PNNL-14831

Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

Overview of Hanford Site High-Level Waste Tank Gas and Vapor Dynamics

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Summary

The storage of volatile and semivolatile species in Hanford Site waste, their transport through any overburden of waste to the tank headspaces, the physical phenomena affecting their concentrations in the headspaces, and their eventual release into the atmosphere above the tanks are examined. The physical and chemical phenomena that cause and influence the transport of gases and vapors from within the waste to the tank headspaces are described, and available supporting evidence from tank observations are provided.

Key findings are that the rate that volatile species from within the waste are transported to the tank headspaces is limited by its transport through the interstitial liquid. Transport through convective liquids (e.g., a liquid pool), through drained porous solids and through the boundary layer of the headspace itself is rapid compared to the rate that species migrate through interstitial liquids. Nonpolar organic compounds do not diffuse through aqueous wastes as rapidly as polar species, and their transport may be governed by the rate they are carried to the surface with rising gas bubbles. The inventory of waste in trapped gas bubbles is probably only important for hydrogen, nitrous oxide, and methane. Headspace concentrations for most species are determined by the balance between the rate they are released by the waste and the rate they are removed via the ventilation system. Headspaces are convectively mixed by temperature differences between the waste surface and the tank dome. Vapor condensation in the headspace, either on the dome and walls or as an aerosol, can cause the absorption of soluble species (e.g., ammonia in water condensate) diminishing the concentrations of soluble species both in the headspace and in air released to the atmosphere.

Passive ventilation is thought to be due to barometric pressure fluctuations, a difference between temperature of the ambient air and the headspace (the chimney effect), and the effects of wind on risers, pits, and instruments that are connected to the tank headspace (or to connected tanks). Passive ventilation rates vary significantly from tank to tank and from one time period to another. Higher passive ventilation rates appear to be associated with multiple and larger ventilation pathways. Headspace composition varies with a variety of factors that tend to be tank-specific, and no simple relationship between seasonal changes in the tank conditions and headspace compositions has been identified.

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Acronyms and Abbreviations

BDGRE	buoyant-displacement gas release event
DBBP	dibutyl butylphosphonate
DOE	U.S. Department of Energy
DST	double-shell tank
ED1A	ethylenediaminemonoacetate
ED2A	ethylenediaminediacetate
ED3A	ethylenediaminetriacetate
GRE	gas release event
HB2EHP	bis(2-ethylhexyl)phosphoric acid
He	helium
H_3HEDTA	hydroxyethylethylenediaminetriacetic acid
H_3NTA	nitrilotriacetic acid
H_4EDTA	ethylenediaminetetraacetic acid
H_5DTPA	diethylenetriaminepentaacetic acid
IDA	iminodiacetate ion
NPH	normal paraffinic hydrocarbon
NTA	nitrilotriacetate
PNNL	Pacific Northwest National Laboratory
RGS	retained gas sampler
RSD	relative standard deviations
SF_6	sulfur hexafluoride
SHMS	standard hydrogen monitoring system
SST	single-shell tank
TBP	tributyl phosphate
TNMHC	nonmethane hydrocarbon

1.0 Introduction

Hanford Site processes associated with the chemical separation of plutonium from uranium and other fission products produced a variety of volatile, semivolatile, and nonvolatile organic and inorganic waste chemicals that were sent to high-level waste tanks. These chemicals have undergone and continue to undergo radiolytic and thermal reactions in the tanks to produce a wide variety of degradation reaction products. The origins of the organic wastes, the chemical reactions they undergo, and their reaction products have recently been examined by Stock (2004). Stock gives particular attention to explaining the presence of various types of volatile and semivolatile organic species identified in headspace air samples. This report is intended to complement the Stock report by examining the storage of volatile and semivolatile species in the waste, their transport through any overburden of waste to the tank headspaces, the physical phenomena affecting their concentrations in the headspaces, and their eventual release into the atmosphere above the tanks. A discussion of the atmospheric dispersion and transport of these waste species, once they have been released from the tanks' ventilation systems (their fate subsequent to the scope of this report), is given by Droppo (2004a).

1.1 Background

A considerable amount of work has been done to further the understanding of gases and vapors in the waste tanks and how they are released to the atmosphere. The bulk of the work was conducted to resolve waste storage safety issues in the 1990s.

A great deal of headspace gas and vapor characterization was conducted in the 1990s by a headspace air sampling program designed to provide source-term data to the industrial hygiene worker protection program (Osborne and Huckaby 1994). Samples were collected from a majority of the tanks and analyzed using robust methods that allowed the quantitation of many of the major volatile waste species (hydrogen, nitrous oxide, ammonia, etc.) and the identification of a broad array of trace organic vapors (Huckaby et al. 1995). Over 2,000 headspace samples have been collected and analyzed, and over 1,200 organic vapors have been identified in the waste tank headspaces (Stock and Huckaby 2004).

The potential hazards of flammable waste gases were the subject of the U.S. Department of Energy (DOE) Flammable Gas Safety Program between 1989 and 2001. Numerous theoretical, laboratory, and modeling studies were conducted to specify the chemistry of flammable gas production by the waste (Stock 2001 and references therein) and establish the physics of gas retention within the waste and releases from the waste (Gauglitz et al. 1994, Stewart et al. 1996, Meyer et al. 1997, Johnson et al. 2001 and references therein). Instrumentation was installed on selected tanks to monitor headspace flammable gas concentrations (Schneider 1996, Wilkins et al. 1996), and special core samples were collected to determine the quantity and composition of the retained gases (Schekarriz et al. 1997, Mahoney et al. 1999, 2000). The mixing of hypothetical flammable gas plumes in the tank headspaces was modeled (Antoniak and Recknagle 1997 and references therein), and field studies were conducted to establish the rates that flammable gases were released to the atmosphere via passive ventilation (Huckaby et al. 1997a, 1998).

The DOE Organic Tank Safety Program conducted a similar effort to address potential hazards associated with the chemistry of organic salts and the flammability of organic solvents in the tanks. Waste chemistry studies examined reactions of the organic complexants and the potential for complexant waste to undergo spontaneous combustion (Sandgren 2003 and references therein). Other studies examined organic solvent inventories (Sederburg and Reddick 1994, Huckaby et al. 1996) and the potential for solvent fires on the waste surface (Cowley et al. 1997, Huckaby and Sklarew 1997).

The current understanding of the waste gases and vapors is thus attributable to a very large effort by many scientists and engineers using theoretical and mathematical models, laboratory tests, and waste analyses. This report is primarily a summary of the understanding developed in recent years.

