Pacific Northwest National Laboratory

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Homogeneity of Passively Ventilated Waste Tanks

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July 1997

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Executive Summary

Gases and vapors in the high-level radioactive waste underground storage tanks at the Hanford Site are being characterized to help resolve waste storage safety issues and estimate air emissions. Characterization is accomplished by collecting and analyzing air samples from the headspaces of the tanks. Samples are generally collected from a single central location within the headspace, and it is assumed that they are representative of the entire headspace. The validity of this assumption appears to be very good for most tanks, because thermally induced convection currents within the headspaces mix constituents continuously. In the coolest waste tanks, however, thermally induced convection may be suppressed for several months of each year because of the seasonal soil temperature cycle.

To determine whether composition does vary significantly with location in a cool tank, the headspaces of three waste tanks have been sampled at different horizontal and vertical locations during that part of the year when thermally induced convection is minimized. This report describes the bases for tank selection and the sampling and analytical methods used, then analyzes and discusses the results.

Headspace composition data from two risers at three elevations in Tanks 241-B-103, TY-103, and U-112 have been analyzed by standard analysis of variance (ANOVA) methods, which indicate that these tank headspaces are essentially homogeneous. No stratification of denser vapors (e.g., carbon tetrachloride, dodecane) or lighter gases (e.g., ammonia, hydrogen) was detected in any of the three tanks. A qualitative examination of all tentatively identified organic vapors in SUMMATM and TST samples supported this conclusion.

Though the data from three tanks cannot be used to demonstrate that no tank headspace ever exhibits significant horizontal or vertical concentration gradients at any time of year, the tanks and sampling dates were selected to maximize the possibility of observing inhomogeneities in the headspaces. The results from Tanks 241-B-103, TY-103, and U-112 indicate that, even in very cool tanks, the central region of a tank headspace is homogeneous for all intents and purposes.

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1.0 Introduction

Gases and vapors in the Hanford Site high-level radioactive waste tanks are being characterized to resolve tank safety and industrial hygiene issues and to facilitate estimation of regulated air pollutant emissions (Brown 1997). Characterization is accomplished by collecting a set of headspace air samples, which are then analyzed in a laboratory. The sampling and analytical methods allow identification and quantitation of a selected set of compounds and can be extended to allow tentative identification and estimation of the concentrations of others. The headspaces of 90 single-shell waste tanks have been sampled by this method since February 1994, and the remaining 59 single-shell and 28 double-shell tanks are scheduled to be sampled to satisfy requirements specified in *Recommendation 93-5 Implementation Plan* (DOE-RL 1996).

Tank headspace air samples are collected via one of the tank's access risers from a single elevation, approximately midway between the bottom of the riser and the surface of the waste. This approach assumes that the headspace composition is uniform, or homogeneous, and that air at the sampling point is representative of the whole headspace. The headspace homogeneity assumption is clearly important, because if the samples are not representative of the headspace, decisions based on the characterization data may be flawed.

Theoretical and empirical data indicate that, with the possible exception of several very cool tanks, the homogeneity assumption is quite good for the passively ventilated tanks. This report addresses the possibility that the homogeneity assumption is not valid for the coolest tanks. The primary data are from characterization studies of Tanks B-103, TY-103, and U-112^(a) performed in the fall of 1996. The data are tabulated and analyzed by standard methods to determine whether they indicate statistically significant differences in the composition of different regions or elevations of the headspaces. The sampling methods, sampling events, and analytical procedures are described but only to the extent necessary to understand the tests; detailed descriptions are given in separate reports (NHC 1997a,b,c; Olsen et al. 1997a,b; Sklarew et al. 1997).

Whether the homogeneity assumption holds for actively ventilated tanks depends upon the ventilation rate, the configuration of the ventilation inlets and outlet, and other physical parameters of the headspace. This report is limited to the passively ventilated tanks; the findings presented here should not be applied to actively ventilated tanks. Also, exceptional events such as the sudden release of a large quantity of waste gases require case-by-case consideration and are not addressed in this report.

(a) Hanford tanks are formally designated with the prefix 241-. In this report, the prefix has been dropped, as it is in common usage.

1.1 Headspace Dynamics

The distribution of gases and vapors in a waste tank headspace is determined by the headspace dynamics. The release of gases and vapors at the waste surface results in relatively high concentrations very near the surface, and ventilation of the headspace results in relatively low concentrations wherever ambient air is introduced. Convection and molecular diffusion mix the air between these extremes, and whether the headspace supports significant concentration gradients or is relatively homogeneous depends upon the mixing rate.

Various studies employing numerical modeling and semi-empirical relationships have concluded that thermally induced convection causes rapid mixing of the headspace (Claybrook and Wood 1994; Postma et al. 1994; Epstein 1995).^(a) Radioactive decay of the waste results in waste surface temperatures that are higher than the temperatures of the tank dome and the ground above the dome. Air is warmed by contact with the waste surface and rises, displaced by air cooled by contact with the tank dome. This thermally induced convection mixes the gases and vapors both vertically and horizontally. The studies conclude that transport and mixing of gases and vapors within the convection zone is very rapid compared with their release from the waste surface, so concentration gradients within the convection zone are negligible.

Between the convection zone and the waste surface is the boundary layer region. Here, concentration gradients are limited by molecular diffusion and may be relatively large compared with gradients in the convection zone. However, this region represents a very small fraction of the headspace, and headspace sampling is not done in this region. Epstein (1995) estimated this boundary layer to be on the order of 1.5 to 2.5 cm thick when the waste surface was only 1.4°C warmer than the dome in a typical tank. Larger (and probably more realistic) differences between the waste and dome temperatures would produce more vigorous convection and result in even thinner boundary layer regions.

The potential effects of incoming fresh air on the collection of gas and vapor samples have been examined recently by numerical modeling.^(b) In that study, a time-dependent, three-dimensional model was used to estimate the fate of 5 and 25 ft³/min fresh air inflows into a tank headspace. The model assumed the dome was 78°F and the waste surface 80°F (to support thermally induced convection), and the fresh air entered via a 4-in.-diameter riser in the dome. The model was run for incoming air that was 20°F cooler than the dome (at both 5 and 25 ft³/min) and for incoming air that was 79°F (neutrally buoyant, at 25 ft³/min). Convection patterns were significantly affected by the inflowing air in each of these scenarios. At 25 ft³/min, the inflowing air was predicted to flow directly to the waste surface and would not significantly affect samples collected from adjacent risers at the mid-plane of the headspace. At 5 ft³/min, the

(a) Antoniuk ZI and KP Recknagle. 1996. *Modeling Hydrogen Plume Concentrations in a Single-Shell Tank Dome*. TWSFG96.6, Pacific Northwest National Laboratory, Richland, Washington.

