^{-7} s^{-1} at $150 \text{ }^\circ\text{C}$. Wolfenden (1999) also pointed out that the reaction has an unusually steep temperature dependence.

Generally, the rate constants for the phosphates with larger alkyl groups are smaller than the rate constants for the methyl esters. For example, the rate constant for the hydrolysis of trimethyl phosphate is about 100 times greater than the rate constant for the hydrolysis of tributyl phosphate in alkaline solution (Camaioni et al. 1996).

The information obtained from the chemical literature has been supplemented by targeted investigations of the phosphate esters in the Hanford Site waste. Burger (1955) discussed the rates of hydrolysis of pure TBP under heterogeneous conditions in the presence of 1 M sodium hydroxide at temperatures from $30 \text{ }^\circ\text{C}$ to $100 \text{ }^\circ\text{C}$. The observed rate data were fit to the following expression by Camaioni and coworkers (1996).

$$\ln(R) = 54.8 - 2.55 \times 10^4(1/T) + 2.69 \times 10^6(1/T)^2$$

where T is the temperature in degrees Kelvin and R is the rate in milligrams of tributyl phosphate hydrolyzed per liter per hour. The rate of disappearance of TBP was approximately 15 mg per hour per liter of 1 M sodium hydroxide at $65 \text{ }^\circ\text{C}$. The reaction rate was about 60 percent slower when kerosene, a simulant for the NPH, was added to the reaction system. Burger also reported that the rate of hydrolysis of dibutylphosphate ion was negligible under the same conditions. Camaioni and coworkers (1996) also investigated the hydrolysis of TBP and found the addition of ions including sodium, calcium, iron (II), chromium (III), nickel, lead (II), zirconium (IV), nitrate, aluminate, and stearate had no appreciable influence on the reaction rate. The rate of hydrolysis of TBP is sufficient to alter its concentration during prolonged storage under alkaline conditions.

The investigations described by Cox and Ramsey (1964), Camaioni and coworkers (1996), and Wolfenden and coworkers (1998) imply the rates of hydrolysis of the dialkyl phosphates, DBP and BEHP, and the monoalkyl phosphates, MBP and EHP, are negligible in the aqueous phase of the waste.

The possibility that 1,1 or 1,2 elimination reactions might accelerate the rate of decomposition of BEHP was investigated. Camaioni and Linehan (1999) showed that sodium BEHP suspended in 2.0 M sodium hydroxide (with or without sodium nitrite) did not perceptibly react after sustained boiling at over $100 \text{ }^\circ\text{C}$ for 12 hours. The phosphorous nuclear magnetic resonance (P-NMR) spectrum of the reaction mixture was the same before and after the experiment. Using sensitive analytical methods, no alkenes or 2-ethylhexyl alcohol were detected in the vapor above the solution.

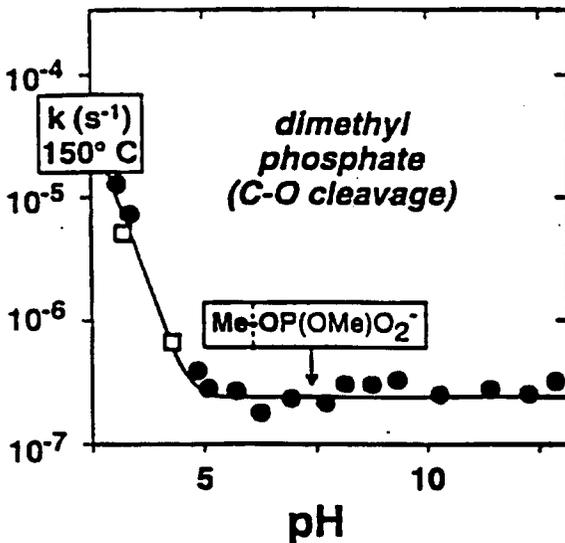
These studies indicate the phosphates used in the PUREX process hydrolyze at very different rates under the conditions at which the compounds are stored in the waste tank. BEPH is not hydrolyzed, but TBP is slowly transformed into DBP.