1.2 Report Overview

For the purposes of this report, the waste tanks can be classified by their ventilation systems –28 tanks are currently connected to mechanical exhausters that actively ventilate their headspaces, and 149 tanks rely on filtered ventilation pathways that allow them to passively exchange air with the atmosphere. This classification scheme currently coincides with another scheme; the 28 actively ventilated tanks are the newer, double-shell tank (DST) design, and the 149 passively ventilated tanks are the older, single-shell tank (SST) design. But the number of shells has little to do with the phenomena discussed here, and at any given time the mechanical exhauster of a DST may be inoperable, in which case its headspace dynamics become those of a passively ventilated tank, and activities in an SST may require the use of a portable exhauster, which would have the opposite effect.

Chapters 2 through 6 of this report discuss phenomena that are generally common to both the actively and passively ventilated tanks. Chapter 2 provides a brief summary of the origins of the waste gases and vapors, leaning heavily on the much more detailed discussions given in Stock (2004). Chapter 3 considers the storage of the gases and volatile species in the aqueous waste, in trapped gas bubbles, in the crystalline matrix of solids, and in organic liquid wastes. (Many of the organic species identified in tank headspace samples are essentially insoluble in the aqueous tank wastes, and their presence in the headspace indicates immiscible organic liquids in the waste.) The transport of gases and volatile species from locations within the waste (because they were either stored or formed there) to the headspace is discussed in Chapter 4. Chapters 5 and 6 describe the dynamics of the tank headspaces and their access piping (risers), the convective mixing within the headspace, the condensation of vapors on cool surfaces, and the effects of condensation on headspace and ventilation air composition.

Passive ventilation is examined in Chapter 7. The physical conditions that induce air exchange between the tank headspaces and the atmosphere are discussed, and qualitative evaluations of their relative importance to the observed ventilation rates are given. Measurements indicate that passive ventilation rates vary significantly from tank to tank and from one time period to another (Huckaby et al. 1997a, 1998), and the available data are examined to determine what factors cause these variations.

Headspace compositions are known to vary with time, due to changes in the rates that the volatile species are released from the waste and changes in the ventilation pathways and rates. These effects and the available data are considered in Chapter 8.

2.0 Gas and Vapor Origins

Many gases and volatile organic liquids evolve from the Hanford Site waste tanks. Some of these volatile materials are the unchanged remnants of the original hydrocarbon diluents that were used in plant operations and discharged to the waste tanks as contaminants of process aqueous wastes. A large volume of organic complexants entered the tanks from the cesium-strontium recovery program in B-Plant in the 1960s and 70s. Others are formed in the aqueous phases of tank wastes through chemical processes that begin with the direct radiolysis of water and nitrate and nitrite ions and lead eventually to the oxidation of the organic compounds in the tanks. Other waste components, such as nitrite, hydroxide, and aluminate ions act as catalysts for the nonradiolytic oxidation of the organic compounds. This chapter discusses the origins of waste gases and vapors; a more detailed discussion has been given by Stock (2004).

2.1 Background

Historical studies established that eleven different complexants, two phosphate esters, and four types of commercial organic diluents were used in large scale plant operations and supporting operations at the Hanford Site (Kupfer et al. 1999). According to the Best Basis Inventory (Tank Characterization Database via DOE’s Tank Waste Information Network System), about 1,280 metric tons of organic carbon is estimated to remain in the tanks. The principal reaction pathway has been, and is, oxidation initiated by radioactive decay processes and by other chemical reactions that involve free radicals and ionic reagents. As a result of this oxidation, the most abundant single organic compound in the tanks is oxalate ion, an end product of oxidation.

Many reactions of interest are radiolytically initiated in the liquid phase along the tracks of beta and gamma particles. The radiolysis of water in strong alkaline solutions of sodium nitrite and nitrate produces hydrogen atoms, hydroxyl radicals, and solvated electrons. Subsequent reactions rapidly progress to produce nitric oxide and nitrogen dioxide, which are among the chief oxidants of the organic solutes. Hydrogen is produced by the radiolysis of water and by hydroxide ion-catalyzed oxidation reactions of the aldehydes that are intermediates in many of the reaction sequences of the organic compounds. Nitrogen and nitrous oxide are formed from nitrate and nitrite ion during the oxidation of organic compounds. Ammonia is formed from the complexants and also as a byproduct of the oxidation reactions.

Chemical degradation and evaporation of process wastes have resulted in a vast array of volatile and semivolatile organic compounds in the tanks. More than 1,200 different organic compounds have been identified in the tank headspaces (Stock and Huckaby 2004). These identified compounds include alkanes; alkenes, alkadienes, and alkynes; cyclic alkanes and alkenes; benzene derivatives; alcohols and ethers; aldehydes and ketones; acids and esters; amines and amides; other nitrogen derivates such as nitroso and nitro compounds; heterocyclic compounds; and halogen-containing compounds.

A species does not have to be stable in the waste to be found in the tank headspace. Many vapor and gas species are continuously formed and destroyed in the waste. If they are volatile, they can escape to the headspace during their short lifespan. Examples include, but are not limited to, nitric oxide, nitrogen dioxide, methanol, ethanol, methylamine, ethylamine, formaldehyde, and acetaldehyde.

2.2 Organic Complexant Derivatives

The original acidic complexants in Hanford processes were ethylenediaminetetraacetic acid (H_4EDTA), hydroxyethylethylenediaminetriacetic acid (H_3HEDTA), diethylenetriaminepentaacetic acid (H_5DTPA), nitrilotriacetic acid (H_3NTA), and acetic, glycolic, tartaric, oxalic, gluconic, and citric acids. The waste streams were treated with sodium hydroxide to convert the acids into salts for storage in the waste tanks. These substances have formed many related anions including ethylenediaminetriacetate (ED3A), ethylenediaminediacetate (ED2A), and ethylenediaminemonoacetate (ED1A), as well as nitrilotriacetate (NTA), iminodiacetate ion (IDA), and glycinate, acetate, formate, and oxalate ions. Many other compounds with one or two carbons, including methane, methanol and ethanol, methylamine and ethylamine are among their organic breakdown products.