(b) Antoniuk ZI. July 10, 1997. *Modeling Breathing Effect on Gas Concentrations in a Single-Shell Tank Dome*. Letter report, Pacific Northwest National Laboratory, Richland, Washington.

inflowing air was predicted to have negligible effects beyond a small region at the bottom of the riser. Though this modeling did not bound all situations, its results do suggest that significant effects on sampling would be difficult to produce given the limited ventilation rates and tank conditions.

This convection-dominated model of the passively ventilated waste tank headspaces is supported by tests performed on Tanks C-103 and C-111 (Huckaby and Story 1994; Huckaby 1994), and has been accepted by the Waste Tanks Advisory Panel Chemical Reactions Subpanel.^(a) However, for tanks with very low heat-generation rates, there may be periods of the year when the ground temperature above the tank is warmer than the waste itself—a situation that does not produce thermally induced convection. Under these conditions, molecular diffusion and convection associated with tank ventilation continue to mix headspace constituents, but possibly at rates too slow to maintain a homogeneous distribution.

To illustrate how seasonal changes in the ground temperature affect the temperatures inside a tank, the waste surface and average headspace temperatures have been plotted as functions of time for Tank BY-107 in Figure 1.1 and for Tank B-103 in Figure 1.2. The annual sinusoidal temperature cycle depicted in both figures is similar in all tanks and is due to seasonal changes in the temperature of the ground above the tanks. Note that in Tank BY-107 the waste surface temperature is consistently higher than the headspace temperature throughout the year, but in Tank B-103 the waste temperature was indicated to be lower than the headspace for much of the latter half of the year. Though temperature measurement uncertainties could account for the differences between Figures 1.1 and 1.2, there is a consistent tendency for the coolest tanks to have small or nonexistent gradients between the waste and headspace temperatures.

If the seasonal rise in soil temperatures results in the concrete tank dome temperature rising above the waste surface temperature, then mixing by thermally induced convection will be reduced. In the absence of convection, gases and vapors released by the waste are transported via molecular diffusion throughout the headspace. As long as the gas and vapor release rates are low, diffusion will prevent large concentration gradients from developing (Claybrook and Wood 1994); however, if release rates are high, significant concentration gradients could develop.

This study was conducted to address issues associated with the headspace homogeneity assumption. Based on the above discussion of headspace dynamics, three cool waste tanks were sampled for evidence of headspace inhomogeneities during that part of the year when thermally induced convection was minimal.

1.2 Selection of Study Tanks

Tanks B-103, TY-103, and U-112 were selected as the subjects of this study because they are the coolest tanks that contain measurable concentrations of the gases and vapors of interest.

(a) Christensen RF. April 5, 1995. Transmittal of Comments and Suggestions Resulting from the Ninth Meeting of the Chemical Reactions Sub-TAP of February 8-10, 1995 (letter 95-TSD-036 to President, Westinghouse Hanford Company).

Figure 1.1. Tank BY-107 Waste Surface and Headspace Temperatures

Figure 1.2. Tank B-103 Waste and Headspace Temperatures

Though other tanks are known to have cooler headspaces, their headspaces either had not been characterized or had been found to contain only very low levels of the gases and vapors of interest. Two of the tanks, B-103 and TY-103, are thought to contain significant amounts of semivolatile organic solvents (Huckaby et al. 1997), and were selected in part to examine the potential accumulation of dense organic vapors near the waste surface. A partial list of the parameters considered in the selection of these tanks is given in Table 1.1.

Waste and average headspace temperatures for 1996 are plotted in Figure 1.2 for Tank B-103 and in Figures 1.3 and 1.4 for Tanks TY-103 and U-112, respectively. Vertical dashed lines in each figure indicate the date that each tank was sampled for this study. The sudden decrease in measured waste temperatures indicated in Figure 1.4 in mid-July is due to a change in the operation of the thermocouple reader, and values obtained after the change are considered better.^(a)

1.3 Selection of Study Analytes

Composition inhomogeneities in the tank headspaces could, in principle, occur with any of the gases or vapors released by the waste. Light gases rising in a plume could accumulate and reside near the top of the headspace, dense organic vapors could linger near the surface, and volatile organic compounds could be nonuniformly distributed because they are produced in only one region of the waste. To demonstrate that all passively ventilated tank headspaces are homogeneous using data from only three tanks, it is important to examine all readily obtainable gas and vapor concentration data from the three selected tanks for any indication of composition inhomogeneities.

The primary target compounds for this study were specified in the sampling and analysis plan of this study (Buckley 1996) and are shown in Table 1.2). Among the target compounds are light gases generated by the waste (e.g., hydrogen and ammonia), vapors from semivolatile organic waste (e.g., tributyl phosphate, n-dodecane, n-tridecane), and a variety of organic vapors associated with the decomposition of organic wastes (e.g., acetone, 1-butanol, acetonitrile).

In addition to the target compounds, the analytical laboratory used standard techniques to tentatively identify and estimate the concentrations of non-targeted organic vapors that were present. This type of data is primarily qualitative and has been used to expand the search for significant inhomogeneities.

Section 2 of this report describes the sample collection devices and methods; Section 3 discusses the analysis of the samples. In Section 4 the statistical analysis and results are found, and the conclusions of the study are contained in Section 5. References cited can be found in Section 6.

(a) Waste and headspace thermocouples in this tank are tied to different reference junctions. In July 1996 changes were made to ensure that these reference junctions were actually at the same temperature.

Table 1.1. Selection Criteria for Study Tanks

	B-103 ^(a)	TY-103 ^(b)	U-112 ^(c)
Waste ^(d)			
Sludge volume	59 kgal	162 kgal	45 kgal
Saltcake volume	0 kgal	0 kgal	0 kgal
Supernate volume	0 kgal	0 kgal	4 kgal
Total waste volume	59 kgal	162 kgal	49 kgal
Headspace			
Volume	3,016 m ³	3,368 m ³	3,054 m ³
Temperature ^(e)	18.9°C	20.0°C	20.6°C
Relative humidity	76%	85%	78%
Hydrogen	< 99 ppmv	60 ppmv ^(f)	232 ppmv
Ammonia	8.8 ppmv	49 ppmv	308 ppmv
Carbon dioxide	432 ppmv	121 ppmv	< 17 ppmv
n-Dodecane	0.037 ppmv	0.81 ppmv	< 0.005 ppmv
n-Tridecane	0.12 ppmv	4.0 ppmv	< 0.005 ppmv
n-Tetradecane	0.082 ppmv	1.7 ppmv	< 0.005 ppmv
Total organic vapors ^(g)	9.8 mg/m ³	60 mg/m ³	2.0 mg/m ³
Notes	Organic Watchlist tank	Organic Watchlist tank with semivolatile organic solvents	Volatile organic vapors present at low levels

(a) Headspace gas and vapor data are from samples collected February 8, 1995; organic vapor data are from triple sorbent traps (TSTs) analyzed by Oak Ridge National Laboratory (Huckaby and Bratzel 1995a).