4.3.3 Phosphate Ester Interchange

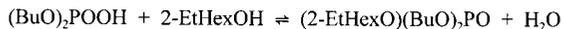
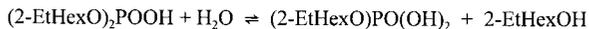
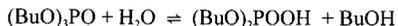
Speciation of the organic compounds in the oil from the sludge in tank 241-C-106 by Campbell and coworkers (Campbell et al. 1995a, 1995b, Campbell and Mong 1999) revealed it was principally sodium bis(2-ethylhexyl)phosphate with lesser amounts of butyl bis(2-ethylhexyl)phosphate, sodium butyl (2-ethylhexyl)phosphate, tributyl phosphate, tris(2-ethylhexyl)phosphate, and NPH.

The formation of the ester with three 2-ethylhexyl groups and other products with both butyl and 2-ethylhexyl groups can be attributed to acid-catalyzed ester interchange reactions during the PUREX process on the basis of three considerations. First, the rates of the reactions between the alcohols and the esters are governed by the same factors governing the rates of the reactions between water and the esters (March 1992). Second, reactions between water and the phosphate esters occur much more rapidly in acid solution, as shown in Figure 4-1. Third, the precedence is substantial for the occurrence of ester interchange reactions in organic solvents such as NPH where the concentrations of the organic alcohols are relatively high compared to the concentration of water.

Figure 4-1. The Dependence of the Rate of Hydrolysis of Dimethyl Phosphate on pH in Aqueous Solution (Wolfenden et al. 1998).



The multistep process is accomplished by the repetitious occurrence of reversible reactions between the esters and water to produce 1-butanol and 2-ethylhexanol and the reactions of the alcohols and the esters to produce compounds containing both alkyl groups.



and so forth.

Prolonged process use presumably led to the formation of the observed compounds:

- tris(2-ethylhexyl)phosphate, (2-EtHexO)₃PO,
- butyl bis(2-ethylhexyl)phosphate, (BuO)(2-EtHexO)₂PO, and
- butyl (2-ethylhexyl)phosphoric acid, (2-EtHexO)(BuO)PO(OH).

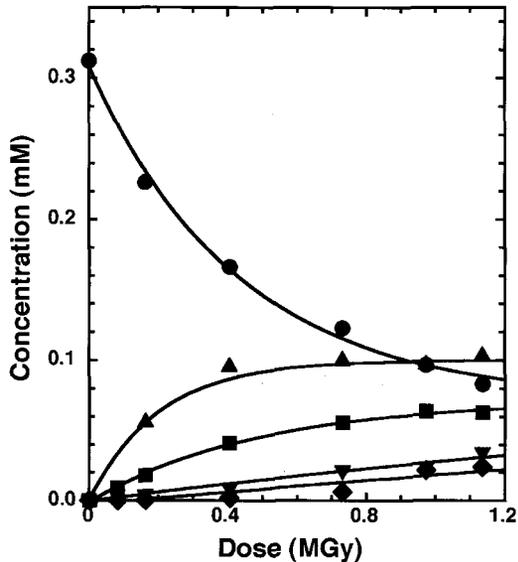
The substances became incorporated in the sludge and were transferred to the tank.

4.3.4 Phosphate Ester Radiolysis

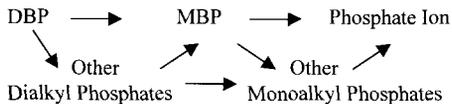
4.3.4.1 Tributyl Phosphate. The radiolysis of TBP has been discussed by Davis (1984). In addition, Camaioni investigated the radiolysis of dibutylphosphate (DBP) in alkaline solution in both the presence and the absence of sodium nitrate and sodium nitrite (Camaioni et al. 1996). The use of P-NMR spectroscopy enabled the simultaneous evaluation of the rates of decomposition of dibutyl and monobutyl phosphate in a single series of experiments. The G value for the disappearance of dibutyl phosphate ranged from 0.20 molecules/100 eV for the reaction in neutral solution in the absence of sodium nitrite or sodium nitrate to between 0.57 and 0.93 molecules/100 eV for reactions in 1 M sodium hydroxide in the presence of the two salts. Monobutyl phosphate forms and decomposes to form phosphate ion under the same conditions.