2.3 Organic Extractants, Diluents, and Their Derivatives

Tributyl phosphate (TBP) and bis(2-ethylhexyl)phosphoric acid (HB2EHP) were used in Hanford Site processes. Some commercial grades of TBP contained dibutylphosphate and tetrabutylpyrophosphate ions as well as dibutyl butylphosphonate (DBBP), butanol, and butanal. Of these, the latter three species are still found in tank waste. Under the alkaline conditions in the tanks, these phosphate esters undergo hydrolysis, oxidation, and fragmentation. The hydrolysis of TBP gives dibutylphosphate and monobutylphosphate ion and butanol. The oxidation and fragmentation reactions lead to methane, ethane, propane, butane, ethene, propene, the butenes, cyclopropane, butadiene, ethyne, propyne, the butynes, methanol, ethanol, 1-propanol and 2-propanol, butanal, acetone, and 2-butanone and cyclic ethers (e.g., tetrahydrofuran) and lactones (e.g., dihydro-2(3H)-furanone) (Stock 2004). Similar families of products are obtained from bis(2-ethylhexyl)phosphate ion.

The organic diluents used included both branched and unbranched paraffins, cyclic aliphatic hydrocarbons, and a small fraction of aromatic hydrocarbons. Many semivolatile alkanes and cycloalkanes currently found in Hanford wastes are recognized as constituents of the hydrocarbon diluents; for example, n-undecane, n-dodecane, n-tridecane, and n-tetradecane with many different methyl derivatives such as 2-, 3-, 4-, 5- and 6-methyldodecane, as well as alkylated cyclopentanes, cyclohexanes, and decalins. The radiolysis of paraffinic hydrocarbons under the oxidizing conditions that prevail in the waste tanks also yields fragmented and oxidized molecules including quite complete homologous series of alkanes and alkenes and oxidized molecules including alcohols, aldehydes and ketones, and nitriles. Hydroperoxides, amines and amides, nitrate and nitrite esters, and nitro and nitroso compounds are formed simultaneously.

2.4 Other Gases and Vapors

Few of the observed species containing halogen, silicon, or sulfur atoms can arise from the compounds that were used in plant operations, but may have come from substances that were used in supporting operations. These include bromine- and chlorine-containing compounds (produced from halocarbon solvents) and even a trifluoro ketone (traced to a trifluoro derivative that was used in supporting operations). The analytical information shows that chlorobiphenyls were discharged to some tanks. However, the origins of the Freons that have occasionally been observed in headspaces have not been definitely established. These substances may derive from refrigerants used near the tanks. The principal silicon-containing compounds, the bis(trimethylsilyl) derivative of 2-hydroxybenzoic acid and cyclic hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane, may originate from silicone fluids that were also used in Hanford Site operations. The origin of N-butylbenzenesulfonamide, the most frequently observed sulfur-containing compound, is uncertain. It apparently arises from a benzenesulfonate resin acid used during operations.

Metallic mercury is in dynamic equilibrium with mercuric and mercurous ions under the waste storage conditions. Investigations at the Savannah River Site have shown soluble mercuric hydroxide is converted into mercury and dimethylmercury. Although unreported, diethylmercury and methylethylmercury are plausible byproducts of this chemistry.

3.0 Waste Gas and Vapor Storage

Waste gases and vapor species exist within the waste dissolved in waste liquids, in trapped gas bubbles, and even in the solid crystalline lattice. This chapter discusses the storage of gases and vapors in terms of their chemical properties and the physical conditions of the waste.

3.1 Storage in Trapped Gas

Some of the gases generated by waste liquids may eventually exceed their saturation concentration and form gas bubbles. Subsequently, generated gases and unsaturated gas species diffuse to existing bubbles and cause them to expand. If the bubbles form in a convective region (e.g., supernatant liquid) they will rise to the surface and release the gases to the headspace when the bubbles pop. If the bubbles form in interstitial liquid in a nonconvective (settled solids) region of the waste, they are constrained by the strength of the surrounding material and may be retained for an indefinite period within the solid matrix. The following sections discuss the mechanisms by which gases are trapped and the composition of the trapped gases.

3.1.1 Gas Retention Mechanisms

Three principal mechanisms have been identified for gas retention: direct attachment of small bubbles to solid particles, trapping of bubbles by liquid capillary forces in the solid matrix, and the trapping of bubbles due to the yield strength of the surrounding waste. In tanks where solids are actively mixed with liquid by pumping, as in tank SY-101 between 1993 and 2000, a substantial amount of the gas inventory may have been retained by the direct-attachment mechanism (Johnson et al. 2000). However, given very limited mixing in many tanks, most significant gas inventories are associated with retention in settled solids, where the two retaining forces are lithostatic load (the weight of the particles above the bubbles) and waste strength (Johnson et al. 2001).

When the lithostatic load is sufficient to hold particles in contact against the force of the bubble's internal pressure trying to push them apart, bubbles are held within the interstitial spaces or pores between particles. This retention mechanism requires either relatively large pores, which reduces the internal bubble pressure(a), or a deep waste column, which increases the lithostatic load, or both. These pore-filling bubbles assume an irregular, dendritic shape conforming to the passages between the particles.

At sufficiently high gas fractions, the bubbles in the pores merge to some extent. The maximum vertical extent of merged bubbles is determined by the balance between capillary forces, which depend on the bubble (i.e., pore) diameter, and the hydrostatic pressure difference between the top and bottom of the bubble. The smaller the pore diameter, the greater the allowable vertical extent. When this vertical extent is exceeded, gas moves upward from the top of the bubble, and liquid flows in under the bottom. Displacement of liquid from the pores that the pore-filling bubble enters, and the flow of liquid into the pores that the bubble vacates, is a very slow process.

(a) Surface tension effects cause very small bubbles to have relatively high internal pressures, which in turn cause a greater resistance to deformation.

If the internal pressure of a bubble is great enough to overcome the lithostatic load, because the bubble is small or the load is light, it pushes the surrounding particles apart. The bubble is then restrained by the yield strength of the bulk waste as a particle-displacing bubble. Bubbles that are relatively small, or located in weak waste, take an approximately spherical or ellipsoidal shape. If the bubble is large enough or the waste strength low enough, the bubble grows into the weakest area of the waste around it and assumes a dendritic shape, usually horizontal or nearly so. For a particle-displacing bubble to rise, the waste near its top and sides must be liquefied or mobilized by the buoyant force imposed by the bubble, flow out of the way, and flow down into the space vacated by the bubble. This process is faster than the liquid displacement required for pore-filling bubbles, since the fluid is not constrained to flow through small pores.

The stronger the waste is, the larger a particle-displacing bubble must be before it rises. When the waste yield strength exceeds a few hundred Pascal, particle-displacing bubbles become flattened in shape and, for high enough gas fraction, form a connected network that allows the gas to escape continuously and prevents further retention (Gauglitz et al. 1996).