(b) Headspace gas and vapor data are from samples collected April 11, 1995; organic vapor data are from TSTs analyzed by Oak Ridge National Laboratory (Huckaby and Bratzel 1995b).

(c) Headspace gas and vapor data are from samples collected July 9, 1996; measurement of n-undecane, n-dodecane, and n-tridecane in Tank U-112 samples was apparently compromised by contaminants; values given are estimated from available data (Evans et al. 1997).

(d) Waste volumes are from Hanlon (1997).

(e) Temperature is headspace average for October 1995.

(f) Value reported is from reanalysis of a single archived SUMMA canister sample from Tank TY-103 (personal communication from BL Thomas to JL Huckaby, July 19, 1996).

(g) Total organic vapor concentration values are from summation of individual constituents detected in TSTs analyzed by Oak Ridge National Laboratory for B-103 and TY-103 (Huckaby and Bratzel 1995a,b) and from EPA TO-12 method analyses for Tank U-112.

Figure 1.3 Tank TY-103 Waste and Headspace Temperatures

Figure 1.3. Tank TY-103 Waste and Headspace Temperatures

Figure 1.4. Tank U-112 Waste and Headspace Temperatures

Table 1.2. Target Analytes

Analyte	CAS Number	Analyte	CAS Number
Ammonia	7664-41-7	1-Butanol	71-36-3
Nitric oxide, NO	10102-43-9	Benzene	71-43-2
Nitrogen dioxide, NO ₂	10102-44-0	Carbon tetrachloride	56-23-5
Methane	74-82-8	Cyclohexane	110-82-7
Carbon dioxide, CO ₂	124-38-9	1,2-Dichloropropane	78-87-5
Carbon monoxide, CO	630-08-0	Trichloroethene	79-01-6
Nitrous oxide, N ₂ O	10024-97-2	n-Heptane	142-82-5
Hydrogen	1333-74-0	cis-1,3-Dichloropropene	10061-01-5
Total Non-Methane Organic Compounds (TNMOC)	n.a.	4-Methyl-2-pentanone (hexone)	108-10-1
Dichlorodifluoromethane	75-71-8	Pyridine	110-86-1
Chloromethane	74-87-3	trans-1,3-Dichloropropene	10061-02-6
1,2-Dichloro-1,1,2,2-tetra-fluoroethane	76-14-2	1,1,2-Trichloroethane	79-00-5
Chloroethene (vinyl chloride)	75-01-4	Toluene	108-88-3
n-Butane	106-97-8	1,2-Dibromoethane	106-93-4
Bromomethane	74-83-9	n-Octane	111-65-9
Chloroethane	75-00-3	Tetrachloroethylene	127-18-4
Ethanenitrile (acetonitrile)	75-05-8	Chlorobenzene	108-90-7
Propanone (acetone)	67-64-1	Ethylbenzene	100-41-4
Trichlorofluoromethane	75-69-4	p/m-Xylene	106-42-3
n-Pentane	109-66-0	Cyclohexanone	108-94-1
1,1-Dichloroethene	75-35-4	Styrene	100-42-5
Dichloromethane (methylene chloride)	75-09-2	1,1,2,2-Tetrachloroethane	79-34-5
1,1,2-Trichloro-1,2,2,2-tri-fluoroethane	76-13-1	o-Xylene	95-47-6
Propanenitrile	107-12-0	n-Nonane	111-84-2
Methanol	67-56-1	1,3,5-Trimethylbenzene	108-67-8
Ethanol	64-17-5	1,2,4-Trimethylbenzene	95-63-6
1-Propanol	71-23-8	n-Decane	124-18-5
1,1-Dichloroethane	75-34-3	1,3-Dichlorobenzene	541-73-1
2-Butanone	78-93-3	1,4-Dichlorobenzene	106-46-7
cis-1,2-Dichloroethene	156-59-2	1,2-Dichlorobenzene	95-50-1
n-Hexane	110-54-3	n-Undecane	1120-21-4
Trichloromethane (chloroform)	67-66-3	1,2,4-Trichlorobenzene	120-82-1
Tetrahydrofuran	109-99-9	n-Dodecane	112-40-3
1,2-Dichloroethane	107-06-2	n-Tridecane	629-50-5
1,1,1-Trichloroethane	71-55-6	n-Tetradecane	629-59-4
1-Butanenitrile	109-74-0	Water	

2.0 Sample Collection

2.1 Sampling Devices and Method

All samples in this study were collected using either sorbent traps or SUMMATM passivated canisters. Sorbent traps use adsorption or chemisorption to selectively remove vapors of interest from a metered amount of sample air. The analytes are extracted in the analytical laboratory, and the amount of each analyte is measured to determine its concentration in the sample air. Sorbent traps are particularly good for the inorganic vapors (e.g., ammonia, water) and many organic vapors but are not effective for permanent gases or highly volatile organic compounds. SUMMA passivated canisters are stainless steel vessels whose internal surfaces have been treated to minimize adsorption of vapors. In this study, evacuated SUMMA canisters were filled with headspace air and taken to the analytical laboratory for analysis. SUMMA canisters are very good for all permanent gases and nonpolar organic vapors, and methods have been adapted to allow their use to measure certain semivolatile organic compounds and polar organic vapors.

All samples were collected using the in situ vapor sampling (ISVS) system, which consists of an air pump and an accurate mass flow metering system to measure sorbent trap volumes and purge SUMMA canister transfer tubing. Sorbent trap samples are connected via narrow tubing to the ISVS manifold and lowered into the tank headspace to the desired elevation. The ISVS system in use at the time of this study allows 14 sorbent traps to be lowered into the headspace at one time for the simultaneous collection of four sorbent traps. SUMMA canister samples are collected via narrow perfluoroalkoxy (PFA) tubing that is lowered into the headspace to the desired elevation. The ISVS system has been demonstrated to be adequate for existing data needs (Huckaby et al. 1996).^(a)

2.2 Collection Date, Location, and Sequence

Tanks B-103, TY-103, and U-112 were sampled for this study on October 16, November 22, and December 6, 1996, respectively. Descriptions of the sampling events are given in NHC (1997a-c). Reported deviations from procedure and anomalous observations were minor, and none appear to have adversely affected results.

Each of the three tanks was sampled at three elevations via two risers, for a total of six sets of samples from each tank. The two risers were selected so that they were as far apart as practicable to investigate horizontal concentration gradients. Samples were collected from approximately two feet above the waste (bottom elevation), two feet below the end of the riser

(a) Ermold LF. August 30, 1996. *Resubmittal of Defense Nuclear Facilities Safety Board Recommendation 93-5 Implementation Plan Revision 1 Commitment 5.6.3.1a, Letter Reporting completion of Comparison Between Truck and Cart Vapor Sampling Systems*. (Letter to JK McClusky, DOE/RL, 9653760), Westinghouse Hanford Company, Richland, Washington.