The product mixture contained residual DBP, MBP, a family of dialkyl phosphates different from DBP, a family of monoalkyl phosphates different from MBP, small quantities of sodium acetate and formate, and an even smaller quantity of sodium oxalate. Excellent material balances for phosphorous and good material balances for carbon were realized in this work establishing that DBP is transformed by the oxidation of the butyl group to produce a family of new dialkyl phosphates in which at least one of the carbon atoms in one of the butyl groups has been oxidized to form a new dialkyl phosphate. The radiolysis of 0.31 M DBP with 1.14 megagray provided a solution containing 0.08 M DBP, 0.06 M MBP, 0.024 M phosphate ion, 0.103 M other dialkyl phosphates, 0.035 M other monoalkylphosphates to account for virtually 100 percent of the phosphorous. The experimental observations are shown in Figure 4-2.

Figure 4-2. Reaction Profile for the Radiolysis of Dibutyl Phosphate. The observations for DBP (▼), MBP (■), phosphate (◆), other dialkyl phosphates (▲), other monoalkyl phosphates (●) are displayed.



The overall reaction pathway is described in the chart.

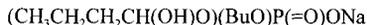


Camaioni and coworkers (1996) also found that sodium acetate and formate were formed in low yield together with much smaller quantities of sodium oxalate. The material balance for carbon was about 80 percent, significantly smaller than for phosphorous, and suggesting that other carbon-containing compounds also were formed during the reaction.

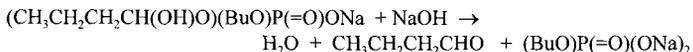
The concentrations of the monoalkyl phosphates and phosphate ion were measured again after several months of storage at ambient temperatures. The concentrations of these substances

were unchanged implying that the oxidized alkyl phosphates formed by radiolysis did not hydrolyze more readily than DPB.

Camaioni and coworkers (1996) suggest the observed products are best understood on the basis of initial oxidation reactions in which hydroxyl or carbonyl groups are introduced into the original butyl groups of DBP. The four alcohols are displayed for convenient inspection.



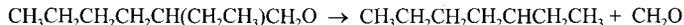
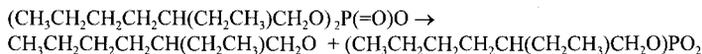
The first molecule in the group is reactive because it has two electronegative oxygen atoms bonded to the 1 carbon atom. Hydrolysis provides butanal, a substance that would have reacted and escaped detection in the experiment. The compound has been detected among the substances in the ventilation stack during sluicing, however.



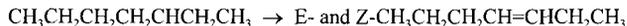
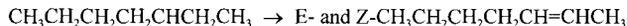
Camaioni and coworkers (1996) also investigated the radiolysis of two possible reaction products, butanol and sodium butyrate, under the same conditions. These substances decomposed much more rapidly than the phosphate esters. The product mixture contained residual butanol together with several monocarboxylates including formate, acetate, and propionate ion, as well as several dicarboxylates including malate, malonate, and oxalate ion. These compounds account for less than 50 percent of the available carbon, suggesting more extensive decomposition reactions occur. Although these other products were not identified, other work shows that inorganic carbonate ion is produced and the butyl group is fragmented (Davis 1984). Spinks and Woods (1990) point out that the radiolysis of low-molecular-weight alcohols in water and in other media provides high yields of hydrogen and the corresponding aldehyde, and lower yields of alkanes, alkenes and alkynes, and other oxygen-containing compounds. Davis (1984) reports the presence of methane, ethane, ethene, ethyne, propane, propene, butane, 1-butane, 2-butane, and 2-methylpropene. The G values for the formation of these products range from 0.2 to 0.4 (Williams and Wilkinson 1961 and Davis 1984). These observations, coupled with the results of Camaioni and coworkers, provide a rational basis for identifying the butyl phosphate esters as one source of methane, ethane, propane, butane, ethene, propene, the butenes, ethyne, propyne, the butynes, methanol, ethanol, 1-propanol and 2-propanol, butanal, propanone, 2-butanone.

4.3.4.2 Sodium Bis(2-Ethylhexyl)Phosphate. The radiolysis of bis(2-ethylhexyl)phosphate has not been investigated. However, as discussed in Section 4.3.3, radiolysis proceeds more slowly in the oil than in the aqueous phase and the rate of radiolysis of this water-insoluble compound is certainly much slower than the rate of radiolysis of water-soluble TBP, DBP, and MBP.