Gas bubbles are present not only in waste beneath the interstitial liquid level but also in waste above the interstitial liquid level that has been partially drained by saltwell pumping. Data from a number of tanks indicate the undrained liquid that remains above the post-pumping interstitial liquid level is effective at retaining gas.(a) This undrained liquid is presumed to be present mostly in regions of fine-particle, poorly draining saltcake, which may be pertinent to the waste's ability to retain gas.

3.1.2 Trapped Gas Volume Fraction

The Retained Gas Sampler (RGS) Program collected and analyzed samples of the retained gases in 14 tanks (Shekarriz et al. 1997, Mahoney et al. 1999, Mahoney 2000). The retained gas constitutes a small fraction of the convective layers ranging from about 0.2% by volume in tank SX-106 to less than 3% by volume in the mechanically mixed bubbly slurry that existed in tank SY-101 before the waste was transferred and diluted in 2000. In contrast, retained gas generally represents a larger fraction of the nonconvective layers ranging from about 4% by volume for the nonconvective layer in tank AW-101 to approximately 26% in the sediment of tanks SX-106 and S-102. However, at typical generation rates it takes many years to accumulate any significant gas volume in the waste sediment. Gas is not retained in unmixed convective layers except in transit.

3.1.3 Trapped Gas Composition

The retained gas samples were found to be predominately nitrogen, hydrogen, nitrous oxide, and ammonia (Mahoney et al. 1999). Most also contained more than 0.1% nitric oxide and nitrogen dioxide, between 0.3 and 2.5% methane, and between 0.2 and 2.7% other hydrocarbons. Because the hydrocarbons with two carbon atoms are often overlooked in conventional analyses of the headspaces, the RGS work provides evidence for the widespread occurrence of ethane, ethene, and ethyne.

(a) Huckaby JL, LA Mahoney, and ER Siciliano. 2001. *Waste Gas Releases Associated with Recent Saltwell Pumping of Single-Shell Tanks.* Letter report TWS01.36, Pacific Northwest National Laboratory, Richland, Washington.

The trapped gas bubbles are essentially in equilibrium with the fluid surrounding them and contain trace levels of whatever volatile organic compounds are present in the surrounding liquid. Analyses of RGS samples did not generally extend to organic compounds with more than two carbon atoms because they were conducted using mass spectroscopy without any chromatographic separation of species. However, one RGS sample collected from the region beneath the crust in tank SY-101 (before the waste was transferred in 1999) was analyzed using a gas chromatograph-mass spectrometer system for organic vapors (Evans et al. 1999). Although the waste in SY-101 was unique in its combination of high density, high concentrations of water-soluble complexants, and relatively high heat load, the findings from this work shed light on the behavior of organic vapors in other tanks.

Evans et al. (1999) found the SY-101 RGS samples contained the common semivolatile hydrocarbon process diluents together with their degradation products – smaller alkanes, alkenes, cycloalkanes, ketones, aldehydes, nitriles, and other compounds. The majority of species identified by Evans et al. (1999) are commonly found in the tank headspaces, although some, notably methylamine, ethylamine, and dimethylamine have not been reported in any tank headspace sample (Stock and Huckaby 2004).

Concentrations of organic vapors present in SY-101 RGS samples, and the volumes of retained gas present in the tanks, suggest that little of the water-soluble organic compounds inventory actually exists in the trapped gas. Table 3.1 lists the 10 most abundant organic species in the SY-101 RGS samples along

Table 3.1. Tank SY-101 Volatile Organic Compound Inventory Estimates

Analyte	Measured Conc. in Trapped Gas near Surface [(a)] (ppmv)	Estimated Conc. in Trapped Gas in Mixed Slurry Layer[(b)] (ppmv)	Trapped Gas Phase Inventory[(c)] (kg)	Conc. in Liquid near Surface[(d)] (g/L)	Conc. in Liquid in Mixed Slurry Layer [(e)] (g/L)	Liquid Phase Inventory[(f)] (kg)
Ethanol	265	1,988	1.7	1.9E-01	1.4E+00	631
Methanol	259	1,943	1.1	2.0E-01	1.5E+00	676
Propene	249	1,868	1.4	2.1E-05	1.6E-04	0.07
Methylamine	206	1,545	0.9	4.5E-02	3.4E-01	153
Propane	152	1,140	0.9	1.3E-05	1.0E-04	0.05
2-Butene, (E)-	151	1,133	1.2	1.7E-05	1.3E-04	0.06
1,3-Butadiene	109	818	0.8	1.2E-05	8.8E-05	0.04
n-Butane	103	773	0.8	1.2E-05	8.9E-05	0.04
1-Butanol	73	548	0.7	4.7E-02	3.5E-01	158
Cyclopropane	49	368	0.3	4.1E-06	3.1E-05	0.01

(a) Evans et al. (1999).
(b) Mahoney et al. (1999).
(c) Calculated by multiplying concentrations in the second and third columns by retained gas inventories given in Appendix B of Mahoney et al. (1999).
(d) Values from Appendix F of Cowley et al. (2003) adjusted for 7.5-fold difference between bubbly and mixed slurry layer gas concentrations.
(e) From Appendix F of Cowley et al. (2003).
(f) Calculated by multiplying concentrations in the fifth and sixth columns by the estimated liquid inventories of 60,900 L and 2,925,000 L for the layer just below the surface and mixed slurry layers, respectively. These liquid inventories are based on an estimated 7% solids fraction, and the measured gas fractions and liquid volumes given in Mahoney et al. (1999).

with their measured concentrations in the mixed slurry layer, their estimated concentrations in the layer directly under the floating crust (Mahoney et al. 1999), their trapped gas-phase inventories using retained gas volumes from Mahoney et al. (1999), their estimated concentrations in the two regions (Cowley et al. 2003), and their estimated liquid phase inventories. Note that the organic vapor concentrations in the mixed slurry layer directly under the crust were extrapolated by Mahoney et al. (1999) from the measured values in the layer directly under the crust, and inventories given assume all liquids in the tank are at equilibrium with the bubbles. Table 3.1 illustrates that the trapped gas phase inventories of the water-soluble compounds (i.e., ethanol, methanol, methylamine, and 1-butanol) are much smaller than the corresponding liquid phase inventories. Although the nonwater-soluble species are favorably partitioned into the trapped gas phase, their inventories are still very small. As noted above, it is not possible to estimate the organic liquid inventories in tank SY-101 from the measurement of organic vapor concentrations.