(top elevation), and at an elevation halfway between the top and bottom elevations (middle elevation). Table 2.1 lists the risers used to collect samples; vertical distances from the middle sampling point to the waste surface, low and high sampling points, and riser bottom; and horizontal distances from each riser to the center of the tank and between the two risers.

Samples were collected in sets of four at each level in each riser, giving a total of 24 samples of each type from each tank. Sampling limitations prevented the simultaneous collection of all samples, but time between samples of each type at the various levels was minimized by collecting samples in two batches. Sorbent traps for ammonia, nitrogen oxides, and water vapor were collected in the first batch, and the permanent gases and organic vapors were collected in the second batch. Using this approach, all samples of a given type from a given tank were collected in less than about 80 minutes.

To determine whether sample results are correlated with the time they were collected (i.e., whether results were affected by the collection sequence), the four middle elevation samples were collected in two subsets. Specifically, for each type of sample and in each riser the sampling sequence was

Table 2.1. Sample Collection Points^(a)

	B-103		TY-103		U-112	
Riser Number	2	7	8	18	3	6
Elevations ^(b) (m)						
Bottom of Riser	6.7	6.7	9.5	8.6	6.7	6.7
High Sampling Point	5.8	5.8	7.8	7.5	5.5	5.5
Middle Sampling Point	3.4	3.5	5.0	4.9	3.4	3.2
Low Sampling Point	1.1	1.2	2.3	2.3	1.2	1.1
Waste Surface	0.4	0.4	1.5	1.5	0.5	0.3
Horizontal Distances (m)						
To center of tank	9.9	9.9	1.5	7.9	9.9	9.9
Between risers	19.8		7.2		19.8	
(a) Values were received from DD Wanner (NHC) in a personal communication to JL Huckaby, May 1997.						
(b) Elevations are measured from the bottom of the sidewall in each tank.						

1. two samples were collected from the middle elevation
2. four samples were collected from the bottom elevation
3. four samples were collected from the top elevation
4. the remaining two samples were collected from the middle elevation.

This sequence allows direct comparison of the initial and final samples independent of elevation.

3.0 Sample Analysis

3.1 Quality Assurance

Samples were analyzed in accordance with *Hanford Analytical Services Quality Assurance Plan* (DOE 1995), *Quality Assurance Project Plan for Tank Vapor Characterization* (Keller 1994), and *Quality Assurance Plan for Activities Conducted by the Pacific Northwest National Laboratory Vapor Analytical Laboratory (VAL) and the Pacific Northwest National Laboratory Tank Vapor Characterization Project*.^(a) Deviations from these plans are documented in the individual analytical reports (Olsen et al. 1997a-b; Sklarew et al. 1997).

3.2 Analytical Methods

Sample analyses for this study were performed according the same PNNL procedures and guidelines as have been used to characterize tank headspaces. To minimize analytical biases, all samples of a given type from the six different sampling locations in each tank were analyzed in a randomized sequence. All analytical results are provided and discussed by Olsen et al. (1997a, 1997b) and Sklarew et al. (1997) for Tanks B-103, TY-103, and U-112, respectively.

3.2.1 Ammonia and Water Vapor

Ammonia analyses were conducted on acidified carbon bead sorbent trap samples. Ammonia was removed from the sorbent media by liquid extraction and analyzed by an ion-specific electrode. Quality control objectives were achieved using both initial and continuing calibration verifications. Blank samples were run to detect the presence of any contamination, and field samples were analyzed for comparative purposes.

Water vapor was measured by a gravimetric method. Water vapor was collected by the hygroscopic ammonia sorbent traps and two silica gel sorbent traps connected in series behind the ammonia sorbent trap. Each sorbent trap was accurately weighed before and after sample collection, and the difference in weights was assumed to be due to collected water vapor (all other condensible constituents are negligible). Quality control objectives were achieved by balance calibration and the use of standard weights and field and trip blanks.

(a) PNNL. 1996. *Quality Assurance Plan for Activities Conducted by the Pacific Northwest National Laboratory Vapor Analytical Laboratory (VAL) and the Pacific Northwest National Laboratory Tank Vapor Characterization Project*. ETD-002, Pacific Northwest National Laboratory, Richland, Washington.

3.2.2 Permanent Gases

The permanent gases analyzed in tank vapor headspace samples included hydrogen, carbon dioxide, carbon monoxide, methane, and nitrous oxide. The method was based on samples collected in SUMMA canisters. Aliquots of the collected vapor were analyzed using a gas chromatograph coupled with a thermal conductivity detector (GC/TCD). The analytes were identified by matching the sample peak retention time with that of a traceable gas standard mixture. The same standard mixture was used to calibrate the method for quantitation. Quality control objectives were achieved using both initial and continuing calibration verifications. Blank samples were run to detect the presence of any contamination, and ambient air samples taken in the tank farm were analyzed for comparative purposes. All SUMMA canister samples from the six different sampling locations in each tank were analyzed on the same day.

3.2.3 Total Non-Methane Organic Compounds

An analysis was performed for total organic compounds (excluding methane) present in the tank headspace vapor samples using a method based on Environmental Protection Agency (EPA) procedure TO-12 for total non-methane organic compound (TNMOC) vapors in ambient air samples. The method was applied to samples collected in SUMMA canisters. The TNMOC vapors were pumped through a cryogenic concentrator and then analyzed using a flame ionization detector. Quantitation was achieved using a multiconcentration calibration curve generated using a traceable propane standard of known concentration. Quality control objectives were achieved using both initial and continuing calibration verifications. Blank samples were run to detect the presence of any contamination, and ambient air samples taken in the tank farm were analyzed for comparative purposes.

3.2.4 Organic Vapors in SUMMA Canisters

Analysis of organic vapors in SUMMA canisters was based on EPA procedure TO-14 for speciating organic vapors in ambient air samples but modified for use on tank headspace samples. Tank headspace samples typically have higher concentrations and constituents with a wider variety of physical and chemical properties than ambient samples. The tank headspace vapor samples were pumped through a cryogenic concentrator and then analyzed using a gas chromatograph-mass spectrometer (GC/MS). Quantitation was achieved using two methods. One was the use of a traceable TO-14 standard containing 39 compounds of known concentration. Calibration for tank headspace constituents not found in commercially available TO-14 standards was achieved using gas standards prepared from calibrated permeation tubes. Quality control objectives were achieved using both initial and continuing calibration verifications. Blank samples were run to detect the presence of any contamination, and ambient air samples taken in the tank farm were analyzed for comparative purposes.

3.2.5 Organic Vapors in Triple Sorbent Traps (TSTs)

Analysis of organic vapors was also performed on commercially produced, graphitized carbon TSTs. The volatile organic compounds adsorbed on the traps were thermally desorbed from the traps and analyzed using a GC/MS. Quantitation was achieved using the same two

methods as used for SUMMA canister organic vapor analysis. Quality control objectives were achieved using both initial and continuing calibration verifications. Blank samples were run to detect the presence of any contamination.