One plausible pathway for the radiolysis of BEHP in the oil is outlined here. The three step reaction sequence is initiated by removing an electron from the anion to give a phosphate-centered radical. Conventional bond scission of the initial product provides a reactive alkoxy radical. The alkoxy radical then forms formaldehyde and heptan-3-yl radical shown in the third equation.

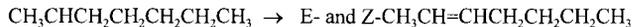
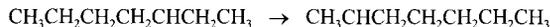


From this point, the chemistry follows the same pathways outlined for the NPH in Section 4.3.3. Hydrogen atom loss from the heptan-3-yl radical provides E- and Z-2-heptene and E- and Z-3-heptene.



and reactions with the oxidizing agents provide 3-heptanone, the most abundant ketone in the VOC mixture.

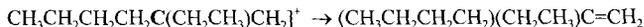
E- and Z-2-Heptene and 1-heptene are formed from heptan-2-yl radical which is obtained through a 1,4 hydrogen transfer reaction of 3-heptanyl radical (Leffler 1993).



Alternative reaction pathways involve hydrogen removal from the 2-ethylhexyl group to provide eight radicals. The most stable radical is obtained by the loss of the tertiary hydrogen atom.



As originally described by Camaioni and coworkers (1996) during their investigation of TBP and DBP, this radical decomposes to eliminate the phosphate dianion and form the cation radical of 3-methyleneheptane, one of the other prominent volatile compounds.

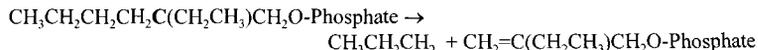


The other radicals obtained through hydrogen atom abstraction undergo the same reactions as the NPH. Hydrogen loss, for example, produces unsaturated molecules, and recombination reactions provide oxidized compounds of the kind shown in Section 4.2.3.

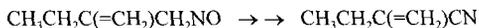
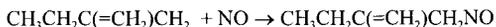
The novel unsaturated nitrile, 2-methylenebutanenitrile, which has five carbon atoms and is not a member of a homologous series also is logically produced from BEHP instead of TBP or NPH. The compound is topologically related to BEHP, as shown by the bold portions of the following structure.



There is not sufficient information to define the explicit pathway for the formation of the nitrile, but the tertiary radical mentioned in the previous paragraph can decompose to give a propyl radical and an allylic phosphate



The radiolysis of the allylic phosphate leads to the allylic radical necessary for the formation of the observed nitrile.



In conclusion, many of the abundant constituents of the VOC can be traced to the radiolysis reactions of BEPH. Less abundant compounds in the VOC, especially the lower molecular weight substances, also are formed indirectly from this compound in the same kinds of reactions described for TBP and NPH.

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5.0 SUMMARY

Characterization studies imply the organic material in tank 241-C-106 is located in the topmost sludge layer, consisting of about 318 kL (84 kgal) of a mixture of low-level waste from B Plant rich in organic material and strontium, and washed PUREX sludge from the AR vault, even richer in strontium. The organic compounds, which were used for strontium removal, included two complexants, glycolic and citric acid; two phosphate esters, bis(2-ethylhexyl)phosphoric acid and tributyl phosphate; and NPH. The best basis inventory suggests the tank contains 15,200 kg of TOC. The oxalate ion content, which is apparently large, is not known with confidence. The organic constituents in the aqueous phase of the waste have not been investigated. However, an organic oil, which was separated from the sludge during centrifugation, is about 45 percent sodium bis(2-ethylhexyl)phosphate with lesser quantities of butyl bis(2-ethylhexyl)phosphate and sodium butyl 2-ethylhexylphosphate, as well as other phosphate esters and residual NPH. The grab samples of sludge collected in 1996 contained 0.5 to 3.0 volume percent oil.

Approximately 370 L of hydrogen are released each day. Approximately 45 organic compounds including alkanes, alkenes, alcohols, ethers, aldehydes, ketones, esters, and nitriles also evolve continuously. About 50 percent of these compounds are soluble in water.