3.2 Storage in Aqueous Solution

Much of the waste gases and vapors are dissolved in the aqueous liquid wastes. The amount of any given species dissolved in the aqueous liquids depends heavily on its solubility. Ammonia is very soluble; more than 97% of it is stored in the liquid phase in the tanks sampled by RGS (Mahoney et al. 1999). At the other end of the solubility range, more than 99% of hydrogen and nitrogen is stored in the gas phase. The solubility of a gas or vapor in a liquid is governed by Henry's Law, one form of which is

$$p_i = K_{Hi} c_i \, . \tag{3.1}$$

Here p_i is the partial pressure of the gas above a solution of it, K_{Hi} is the Henry's Law proportionality constant (solubility, in effect), and c_i is the dissolved gas concentration. If the sum of the equilibrium partial pressures of all the dissolved gases and vapors in waste liquid is at least equal to the local hydrostatic pressure, a separate gas phase (a bubble) can be formed.

The chemical thermodynamic model ESP[(a)] (version 6.7) was used to model the solubility of ammonia, nitrous oxide, hydrogen, acetone, 1-butanol, TBP, and n-dodecane in an aqueous solution of sodium nitrate and sodium hydroxide that was about 7 M in sodium and had a pH of 12.4 at 25°C. These gases and organic vapors are found in many Hanford waste tanks. Table 3.2 shows the calculated solubilities and Henry's Law constants. For gases, a high Henry's Law coefficient (as for hydrogen) indicates a high preference for the gaseous state and low solubility. For organic vapors, the Henry's Law constant is affected both by the solubility of the vapor and the volatility of the vapor. The concentrations are expressed in terms of grams of water in the salt solution.

The far right column of Table 3.2 shows the calculated dissolved inventories of each gas and vapor that would be expected in 100 kgal of the aqueous solution at equilibrium under the prescribed conditions. For the inorganic species (H_2, N_2O, and NH_3) the inventories given in this column are for typical observed trapped gas partial pressures of 0.75 atm H_2, 0.6 atm N_2O, and 0.01 atm NH_3 and represent rough

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(a) ESP was developed by OLI Systems, Inc., Morris Plains, New Jersey.

Table 3.2. ESP-Predicted Solubilities and Henry's Law Coefficients for Some Species

Solute	K_{Hi} (atm/(g solute/g H_2O))	Solubility (g solute/g H_2O in solution)	kg Solute/100 kgal of 7M Na solution
Hydrogen	1.2×10^6	$6.2 \times 10^{-7(b)}$	0.16
Nitrous Oxide	1.8×10^3	$3.3 \times 10^{-4(b)}$	85
Ammonia	1.8×10^0	$0.011^{(b)}$	2,800
Acetone	6.0×10^{-1}	$0.45^{(c)}$	88,000
1-Butanol	1.2×10^{-1}	$0.093^{(c)}$	24,000
Tributyl Phosphate	9.8×10^{-5}	$0.0031^{(c)}$	830
n-Dodecane	6.6×10^4	$2.7 \times 10^{-9\ (c)}$	0.00073

(a) Properties were predicted for an aqueous solution of sodium nitrate and sodium hydroxide that was about 7 M in sodium and had a pH of 12.4 at 25°C.
(b) The solubilities of the gases are based on the dissolved gas being in equilibrium with typical partial pressures of gas in retained bubbles: 0.75 atm H_2, 0.6 atm N_2O, and 0.01 atm NH_3.
(c) The solubilities of the organic vapors are based on the dissolved vapors being in equilibrium with the pure organic liquid.

estimates of the inventories of these species per 100 kgal of liquid in a typical saltcake tank. The organic vapor inventories (acetone, 1-butanol, tributyl phosphate, and n-dodecane) given in the far right column are estimates of the inventories of these species if the aqueous solution were in equilibrium with the pure organic liquid; consequently, these are not meaningful estimates of any existing inventories but are included here to provide maximums for qualitative comparison.

In general, the aqueous waste liquids are very polar (water molecules are polar) and the solubility of polar solutes (e.g., ammonia, methanol) will be greater than nonpolar solutes (e.g., alkanes). Another general rule is that the presence of dissolved salts reduces the solubility of other solutes, including gases and vapors, below their solubilities in pure water. Thus, the solubility of these species is lower in saltcake tanks, which have aqueous waste with high salt contents, than in sludge tanks, which have lower salt contents.

It is important to note that while headspace gas and vapor concentrations indicate the presence of the species in the condensed phase, and given that ventilation rates can even be used to estimate the surface area from which the species evaporate (Huckaby and Sklarew 1997), they cannot be used to estimate inventories.

3.3 Storage in Organic Liquid Solution

Organic liquid wastes from the various Hanford separations processes are known to exist in significant quantities in several tanks. Waste samples from tanks BY-108, BY-110, C-102, C-103, C-104, and C-203, for example, have been found to contain TBP and the semivolatile normal paraffinic hydrocarbon (NPH) diluents as a separated organic liquid phase (Tank Characterization Database via DOE's Tank Waste Information Network System). In general, the organic liquid wastes are solutions of nonpolar species that tend to store nonpolar species better than the aqueous wastes.

The presence of the semivolatile NPH vapors in many tanks also indicates at least trace quantities of organic liquids are also common in the tank farms. The organic vapor inventories given in the last column of Table 3.2 suggest that while relatively large amounts of acetone, 1-butanol, and even tributyl phosphate can be dissolved in the aqueous wastes, only a very small amount of n-dodecane could be present in the aqueous wastes. Given the inventory of n-dodecane dissolved in the aqueous waste of any tank is no more than a few grams, the observation of n-dodecane in the headspace of a tank at concentrations of more than a few ppbv implies a separate organic liquid phase is present in the tank from which the n-dodecane is evolving.(a)

Consider as a specific example tank C-107, which was found to have an n-dodecane concentration in its headspace of about 0.22 mg/m^3 at 25 °C (32 ppbv) (Pool et al. 1995). The passive ventilation rate of this tank was measured in 1997 to be 1.9 m^3/h, which is one of the lowest measured passive ventilation rates (Huckaby et al. 1997a). Assuming the air vented from tank C-107 also contains 0.22 mg/m^3, the estimated yearly emissions of n-dodecane would be (0.22 mg/m^3)x(1.9 m^3/h)x(8,766 h/year)x(0.001 g/mg) = 3.7 g/year. Given a total waste inventory of about 248 kgal, a bounding estimate of the dissolved n-dodecane is (248 kgal)x(0.00073 kg/100 kgal)x(1,000 g/kg) = 1.8 g. Because the estimated yearly emissions of n-dodecane are about twice the estimated possible inventory dissolved in the aqueous phase, it can be concluded that either tank C-107 has an additional (organic liquid phase) inventory of n-dodecane or the n-dodecane in the tank C-107 headspace came from the headspace of a connected tank.