3.3 Anomalous Results

The analytical results of certain samples indicated there had been problems associated with their handling, collection, or analysis. Some samples were apparently exposed to contaminants during handling or storage, and some TST samples were adversely affected by passive sampling that occurred during their extended time in the tank headspace. Several results, marked as suspect by the analysts, were also subject to unidentified problems.

3.3.1 Sample Contamination

Tank TY-103 and U-112 TST samples were apparently contaminated with organic vapors. The samples and field blanks^(a) from both tanks had comparable levels of many tentatively identified volatile branched and cyclic alkanes. It was concluded that these were contaminants (i.e., not from the headspaces) because, if they had been present in the headspaces, their concentrations would have been much higher in the samples than in the field blanks. Many of the positively identified (target) compounds (e.g., toluene, xylenes) were also found in both the field blank and sample TSTs from these tanks.

Field blank-based corrections to the sample results were not made, because the measured concentrations of these suspected contaminants varied greatly between the two field blanks and among the samples of both tanks. Instead, to ensure contaminants were excluded from this study but valid constituents were included, only constituents that were positively identified in the field blanks were excluded. This rule resulted in excluding 15 of the 23 quantitatively measured^(b) constituents in TY-103 TSTs, and all 7 of the quantitatively measured constituents in U-112 TSTs.

3.3.2 Passive Sampling

Since sorbent traps in the ISVS method are physically exposed to the tank vapor for some time before and again after actual sample collection, some amount of passive sampling by diffusion of vapors to the sorbent media is to be expected. (SUMMA canister samples are not affected by passive sampling.) To estimate the impact of passive sampling, field blanks are included in the ISVS bundle. The field blanks are physically configured identically to other samples, but no sample air is drawn through them. Field blank data were used by the analysts to correct both the ammonia and water vapor measurements, where the amount of analyte trapped

(a) Field blanks are included in the sample bundle and treated like samples except that no sample air is intentionally drawn through them.

(b) As described in Section 4, it was decided that at least 75% of all reported concentrations for a given constituent must be within the instrumental calibration range to be considered quantitatively measured and be included in the statistical analyses of this study.

due to passive sampling is relatively small. There was also evidence of passive sampling in U-112 TSTs, but because there was a contamination issue with these samples, the data from these samples were not used anyway.

4.0 Statistical Analysis and Results

4.1 Selection of Data for Statistical Analysis

Not all sample analysis data were incorporated into the statistical analysis of this study because some did not meet criteria established in *Vapor Sampling and Analysis Plan for Headspace Homogeneity Tests of Tanks B-103, TY-103, and U-112* (Buckley 1996). The sampling and analysis plan requires that the concentrations of study analytes be quantitatively measured, and this criterion eliminates many targeted compounds that were either below analytical quantitation limits or below analytical detection limits. All data for a given compound in a given type of sample were included in the statistical analyses when at least 75% of the concentration data were within the quantitation limits.

Though sample analyses included tentative identification of non-targeted organic vapors, their concentrations were estimated (i.e., not quantitated), and these results have been deemed inappropriate for statistical analysis. Data not included in the statistical analyses have been examined for qualitative agreement with other study findings and are discussed in Section 5.

4.2 Statistical Model

The analysis of variance (ANOVA) model fit to the vapor sampling data has the following form:

$$\begin{aligned} y_{ijkm} &= \mu + R_i + D_j + RD_{ij} + T_{ijk} + E_{ijkm}, \\ i &= 1, 2, \dots, a; \quad j = 1, 2, \dots, b; \\ k &= 1, 2, \dots, n_{ij}; \quad m = 1, 2, \dots, p_{ijk}. \end{aligned} \tag{4.1}$$

The variable y_{ijkm} is the measured concentration of a vapor from the i th riser, the j th depth, the k th subsample, and the m th sample. The data set is "unbalanced" because the range of the subscripts (a , b , n_{ij} , and p_{ijk}) depend on the riser and depth. Table 4.1 gives the unbalance in the vapor data.

Table 4.1. Range of Subscripts for the Vapor Data

i	j	k	m
1	1	$n_{11}=1$	$p_{111}=4$
1	2	$n_{12}=2$	$p_{121}=2$ and $p_{122}=2$
1	3	$n_{13}=1$	$p_{131}=4$
2	1	$n_{21}=1$	$p_{211}=4$
2	2	$n_{22}=2$	$p_{221}=2$ and $p_{222}=2$
2	3	$n_{23}=1$	$p_{231}=4$

The symbols on the right side of equation (4.1) are defined as follows:

μ is the mean concentration of a gas

R_i is the effect of the i th riser, $i = 1, 2, \dots, a$, where a is the number of riser

D_j is the effect of the j th depth, $j = 1, 2, \dots, b$, where b is the number of depths

RD_{ij} is the "riser-by-depth" interaction term

T_{ijk} represents the deviations of the k th sample in location ij , $k = 1, 2, \dots, n_{ij}$, where n_{ij} is the number of samples

E_{ijkm} represents the deviations of the m th subsample from location ijk , $m = 1, 2, \dots, p_{ijk}$, where p_{ijk} is the number of subsamples.

The crossed effect variables, R_i , D_j , and RD_{ij} , are assumed to be uncorrelated and normally distributed with means zero and variances $\sigma^2(R)$, $\sigma^2(D)$, $\sigma^2(RD)$. The sampling and subsampling variables T_{ijk} and E_{ijkm} are also assumed to be uncorrelated and normally distributed with means zero and variances $\sigma^2(T)$ and $\sigma^2(E)$. The crossed and nested variables are assumed to be uncorrelated with each other.

ANOVA methods were used to test the significance of four variance components, $\sigma^2(R)$, $\sigma^2(D)$, $\sigma^2(RD)$, and $\sigma^2(T)$ where

$\sigma^2(R)$ represents variance of samples taken from different risers (horizontal variability)

$\sigma^2(D)$ represents variance of samples taken at different depths (vertical variability)

$\sigma^2(RD)$ represents variances of the riser-by-depth interaction

$\sigma^2(T)$ represents variance between the repeated samples taken from the middle location.

4.3 Variance Components and Significance Tests

For each analyte, the variance components $\sigma^2(R)$, $\sigma^2(D)$, $\sigma^2(RD)$, $\sigma^2(T)$, and $\sigma^2(E)$ of equation (4.1) were estimated using restricted maximum likelihood methods. The restricted maximum likelihood method, as applied to variance component estimation, is discussed in Harville (1977). The relative magnitude of the variance components give an indication of which source(s) of variability are dominant.

ANOVA methods were used to test hypotheses that the variance components could not be distinguished from zero. In the case of a balanced data set, the method used to determine the significance of the variance components is straightforward. Specifically, the ANOVA table and tests for significance of the variance components for the balanced version of the model, equation (4.1), are given in chapter 11 of Ostle (1963).