The initiation of sluicing leads to a two- to threefold increase in the hydrogen release rate. The increase in the nitrous oxide release rate appears to be larger. In addition, more than 200 organic compounds representing 8 different organic structural groups appear in the ventilation stack during sluicing. Linear alkanes from propane to tetradecane are present, together with smaller amounts of some methylated linear alkanes. Linear alkenes from propene to decene are observed with smaller amounts of linear alkadienes and alkynes. Cycloalkanes with three-, five-, and six-membered rings and certain decalins are present in low concentrations. Aromatic compounds including benzene, toluene, and the xylenes are much less abundant than the alkanes or alkenes. Several alcohols and ethers with structures topologically related to butanol and 2-ethylhexanol are found. Homologous series of linear aldehydes, ketones, and nitriles are present together with one allylic nitrile.

Inasmuch as the concentrations of organic substances increase appreciably during sluicing, these substances must have been retained in the sludge in tank 241-C-106.

A ninth group of compounds containing fluorine or chlorine atoms was detected. However, the absolute concentrations of these halocarbons are so low that no definite conclusions can be drawn about their origins.

The sludge has between 3 and 6 percent gaseous void space. Portions of the retained gas, principally hydrogen, nitrous oxide and presumably also nitrogen, are released when the waste is disturbed. The retained organic compounds distributed among the void space, the water, and the oil in the sludge are released simultaneously. When sluicing is initiated, the concentrations

of water-soluble organic substances increase, but the concentrations of water-insoluble compounds increase even more.

The topological structures, volatility and reactivity of the PUREX chemicals and the VOC provide a technical basis for relating the VOCs to the original process chemicals. In brief, the NPHs are more volatile than the phosphate esters and their concentrations have been substantially depleted by evaporation during interim storage. Tributyl phosphate is partially water-soluble and has been largely converted into dibutyl- and monobutylphosphate ions. Sodium bis(2-ethylhexylphosphate) is neither volatile, soluble in water, nor chemically reactive and, is now the most abundant organic compound in the oil. The remaining original compounds and the molecules formed from them and retained in the waste have undergone oxidative radiolytic reactions leading to the formation of hydrogen-deficient hydrocarbons and alcohols, aldehydes, ketones, nitriles, and carboxylate ions. Hydrogen, nitrous oxide, nitrogen, and ammonia are simultaneously formed during these oxidation reactions.

Some evolving alkanes, for example the linear paraffins and their monomethyl derivatives with more than nine carbon atoms, were original constituents of the NPH mixture. The other alkanes with less than nine carbon atoms originate from the radiolytic reactions of the NPHs and the phosphate esters. The numerous alkenes among the VOCs also have predominantly linear structures. The heptenes are formed by radiolysis of sodium bis(2-ethylhexyl)phosphate ion. The cycloalkanes and certain decahydronaphthalenes and aromatic hydrocarbons are present in low concentrations. Compounds of this structural class were present in the original NPH mixture. The high abundance of 1-butanol is related to the hydrolysis and radiolysis of the remaining butylphosphates. The concentration of 2-ethyl-1-hexanol is much smaller because the rates of hydrolysis and radiolysis of the corresponding ester are much slower. Methanol, ethanol, and propanol are formed as intermediates in the oxidation sequences leading to formate, acetate, and propionate ions. Most of the ethers have structures topologically related to the original butyl or 2-ethylhexyl groups. The homologous series of linear aldehydes, ketones, and nitriles result in part from radiolysis reactions of the hydrocarbons and the decomposition products of the phosphate esters. In particular, the abundant ketones with seven and eight carbon atoms are produced during radiolysis of sodium bis(2-ethylhexyl)phosphate.

In combination, the inherently slow rate of hydrolysis of sodium bis(2-ethylhexyl)phosphate coupled with its insolubility in water and its very low vapor pressure have led to the selective retention of this molecule in the sludge. Its slow radiolytic decomposition will produce VOCs for years.