Nonpolar organic compounds may also be subject to a phase separation similar to that observed when the concentration of a gas exceeds its solubility. Nonpolar organic species that have exceeded their solubility in the aqueous phase (e.g., due to their generation or a change in solubility due to waste cooling, evaporation, etc.) will form a separate organic liquid phase. This may take the form of a continuous layer, a coating on solids, or droplets attached to solids. Similar to the nucleation and expansion of gas bubbles, once one species exceeds its solubility and produces a separate organic phase, all the other organics will partition themselves between the organic and aqueous phases according to their relative solubilities in the two solvents. Thus, an excess over-solubility of one species causes the aqueous concentrations of all the organic species to decrease to some extent, even though none of them has exceeded its respective solubilities.

3.4 Storage in Solids

In addition to the storage of gases in vapors, in trapped bubbles, and in solution, there is the potential to store gases and volatile species in the crystalline lattice of waste solids. Not to be confused with gas bubbles trapped by interstitial liquid in a porous solid matrix, the possibility exits that radiolysis of the waters of hydration or other constituents present in the crystalline structure of certain solids could produce hydrogen or other volatile species that remain trapped in the solid phase. While this must occur to some small extent, and could potentially be a significant issue under very special circumstances, evidence suggests it is probably negligible when compared to other means of storing gases and vapors (see related work by Johnson 1956, Tandon 2000, and discussions in Spinks and Woods 1990).

(a) A notable exception to this statement occurs when the vapor in question was introduced to the headspace via ventilation pathways to/from another tank headspace.

4.0 Transfer of Gases and Vapors to the Headspace

Gases and volatile species formed or stored below the waste surface must be transported through any overlaying waste before they are released into the headspace. This chapter discusses the various modes of mass transfer through the waste and the relative importance of each mode for different types of gases and vapors.

4.1 Overview of Mass Transfer Routes

The rates at which gases and vapors are transferred to tank headspaces clearly depend on where they originate and the configuration of waste between their origin and the headspace. An overview of the mass transfer of gases and vapors from the waste to the headspace is depicted in Figure 4.1. In this figure, gases and vapors dissolved in the interstitial liquid at Point A are transferred to the headspace via diffusion, convection, and bubble migration.

Diffusion through the interstitial liquid may transport the dissolved gases and vapors from Point A directly to an interface with the headspace, as marked by Point B in Figure 4.1, from which they may be released into the headspace. If there is an overlaying bed of drained waste, as above Point C in Figure 4.1, the gas and vapors must also transfer via diffusion and/or convection through the open air-filled pores of the drained waste to reach the headspace. If a liquid surface is present, as depicted above Point D, the gases and vapors may be carried by diffusion and convection to the surface of the liquid and eventually may be released into the headspace by evaporation or off-gasing.

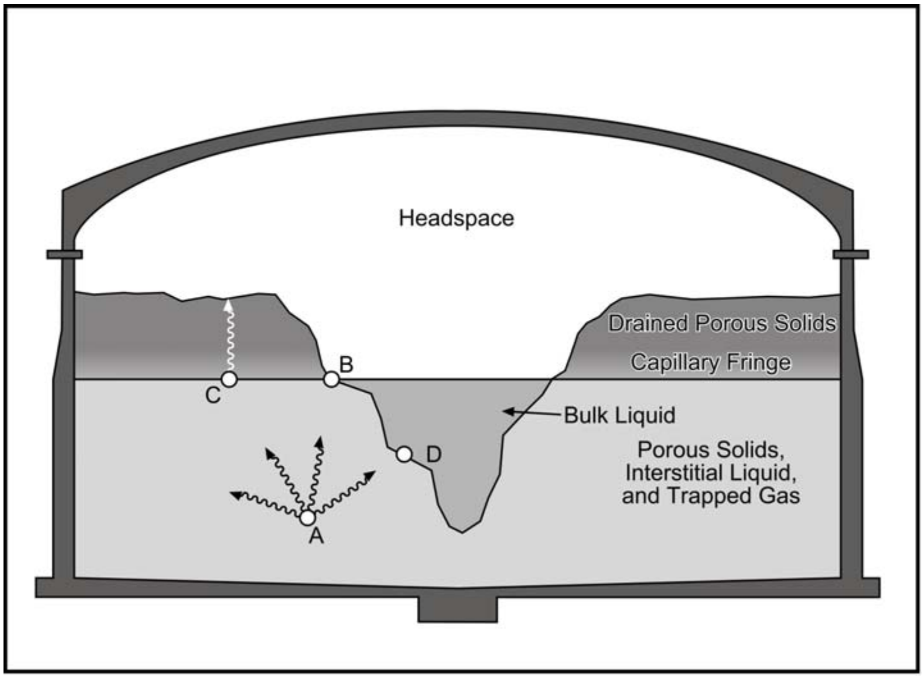

Figure 4.1. Schematic of Tank Waste and Possible Mass Transfer Paths

Rising bubbles of waste gases represent an alternative mode of mass transfer through the solid waste. Bubbles formed within the waste migrate upward carrying the gases and vapors they contain to the surface. Although the mechanisms controlling this bubble migration are poorly understood, it is observed that the release of gas bubbles increases during periods of low atmospheric pressure (McCain 2001, Hedengren et al. 2001), which causes the gas retained in the waste solids to expand and migrate.

4.2 Transport via Interstitial Liquid

In layers of settled solids, which are present in all SSTs and most DSTs, dissolved gases and vapors diffuse through the interstitial liquid from lower regions in the layer to the upper surface of the layer. Compared to other mass transfer mechanisms discussed here, liquid-phase diffusion is relatively slow and made even slower by the presence of a solid matrix. The solid matrix diminishes the cross-sectional area available for diffusive transport, and because the diffusing molecules must circumnavigate the solid particles and blocked pores, it effectively increases the distance that the diffusing molecules must travel. The rate at which the species diffuses though the liquid-filled solid matrix thus depends on the pore structure of the solid.

The rate of diffusion also depends on the diffusivity of the species in the interstitial liquid and its concentration gradient at any point.(a) Diffusivity depends on the temperature and chemical properties of both the diffusing species and the fluid through which it is diffusing. In general, diffusivity tends to increase with increasing temperature and decrease with increasing molecular weight of the diffusing species. Concentration gradients are essentially the “driver” for diffusion just as temperature gradients drive heat transfer, and higher concentration gradients result in proportionally higher mass transfer rates. Concentration gradients in the waste are inherently limited for many species of interest by the solubility of the species in the aqueous interstitial liquid.