Because the data in this study was not balanced, the procedure used to determine the significance of the variance components cannot easily be done without the use of a computer. To test the significance of the variance components, the TEST option of the SAS GLM procedure (SAS 1990) was used. In the GLM procedure, appropriate F-ratios are formed using linear combinations of the mean squares from the ANOVA. The degrees of freedom in the F-tests are based on approximations. A good set of references which describe the statistical methodology are given in chapter 24 of the SAS/STAT User's Guide (SAS 1990).

An iterative approach was used in the analysis. For each constituent, the full model defined by equation (4.1) was fit to the data, and the significance of the sampling effect, T_{ijk} , was determined. Some constituents had p-values less than 0.2, and some had p-values greater than 0.2. In cases where the p-value was less than 0.2, the full model, equation (4.1), was used to evaluate the significance of each variance component. In these cases no additional models were fit to the data.

In cases where the p-value corresponding to the T_{ijk} term was greater than 0.2, a second iteration was completed. In this iteration, the T_{ijk} term was "pooled" with E_{ijkm} . The significance of riser-by-depth interaction variance component was then tested with the new (reduced) model. If the p-value corresponding to $\sigma^2(RD) = 0$ was less than 0.2, the significance of the riser and depth variance components were evaluated without fitting an additional model. In cases where the p-value was greater than 0.2, a third iteration was completed. In this iteration, the RD_{ij} term was "pooled" with T_{ijk} and E_{ijkm} and a third, and final, model was fit to the data. The significance of the riser and depth variance components were then tested using the reduced model.

4.4 Statistical Results

For each tank, the statistical results are given in two tables. The first table indicates the constituents which had significant variance components. The second table gives the variance components as a percentage of the overall variability.

Any variability that could be attributed to changes in gas composition at different depths was either negligible or extremely small. Variability which could be attributed to changes in

concentration for different riser locations was generally less than or approximately equal to the repeated samples variability, $\sigma^2(T)$, and within sample variability, $\sigma^2(E)$. These results support the hypothesis that the composition of gas in each tank's headspace is homogenous.

4.4.1 Tank B-103

A summary of the significance tests for Tank B-103 is given in Table 4.2. In this table an "x" denotes the variance components that are significantly different from zero (at the 0.05 level of significance). To help judge the magnitude of the results, Table 4.2 also includes the mean value, the units of the mean value, and the percent relative standard deviation (%RSD) for each set of measurements. Three of the 45 sets of measurements analyzed indicated results were riser-dependent, two indicated results were depth-dependent, and none indicated a significant interaction between riser and depth results.

As a percentage of the measurements, about 7% indicated a riser-dependence, about 4% indicated a depth-dependence, and 0 % indicated a riser-by-depth interaction. These percentages are similar to the number of false positives that one would expect using a 0.05 level of significance.

The variance components of the statistical model are given for each set of Tank B-103 measurements as a percentage of the total variance in Table 4.3. The estimate of the variance within a sample, $\hat{\sigma}^2(E)$, is the dominant term for 43 of the 45 measurements. Relative to the size of the sample within measurement variability, the other estimates of variances components are small.

4.4.2 Tank TY-103

Tank TY-103 significance tests are summarized in Table 4.4. As in Table 4.2, an "x" denotes the variance components that are significantly different from zero at the 0.05 level of significance. Table 4.4 also includes the mean value, the units of the mean value, and the %RSD for each set of measurements. Four of the 36 sets of measurements analyzed indicated results were riser-dependent, one indicated results were depth-dependent, and one indicated a significant interaction between riser and depth results.

As a percentage of the measurements, about 11% indicated a riser-dependence, about 3% indicated a depth-dependence, and 3% indicated a riser-by-depth interaction. These percentages are similar to the number of false positives that one would expect using a 0.05 level of significance.

The variance components of the statistical model are given for each set of Tank TY-103 measurements as a percentage of the total variance in Table 4.5. The estimate of the variance within a sample, $\hat{\sigma}^2(E)$, is the dominant term for 18 of the 36 measurements, and variances associated with T_{ijk} , $\hat{\sigma}^2(T)$, and riser, $\hat{\sigma}^2(R)$, being the dominant terms for 9 and 8 of the measurements, respectively. The $\hat{\sigma}^2(D)$ term was not a major source of variability for any constituent.

Table 4.2. Tank B-103 Significance of Variance Components, Means, and RSDs

Analyte	Sampling Device	Significance of Variance Components			Mean	Units	%RSD
		Riser	Depth	Interaction			
Acetone	SUMMA				316	ppbv	11
Acetone	TST				226	ppbv	16
Acetonitrile	SUMMA				101	ppbv	12
Acetonitrile	TST				74	ppbv	17
Ammonia	Sorbent Trap				8	ppmv	10
n-Butane	SUMMA				177	ppbv	10
n-Butane	TST				169	ppbv	13
Butanenitrile	SUMMA				36	ppbv	14
Butanenitrile	TST				28	ppbv	11
1-Butanol	SUMMA				964	ppbv	17
1-Butanol	TST				742	ppbv	11
2-Butanone	SUMMA				92	ppbv	13
2-Butanone	TST				94	ppbv	16
Carbon dioxide	SUMMA				1,370	ppmv	4
Cyclohexanone	SUMMA	x			15	ppbv	16
n-Dodecane	SUMMA	x			58	ppbv	16
n-Dodecane	TST				12	ppbv	60
Ethanol	SUMMA				62	ppbv	28
n-Heptane	SUMMA				6	ppbv	23
n-Heptane	TST				7	ppbv	14
n-Hexane	SUMMA				16	ppbv	9
n-Hexane	TST				20	ppbv	11
Methanol	SUMMA				205	ppbv	20
Methanol	TST		x		554	ppbv	38
Nitrous oxide (N ₂ O)	SUMMA				60	ppmv	4
Nitrogen dioxide (NO ₂)	Sorbent Trap				477	ppbv	21
n-Pentane	SUMMA				40	ppbv	9
n-Pentane	TST				41	ppbv	11
Pentanenitrile	TST				6	ppbv	16
Propanenitrile	SUMMA				36	ppbv	11
Propanenitrile	TST				35	ppbv	14
1-Propanol	SUMMA				87	ppbv	15
1-Propanol	TST				99	ppbv	18
Tetrachloroethylene	SUMMA				6	ppbv	11
n-Tetradecane	SUMMA				83	ppbv	40
n-Tetradecane	TST				68	ppbv	90
Tetrahydrofuran	SUMMA				28	ppbv	25
Tetrahydrofuran	TST				22	ppbv	6
TNMOC	SUMMA	x	x		15	mg/m ³	6
Toluene	TST				24	ppbv	48
Trichlorofluoromethane	SUMMA				165	ppbv	10
Trichlorofluoromethane	TST				162	ppbv	5
n-Tridecane	SUMMA				141	ppbv	24
n-Tridecane	TST				42	ppbv	62
Water	Sorbent Trap				13	mg/L	7