6.0 REFERENCES

- Agnew, S. F., 1995, Hanford Defined Wastes: Chemical and Radionuclide Compositions, LA-UR-2657, Rev. 2, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Agnew, S. F., 1996, *Hanford Defined Wastes: Chemical and Radionuclide Inventories: HDW Model*, LA-UR-96-858, Rev. 3, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Agnew, S. F., R.A. Corbin, T. B. Duran, K.A. Jurgenson, T. P. Ortiz, and B. L. Young, 1995, *Waste Status and Transaction Record Summary (WSTRS)*, Rev. 1, WHC-SD-WM-TI-615, Westinghouse Hanford Company, Richland, Washington.
- Agnew, S. F., R. A. Corbin, T. B. Duran, K. A. Jurgenson, J. Fitzpatrick, B. L. Young, J. Boyer, and T. P. Ortiz, 1997, *Hanford Tank Chemical and Radionuclide Inventories: Hanford Defined Wastes (HDW) Model*, WHC-SD-WM-TI-615, Rev. 4, Westinghouse Hanford Company, Richland, Washington.
- Bailey, J., 1999, Private Communication.
- Bartley, P. L., G. T. Dukelow, M. J. Klem, and J. A. Reddick, 1996, *Tank 241-C-103 Systems Engineering Study: Speerable Organic Phase Skimming, Storage, Treatment, and Disposal Options*, WHC-SD-WM-ES-384, Westinghouse Hanford Company, Richland, Washington.
- Bartley, P. L., 1999, *Hazard Characterization and Analysis of Waste, Tank 241-C-106 Sluicing*, Interim Report, HNF-4167, Richland, Washington.
- Bonfoey D. B., M. J. Duchsherer, G. A. Fies, L. D. Lockard, K. O. Pennock, L. A. Pingel, J. Y. Smith, M. Stauffer, R. S. Viswanath, M. L., Myers, and L. L. Lockrem, 1999a, *Tank Vapor Sampling and Data Analysis Package for Tank 241-C-106 Waste Retrieval Sluicing System Process Test, Sampled December 16, 1998*, HNF-3949, Rev. 0, Numatec Hanford Corp., Richland, Washington.
- Bonfoey D. B., M. J. Duchsherer, G. A. Fies, L. D. Lockard, K. O. Pennock, L. A. Pingel, J. Y. Smith, M. Stauffer, R. S. Viswanath, M. L., Myers, and L. L. Lockrem, 1999b, *Tank Vapor Sampling and Data Analysis Package for Tank 241-C-106 Waste Retrieval Sluicing System Process Test, Sampled March 7, 1998*, HNF-XXX, Rev. 0, Numatec Hanford Corp., Richland, Washington.
- Burger, L. L., 1955, *The Chemistry of Tributyl Phosphate: A Review*, HW-40910, Hanford Atomic Products Operation, Richland Washington.