The rate of diffusion also depends on the volume fraction of gas that is retained in the waste. Diffusivities are four orders of magnitude greater in gas phase than in liquid phase, so gas bubbles can provide “short circuits” through which a species can pass more rapidly than it would through an equivalent length of liquid.

Species that are relatively insoluble in the interstitial liquid, having correspondingly small concentration gradients, are generally transferred at lower rates than species that are more soluble. This has the following two important implications:

- Gases and vapors that are less soluble in the interstitial liquid are preferentially retained within the waste. This may result in the accumulation of the less soluble species within the waste, and an increase in the likelihood of reactions involving the less soluble species (and the products of those reactions).

(a) The diffusion of a substance due to temperature gradients, thermophoresis, is assumed to be negligible in this discussion.

- Headspace composition measurements made in a quiescent tank may not be a good representation of emissions during a waste-disturbing activity. This was observed in 1999 when sluicing disturbed the waste in tank C-106 and resulted in the unexpected release of many nonpolar (lower solubility) vapor species (Stauffer and Stock 1999).

Species dissolved in the interstitial liquid may also be transported by thermally driven convection of the interstitial liquid itself. Convection has been hypothesized to occur when hot regions of the waste induce the dissolution of salts, which raises the density of the interstitial liquid. The denser liquid migrates downward displacing other liquids to cooler regions. As the displaced liquid circulates to cooler regions, some of the dissolved salts precipitate, decreasing its density. This results in a continuous circulation of interstitial liquid between the warmer and cooler regions of the waste, with dissolution of waste in warmer regions and precipitation of salts in the cooler regions. The convection must diminish with time as the precipitation of salts in cooler regions plugs the pores and as the waste cools. This phenomenon was examined in detail by Meyer and Kuhn (2002). It is not addressed further here because the wastes in most tanks have cooled to a point at which convection of interstitial liquid is negligible.

Because interstitial liquid phase transport is characteristically slow, it generally represents the rate-limiting process in the transfer of gases and vapors from within the waste. Months would be required for a concentration change near the bottom of a 1-m-thick layer of settled solids to have a substantial effect on the release rate from the top of the layer, if the only way the constituent could travel was by diffusion through liquid-filled pores.

4.3 Transport via Air in Porous Solids

The drainable liquids in SSTs have been removed to reduce the possibility and potential impact of a tank leak. The drainage of interstitial liquid, accomplished using the saltwell pumping process,[a] has not removed all of the liquid from the waste and generally several feet of interstitial liquid remain at the bottom of the tanks. A significant fraction of the interstitial liquid above that level has not drained.

However, drainage has opened air-filled pathways down to the top of the capillary fringe (see Figure 4.1), and diffusion of gases and vapors is more rapid in the gas phase than in the liquid phase. A concentration change in the gas near the bottom of a drained 1-m-thick porous layer would take a day or less to reach the top by diffusion through the air-filled pores. This is clearly a much higher transport rate than for diffusion through stationary liquid, making air-filled pores a significant transport pathway. The speed of diffusive transport was shown by computational modeling of drainage and vapor releases during salt-well pumping, discussed by Peurrung et al. (1996).

Diffusion is not the only mechanism for gas-phase transport in pores. Air may also be circulated in the drained porous region of waste by convection in tanks where there are significant radial thermal gradients (e.g., the waste is warmer in the center of the tank and cooler at the tank walls). In general, convection would increase the mass transfer of gases and vapors through the drained waste region,

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(a) The saltwell pumping process involves installing a well casing and pump into the waste to allow collection and pumping of liquids that drain into the well casing. All SSTs have had their drainable liquids removed, so no saltwell pumping is currently being conducted and none is planned.

compared to diffusion. The effects of convection could outweigh those of diffusion in wastes with higher temperatures. However, whether the main mechanism is diffusion or thermal convection, it is clear that transport through the connected gas-filled pores in drained waste is not rate-limiting in gas and vapor releases.

Both the diffusion and convection rates depend on the completeness with which the waste was drained. Any residual liquid in the drained upper region of waste reduces the pore space available for transport and so decreases the gas-phase transfer rate. The residual liquid also provides a potentially large, temporary source of releases of soluble gases and vapors, as well as a short-term sink for moderately soluble gases and vapors rising from lower in the waste.

The first of these effects has been observed to control ammonia releases in a number of saltwell-pumped tanks.(a) The residual liquid was spread though the drained region and provided a large wetted surface area in contact with gas-filled pore space. Ammonia dissolved in the residual liquid was released at a much higher rate than in the pre-drained tank because of the increased liquid surface area in the drained region. The same behavior could be expected for other water-soluble species – those present predominantly in dissolved form, not in gas bubbles.

The residual liquid in the drained region can serve either as a source or a sink for species that are moderately dissolved–those present in dissolved and bubble form in very roughly equal amounts. A recently drained region begins by releasing some fraction of the species that was present in the bubbles in the region; concurrently and afterwards, the dissolved fraction of the species is released through the wetted area. This latter release leaves behind liquid that is depleted by comparison to the liquid that lies below it in regions as yet undrained. Once this happens, any gas releases that originate below the drained region and pass through it are preferentially stripped of soluble species as the gas comes into contact with the depleted liquid.

This stripping behavior was seen during tank S-106 saltwell pumping.(a) Figure 4.2 depicts the headspace hydrogen-to-nitrous oxide ratio for about 10 months after the start of saltwell pumping and the ratio measured in retained gas samples from this same tank (Mahoney et al. 1999). During the first three months of pumping, gas releases caused the hydrogen-to-nitrous oxide ratio to be much higher than had been measured in the retained gas sample. This initially high ratio was apparently due to the absorption of nitrous oxide, a moderately soluble gas, from the gas releases by interstitial liquid near the waste surface and liquid in the wetted recently drained solids region. Because the hydrogen in these gas releases was much less soluble, it was not appreciably absorbed, and a much higher fraction of hydrogen reached the headspace.

After about three months of pumping, the liquid near the waste surface had apparently become saturated with nitrous oxide, the rate of gas releases had slowed, and the headspace ratio dropped to roughly the same as had been reported from the retained gas samples. With continued pumping and the decline of the overall trapped gas release rate, the headspace hydrogen-to-nitrous oxide ratio became

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(a) Huckaby JL, LA Mahoney, and ER Siciliano. 2001. *Waste Gas Releases Associated with Recent Saltwell Pumping of Single-Shell Tanks.* Letter report TWS01 36, Pacific Northwest National Laboratory, Richland, Washington.

dominated by the off-gasing of nitrous oxide from the liquid near the surface, and the headspace ratio dropped to well below that reported for retained gas samples.