Table 4.3. Tank B-103 Variance Components as Percent of Total

Analyte	Method	$\sigma^2(R)$ (%)	$\sigma^2(D)$ (%)	$\sigma^2(RD)$ (%)	$\sigma^2(T)$ (%)	$\sigma^2(E)$ (%)
Acetone	SUMMA	6	4	0	0	90
Acetone	TST	0	23	0	0	77
Acetonitrile	SUMMA	8	10	0	0	82
Acetonitrile	TST	0	0	0	0	100
Ammonia	Sorbent Trap	0	1	0	0	99
n-Butane	SUMMA	0	0	0	0	100
n-Butane	TST	0	3	5	0	91
Butanenitrile	SUMMA	12	2	0	0	86
Butanenitrile	TST	5	0	0	1	94
1-Butanol	SUMMA	6	0	0	0	94
1-Butanol	TST	0	0	0	0	100
2-Butanone	SUMMA	8	9	0	0	82
2-Butanone	TST	0	0	9	0	91
Carbon dioxide	SUMMA	4	64	0	26	6
Cyclohexanone	SUMMA	27	0	0	0	73
n-Dodecane	SUMMA	16	0	0	0	84
n-Dodecane	TST	0	0	0	0	100
Ethanol	SUMMA	0	11	0	0	89
n-Heptane	SUMMA	0	0	0	0	100
n-Heptane	TST	0	0	0	0	100
n-Hexane	SUMMA	0	0	0	0	100
n-Hexane	TST	0	13	0	0	87
Methanol	SUMMA	0	0	0	0	100
Methanol	TST	0	44	0	0	56
Nitrous oxide (N ₂ O)	SUMMA	0	3	0	0	97
Nitrogen dioxide (NO ₂)	Sorbent Trap	0	0	26	56	17
n-Pentane	SUMMA	0	0	0	0	100
n-Pentane	TST	0	8	3	5	85
Pentanenitrile	TST	7	0	0	0	93
Propanenitrile	SUMMA	8	11	0	0	81
Propanenitrile	TST	4	0	0	0	96
1-Propanol	SUMMA	0	0	10	0	90
1-Propanol	TST	1	0	0	0	99
Tetrachloroethylene	SUMMA	0	0	0	0	100
n-Tetradecane	SUMMA	0	0	0	0	100
n-Tetradecane	TST	0	0	0	0	100
Tetrahydrofuran	SUMMA	0	0	0	22	78
Tetrahydrofuran	TST	0	0	0	0	100
TNMOC	SUMMA	17	26	0	0	57
Toluene	TST	0	0	0	0	100
Trichlorofluoromethane	SUMMA	0	0	0	0	100
Trichlorofluoromethane	TST	0	0	0	17	83
n-Tridecane	SUMMA	1	0	0	0	99
n-Tridecane	TST	0	0	0	0	100
Water	Sorbent Trap	0	7	0	44	49

Table 4.4. Tank TY-103 Significance of Variance Components, Means, and RSDs

Analyte	Sampling Device	Significance of Variance Components			Mean	Units	%RSD
		Riser	Depth	Interaction			
Acetone	SUMMA				145	ppbv	7
Acetonitrile	SUMMA	x			76	ppbv	4
Ammonia	Sorbent Trap				46	ppmv	9
n-Butane	SUMMA	x	x		47	ppbv	8
Butanenitrile	SUMMA				14	ppbv	11
Butanenitrile	TST				18	ppbv	10
1-Butanol	SUMMA				307	ppbv	9
1-Butanol	TST				187	ppbv	14
2-Butanone	SUMMA				21	ppbv	16
Carbon dioxide	SUMMA				210	ppmv	2
Carbon tetrachloride	SUMMA				11	ppbv	13
Carbon tetrachloride	TST				8	ppbv	9
n-Decane	SUMMA				7	ppbv	9
n-Dodecane	SUMMA	x			1,290	ppbv	26
n-Dodecane	TST				168	ppbv	60
Ethanol	SUMMA			x	69	ppbv	24
n-Heptane	SUMMA				8	ppbv	31
Hydrogen	SUMMA				62	ppmv	2
Methanol	SUMMA				400	ppbv	28
Nitrous oxide (N ₂ O)	SUMMA				205	ppmv	1
n-Pentane	SUMMA				14	ppbv	7
Pentanenitrile	TST				5	ppbv	12
Propanenitrile	SUMMA				18	ppbv	6
Propanenitrile	TST				14	ppbv	17
1-Propanol	SUMMA				34	ppbv	8
1-Propanol	TST				26	ppbv	15
Tetrachloroethylene	SUMMA				9	ppbv	11
Tetrachloroethylene	TST				6	ppbv	26
n-Tetradecane	SUMMA	x			2,370	ppbv	60
Tetrahydrofuran	SUMMA				15	ppbv	10
TNMOC	SUMMA				45	mg/m ³	14
Toluene	SUMMA				24	ppbv	45
Trichlorofluoromethane	SUMMA				143	ppbv	11
1,1,2-Trichloro- 1,2,2-trifluoroethane	SUMMA				8	ppbv	43
n-Tridecane	SUMMA				6,100	ppbv	29
Water	Sorbent Trap				14	mg/L	18

Table 4.5. Tank TY-103 Variance Components as Percent of Total

Analyte	Method	$\sigma^2(R)$ (%)	$\sigma^2(D)$ (%)	$\sigma^2(RD)$ (%)	$\sigma^2(T)$ (%)	$\sigma^2(E)$ (%)
Acetone	SUMMA	16	0	11	37	36
Acetonitrile	SUMMA	49	11	0	0	41
Ammonia	Sorbent Trap	14	0	0	0	86
n-Butane	SUMMA	35	3	0	20	41
Butanenitrile	SUMMA	36	0	11	25	27
Butanenitrile	TST	0	5	0	7	88
1-Butanol	SUMMA	50	0	15	17	18
1-Butanol	TST	0	0	0	0	100
2-Butanone	SUMMA	0	35	0	23	41
Carbon dioxide	SUMMA	4	0	0	0	96
Carbon tetrachloride	SUMMA	68	0	0	20	12
Carbon tetrachloride	TST	0	2	0	0	98
n-Decane	SUMMA	50	0	0	37	14
n-Dodecane	SUMMA	87	0	0	8	5
n-Dodecane	TST	0	0	0	16	84
Ethanol	SUMMA	35	4	38	0	24
n-Heptane	SUMMA	0	0	0	65	35
Hydrogen	SUMMA	12	0	0	0	88
Methanol	SUMMA	27	0	0	48	25
Nitrous oxide (N ₂ O)	SUMMA	10	0	0	0	91
n-Pentane	SUMMA	38	0	0	38	24
Pentanenitrile	TST	0	0	0	17	83
Propanenitrile	SUMMA	14	0	0	68	18
Propanenitrile	TST	11	0	0	0	89
1-Propanol	SUMMA	37	0	0	51	12
1-Propanol	TST	0	23	0	0	77
Tetrachloroethylene	SUMMA	29	0	0	49	22
Tetrachloroethylene	TST	0	3	0	0	97
Tetradecane	SUMMA	41	2	0	6	51
Tetrahydrofuran	SUMMA	0	0	0	87	13
TNMOC	SUMMA	85	0	0	9	6
Toluene	SUMMA	0	0	0	73	27
Trichlorofluoromethane	SUMMA	45	0	0	40	14
1,1,2-Trichloro- 1,2,2-trifluoroethane	SUMMA	1	0	0	49	50
n-Tridecane	SUMMA	16	0	0	31	53
Water	Sorbent Trap	0	4	0	23	73