- Camaioni, D. M., W. D. Samuels, S. A. Clauss, A. K. Sharma, and K. L. Wahl, 1996, *Alkaline Hydrolysis of Simulated Tank 241-C-103 Separable Organic Phase*, Letter Report OT: 040896, Pacific Northwest National Laboratory, Richland, Washington.
- Camaioni, D. M., and J. Linehan, 1999, Letter Report to K. G. Carothers on *Tests for the Decomposition of Bis(2-Ethylhexyl)phosphate in Molar Sodium Hydroxide*, Pacific Northwest National Laboratory, Richland, Washington.
- Campbell, J. A., and G. M. Mong, 1999, *Analysis of Components in Hanford Waste Tanks*, J. Rad. Nuc. Anal. Chem., 00, 0000. In press.
- Campbell, J. A., S. A. Clauss, K. E. Grant, V. Hoopes, B. D. Lerner, R. B. Lucke, G. M. Mong, J. K. Rau, R. Steele, and K. L. Wahl, 1994, *Waste Tank Organic Safety Program Analytical Methods Development: FY 1994 Progress Report*, PNNL-10128, Pacific Northwest National Laboratory, Richland, Washington.
- Campbell, J. A., M. Bean, K. L. Wahl, G. M. Mong, K. E. Bell, K. B. Werner, A. D. Rice, R. J. Ray, D. B. Bechtold, B. R. Wels, R. W. Schroeder, J. W. Ball, B. D. Valenzuela, J. M. Frye, S. L. Fitzgerald, P. P. Bachelor, B. Griffin, R. K. Fuller, A. B. Benally, and S. M. Parong, 1995a, *Waste Tank Analytical Safety Project. Analysis of Samples from Hanford Waste Tanks 241-C-102, 241-BY-108, and 241-C-103*, PNNL-10531, Pacific Northwest National Laboratory, Richland, Washington.
- Campbell, J. A., S. A. Clauss, V. Hoopes, J. Rau, K. L. Wahl, B. D. Lerner, K. E. Grant, G. M. Mong, and R. Scheele, 1995b, *Flammable Gas Program Organic Analysis and Analytical Methods Development: FY 1995 Progress Report*, PNNL-10776, Pacific Northwest National Laboratory, Richland, Washington.
- Campbell, J. A., K. L. Wahl, S. A. Clauss, K. E. Grant, V. Hoopes, G. M. Mong, J. Rau, and R. Steele, 1996a, *Organic Tanks Safety Program: Advanced Organic Analysis FY 1996 Progress Report*, PNNL-11309, Pacific Northwest National Laboratory, Richland, Washington.
- Campbell, J. A., S. A. Clauss, K. E. Grant, V. Hoopes, G. M. Mong, J. Rau, R. Steele, and K. H. Wahl, 1996b, *Flammable Gas Safety Program: Actual Waste Organic Analysis FY 1996 Progress Report*, PNNL-11307, Pacific Northwest National Laboratory, Richland, Washington.
- Campbell, J. A., S. A. Clauss, K. E. Grant, V. Hoopes, G. M. Mong, R. Steele, D. Bellofatto, and A. Sharma, 1997, *Organic Analysis Progress Report FY 1997*, PNNL-11738, Pacific Northwest National Laboratory, Richland, Washington.
- Cox, J. R., Jr. and O. B. Ramsey, 1964, *Mechanisms of Nucleophilic Substitution in Phosphate Esters*, Chemical Reviews, 64, 317.

- Cowley, W. L., and J. E. Meacham, 1998, *Organic Solvent Topical Report*, HNF-SD-WM-CN-032, Rev. 1, Duke Engineering and Services Hanford, Inc., Richland Washington.
- Davis, W., Jr., 1984, "Radiolytic Behavior," in *Science and Technology of Tributyl Phosphate*, W. W. Schultz and J. D. Navratil, editors, Volume I, CRC Press, Boca Raton, Florida.
- Huckaby, J. L., and J. C. Evans, 1999, Letter Report to K. G. Carothers, *Chemical Analysis of Air Samples Collected on November 18, 1998 during Sluicing Activities at Tank 241-C-106*, Pacific Northwest National Laboratory, Richland, Washington.
- Hu, T. A., 1999, Private Communication.
- Hu, T. A., 1999, *Empirical Rate Equation Model and Rate Calculations for Hydrogen Generation for Hanford Tank Waste*, HNF-3851, Rev. 0, Lockheed Martin Hanford Corporation, Richland, Washington.
- Jenkins, R. A., A. B. Dinal, C. E. Huggins, C. Y. Ma, J. T. Skeen, and R. R. Smith, 1994, *Analysis of Tank 241-C-103 Headspace Components from Sampling Job 7b*, Oak Ridge National Laboratory, Oak Ridge Tennessee.
- Ma, C. Y., J. T. Skeen, A. B. Dinal, C. K. Bayne, and R. A. Jenkins, 1997, *Performance Evaluation of a Thermal Desorption/Gas Chromatographic/Mass Spectrometric Method for the Characterization of Waste Headspace Samples*, Environmental Science and Technology, 31, 853.
- Rasmussen, D. A., 1994, *Air Samples Collected At Waste Tanks 241-C-104, -105 and -106 on March 3 and February 15 and 16, 1994*, Oregon Graduate Institute, Beaverton, Oregon.
- Reynolds, D. A., 1997, *Chemical and Chemically-Related Considerations Associated with Sluicing Tank C-106 Waste to Tank AY-102*, HNF-SD-WM-TI-756, Rev. 2, Lockheed Martin Hanford Corporation, Richland, Washington.
- Reynolds, D. A., 1999, Private Communication.
- Scheele, R. D., J. L. Sobolik, R. L. Sell, and R. L. Burger, 199X, *Organic Tank Safety Project: Preliminary Results of Energetics and Thermal Behavior Studies of Model Organic Nitrate and/or Nitrite Mixtures and a Simulated Organic Waste*, PNL-10213, Pacific Northwest National Laboratory, Richland, Washington.
- Schreiber, R. D., 1996, *Tank Characterization Report for Single-Shell Tank 241-C-106*, WHC-SD-WM-ER-615, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Stewart, C. W., and G. Chen, 1998, *Baseline Estimate of Retained Gas Volume in Tank 241-C-106*, PNNL-11890, Pacific Northwest National Laboratory, Richland, Washington.