Table 4.6. Tank U-112 Significance of Variance Components, Means, and RSDs

Analyte	Sampling Device	Significance of Variance Components			Mean	Units	%RSD
		Riser	Depth	Interaction			
Acetone	SUMMA				34	ppbv	19
Ammonia	Sorbent Trap	x			304	ppmv	3
n-Butane	SUMMA				32	ppbv	5
1-Butanol	SUMMA				167	ppbv	10
Ethanol	SUMMA	x			443	ppbv	23
Hydrogen	SUMMA			x	99	ppmv	5
Methanol	SUMMA				814	ppbv	10
Nitrous oxide (N ₂ O)	SUMMA				181	ppmv	1
1-Propanol	SUMMA				38	ppbv	10
Tetrahydrofuran	SUMMA				7	ppbv	12
TNMOC	SUMMA	x			3	mg/m ³	8
Toluene	SUMMA	x			36	ppbv	6
Trichlorofluoromethane	SUMMA				35	ppbv	4
Water	Sorbent Trap	x			14	mg/L	8

4.4.3 Tank U-112

The significance tests for Tank U-112 are summarized in Table 4.6. As in Tables 4.2 and 4.4, an "x" denotes the variance components that are significantly different from zero at the 0.05 level of significance. The mean value, the units of the mean value, and the percent relative standard deviation (%RSD) for each set of measurements is also included in Table 4.6. Five of the 14 sets of measurements analyzed indicated results were riser-dependent, none indicated results were depth-dependent, and one indicated a significant interaction between riser and depth results.

As a percentage of the measurements, about 36 % indicated a riser-dependence, 0 % indicated a depth-dependence, and about 7 % indicated a riser-by-depth interaction. With the exception of the riser term, these percentages are similar to the number of false positives that one would expect using a 0.05 level of significance. Even though some of the riser terms, $\hat{\sigma}^2(R)$, are significantly greater than zero, the actual concentration differences measured from the two risers were quite small. Table 4.7 lists mean measured concentrations for the Tank U-112 analytes, and their percent difference. Note that the highest percent difference between the means is only 20 %, and that the means for 11 of the 14 analytes agree to within 10 %.

The variance components of the statistical model are given for each set of Tank U-112 measurements as a percentage of the total variance in Table 4.8. Variance within a sample, $\hat{\sigma}^2(E)$, is the dominant term for 11 of the 14 measurements. Relative to the size of the within sample measurement variability, the other variances are small.

Table 4.7. Tank U-112 Result Means by Riser

Analyte	Sampling Device	Units	Riser 3		Riser 6		% Difference Between Means
			Mean	Std. Dev.	Mean	Std. Dev.	
Acetone	SUMMA	ppbv	34.3	7.5	33.3	5.5	3
Ammonia	Sorbent Trap	ppmv	299	9	308	9	-3
n-Butane	SUMMA	ppbv	31.9	1.7	32.3	1.7	-1
1-Butanol	SUMMA	ppbv	165	11	171	20	-4
Ethanol	SUMMA	ppbv	394	42	482	119	-20
Hydrogen	SUMMA	ppmv	97	2	98	1	-1
Methanol	SUMMA	ppbv	772	52	854	91	-10
Nitrous oxide (N ₂ O)	SUMMA	ppmv	182	2	181	1	0.3
1-Propanol	SUMMA	ppbv	37.8	3.0	38.5	4.4	-2
Tetrahydrofuran	SUMMA	ppbv	7.0	0.8	6.8	0.9	3
TNMOC	SUMMA	mg/m ³	2.5	0.1	2.8	0.2	-12
Toluene	SUMMA	ppbv	35.5	1.8	36.6	2.4	-3
Trichlorofluoromethane	SUMMA	ppbv	34.5	1.3	34.8	1.4	-1
Water	Sorbent Trap	mg/L	14.8	1.0	13.6	0.9	8

Table 4.8. Tank U-112 Variance Components as Percent of Total

Analyte	Method	$\delta^2(R)$ (%)	$\delta^2(D)$ (%)	$\delta^2(RD)$ (%)	$\delta^2(T)$ (%)	$\delta^2(E)$ (%)
Acetone	SUMMA	0	0	0	2	99
Ammonia	Sorbent Trap	24	0	0	0	76
n-Butane	SUMMA	0	0	0	0	100
1-Butanol	SUMMA	0	0	0	0	100
Ethanol	SUMMA	29	0	0	0	71
Hydrogen	SUMMA	8	0	53	0	39
Methanol	SUMMA	30	0	0	11	58
Nitrous oxide (N ₂ O)	SUMMA	0	0	0	0	100
1-Propanol	SUMMA	0	0	0	4	96
Tetrahydrofuran	SUMMA	0	0	0	0	100
TNMOC	SUMMA	75	0	0	0	25
Toluene	SUMMA	3	0	0	0	97
Trichlorofluoromethane	SUMMA	0	0	0	0	100
Water	Sorbent Trap	30	0	0	35	35

5.0 Summary and Conclusions

Headspace composition data from two risers at three elevations in Tanks B-103, TY-103, and U-112 have been analyzed by standard statistical methods and found to provide essentially no evidence that these tanks exhibit any significant horizontal or vertical concentration gradients. No stratification of denser vapors (e.g., carbon tetrachloride, dodecane) or lighter gases (e.g., ammonia, hydrogen) was detected in any of the three tanks. A qualitative examination of all tentatively identified organic vapors in SUMMA and TST samples supported this conclusion.

The studied tanks had sufficient concentrations of low and high density gases and vapors to provide quantitative concentration data on headspace stratification. The majority of quantitative data were included in the statistical analysis, and only a small number of available data were not used in the study because of a TST contamination problem. At the time the tanks were sampled, the waste surface temperature in each studied tank was reported to be about the same as, or slightly below, the headspace air temperature. For this temperature profile, mixing due to thermally induced convection would be expected to be at a minimum.

Though the data from three tanks cannot be used to demonstrate that no tank headspace ever exhibits significant horizontal or vertical concentration gradients at any time of year, the tanks and sampling dates were selected to maximize the possibility of observing inhomogeneities in the headspaces. The results from Tanks B-103, TY-103, and U-112 indicate that, even in very cool tanks, the central region of a tank headspace is homogeneous for all intents and purposes.

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