Weiss R. L., and K. E. Schull, 1988, *Data Transmittal Package for 241-C106 Waste Tank Characterization*, SD-RE-TI-205, Westinghouse Hanford Company, Richland, Washington.

Wilkinson, R. W., and T. F. Williams, 1961, "The Radiolysis of Tri-n-alkyl Phosphates," *J. Chem. Soc.*, p. 4098

APPENDIX A

TOC AND OXALATE ION CONTENT OF 1996 GRAB SAMPLES

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APPENDIX A

TOC AND OXALATE ION CONTENT OF 1996 GRAB SAMPLES

The analytical results for total organic carbon and oxalate ion in the grab samples removed from Risers 1 and 7 from tank 241-C-106 are summarized in Table A-1. The table shows the large variations in the total organic carbon and oxalate ion measurements.

Table A-1. Analytical Results for Total Organic Carbon and Oxalate Ion in Grab Samples from Tank 241-C-106.

Depth (a)	Sample	Riser 1			Riser 1			Riser 1			Riser 7			Riser 7			Riser 7									
		Solids	TGA	W%	Solids	TOC	W%	Solids	TOC	W%	Solids	TOC	W%	Solids	TOC	W%	Solids	TOC	W%							
		DSC	Wt% Dry	J/g Dry	C in Ox	Wt% Dry	DSC	Wt% Dry	J/g Dry	C in Ox	Wt% Dry	DSC	Wt% Dry	J/g Dry	C in Ox	Wt% Dry	DSC	Wt% Dry	J/g Dry	C in Ox	Wt% Dry	TGA	Wt% Dry	TOC	Wt% Dry	
14	Centrifuged																									
14	Control																									
14	Centrifuged, filtered																									
23	Centrifuged	110	8.28																							
28	Control	0	31.1																							
28	Filtered	325	12.8	3.1	2.11	0	35.4	0.3, 0.3																		
28	Raw in air	142	52.9	2.7																						
28	Raw in N ₂	0	57.9	2.4																						
35	Centrifuged	0	12.9																							
35	Control	0	13.5																							
35	Centrifuged, filtered	111	25.7	3.0	1.87	0	60.3	0.5, 0.5	0.08																	
40	Centrifuged																									
40	Control																									
40	Centrifuged, filtered																									
40	Raw in air																									
40	Raw in N ₂																									
51	Raw	0	3.18	5.7																						
53	Centrifuged	216 (d)	3.59																							
53	Control	0	33.5																							
53	Centrifuged, filtered	0	24.1	2.1	2.18	0	58.0	0.3, 0.5	0.06																	

Notes:
 (a) The samples also are identified by the following numbers: For Riser 1: 14" (5), 28" (7), 28" (9), 35" (10), 51" (3), 53" (4); for Riser 7: 14" (11), 23" (12), and 40" (13).
 (b) Two values are provided when both persulfate and furnace oxidation methods were used.
 (c) The carbon in oxalate ion content was measured to be higher than the total organic carbon content.
 (d) The value is the average of 0, 1037, 0, 14, and 27. Another measurement at the Pacific Northwest National Laboratory provided another zero observation.

REFERENCES

- Reynolds, D. A., 1997, *Chemical and Chemically-Related Considerations Associated with Sluicing Tank C-106 Waste to Tank AY-102*, HNF-SD-WM-TI-756, Rev. 2, Lockheed Martin Hanford Corporation, Richland, Washington.
- Schreiber, R. D., 1996, *Tank Characterization Report for Single-Shell Tank 241-C-106*, WHC-SD-WM-ER-615, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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