These releases had passed through liquid that had been part of the supernate pool and remained as residual liquid in the topmost waste. The supernate, having been in contact with the headspace air, was depleted of nitrous oxide, which is moderately soluble. By comparison, hydrogen is only sparingly soluble and almost entirely present in the gas phase. As a result of the liquid being depleted in N_2O and the differing solubilities of N_2O and H_2, gas releases from the lower waste were stripped of nitrous oxide as they contacted the residual liquid in the drained waste. Eventually, this liquid became resaturated with N_2O, and the large wetted area caused increased release rates of the same type as for ammonia (though not the same magnitude). At this point, the higher nitrous oxide releases drove the H_2/N_2O ratio below that measured in retained gas samples, a situation that lasted for more than a year and a half.

In general, the presence of residual liquid in waste that has been drained enough to have open, connected gas-filled pores implies that 1) relatively rapid release of volatile species is possible, and 2) the composition of released gases and vapors may vary over time, depending on the relative solubilities of the released species.

4.4 Transport via Supernatant Liquid

In some DSTs the entire waste inventory is believed to be liquid; in the majority of DSTs much of the liquid inventory is found as supernatant overlying a bed of settled solids. Both gases and vapors are generated in this liquid and dissolved in it. Waste liquids also generate heat through radioactive decay. Because very small temperature gradients are needed to support natural convection, it is very likely that all of the bulk liquid layers in Hanford tanks are convectively mixed. There is no measurable difference in temperature from the top to the bottom of liquid layers for which measurements are available, indicating that thorough mixing is occurring.

Convection swiftly transfers dissolved species from the bottom of the layer to the top. As discussed by Palmer et al. (1996), the time required for liquid to move from bottom to top is on the order of a minute. Thus, transport within the supernatant layer is much more rapid than transport within the settled solids layer. Once dissolved substances from the solids layer have reached the top of the solids, their subsequent transport to the top of the liquid is instantaneous.

Bubbles released from the solids layer also reach the top of the supernatant layer quickly. X-rays of core samples taken from a number of SSTs and DSTs (Mahoney et al. 1999) showed in situ bubbles, most of which were 3 mm or less in diameter, although some larger bubbles, as well as gaps and caverns, were also present. Even a very small bubble of 0.5-mm diameter would rise through 1 m of stationary supernatant in about 2 minutes. Because bubbles travel with the convective liquid, they transport gas-phase substances even more rapidly than the dissolved-substance transport provided by convection. Bubbles also collect volatile species from the liquid as they rise and release them when they pop at the liquid surface.

The supernatant produces its own gases and vapors beyond those transported to it from the solids layer. In addition, the inventory of species in the layer is often continuously depleted by losses to the headspace. Thus, the composition of gas releases may be modified from the in situ composition of retained gas by passing through the supernatant layer. For example, most of the measured in situ hydrogen-to-nitrous oxide ratios differed to some extent from those in headspace gas in the same tanks (Mahoney et al. 1999, Stock 2001). This may have been due in part to contributions from the headspaces of other tanks in the cascades (see Section 5.3.1), but was probably also caused by contact with the supernatant layers.

4.5 Off-Gasing and Evaporation from the Waste Surface

The waste surfaces in Hanford tanks fall into four categories: open liquid surface, wet solids matrix with liquid in the pores all the way to the top, a floating crust that contains some liquid but does not have a continuous liquid path from bottom to top of the crust, and (in saltwell-pumped SSTs) a thick layer of drained or even dry waste overlying wet solids.

In the absence of a crust, the volatile species present at the open waste liquid surface evolve directly from the surface into the headspace. Gases dissolved in the liquid, e.g., nitrous oxide dissolved in aqueous liquid, exsolve (come out of solution) until the liquid on the surface is in equilibrium with the relatively low concentration of the gas in the headspace. As a result, the liquid that convection brings to the surface becomes depleted of gas compared to the bulk liquid. Diffusion from the subsurface liquid in the flow cannot resupply the near-surface liquid with gas as quickly as it is removed by exsolution. The lower the liquid velocity, the longer the flow stays at the surface, the thicker the depleted zone and the slower the overall gas release, which is limited by liquid-phase diffusion from the bulk liquid to the surface through the depleted zone.

Transport constraints also apply in the headspace gas. The waste gas added to the air at the liquid surface must be transported into the bulk headspace gas to allow exsolution to continue. This gas-phase transport is faster by a factor of a thousand than that in the near-surface liquid-phase (Peurrung et al. 1998), so the depleted zone in the liquid is the rate-limiting process in the transport of gases through an open liquid surface.

The liquid/gas interface within the floating crust, or at the top of a wet-solids layer, is much closer to stagnant conditions than the open-surface interface. Accordingly, surface release rates of dissolved species are much lower for the trapped surface. The crust also serves to obstruct the release of rising gas bubbles.

4.6 Retained Gas Release Events

Gases trapped within the waste can be released to the headspace gradually via the mechanisms discussed in Sections 4.2 through 4.5, or rapidly via gas release events (GREs). GREs are defined broadly here to include the relatively slow gas releases due to upward bubble migration as well as buoyancy-induced episodic gas releases in which large volumes of trapped gases are released over a short time. GREs can be spontaneous, as when the inventory of trapped gases exceeds the capacity of the waste to trap it, or induced, as when waste-disturbing activities cause a portion of trapped gas to be released. The most significant GREs are those caused by rapid buoyant displacement of a portion of a bulk solids layer under a deep layer of supernate (Stewart et al. 2003). Some episodic GREs in DSTs release enough gas to cause a detectable drop in the waste surface level.

Besides the more-or-less well defined gas release events, a semi-continuous background release also occurs in essentially all tanks where bubbles formed in the waste rise and release their contents to the headspace. The background releases depend primarily on waste properties and may change seasonally but usually not dramatically. In some tanks, the background release rate is very steady, but it may also fluctuate due to the occurrence of many small GREs. Waste removal and other inventory modifications also cause changes in background release rates. Background gas releases via bubble migration are generally responsible for the steady-state headspace gas concentrations observed in all tanks, particularly of gases that are relatively insoluble in the aqueous waste (e.g., hydrogen and methane).

Saltwell pumping of SSTs typically causes GREs that are believed to result from the mechanism of “percolation,” in which expanding bubbles eventually reach a size that allows them to begin moving through the surrounding waste and rise to the top of the solids layer. Percolation occurs in pore-filling dendritic bubbles. The parallel phenomenon of bubble disengagement occurs when particle-displacing bubbles grow sufficiently to break free of the surrounding sediment. In addition, bubbles can be released directly when liquid around them is drained and the bubble pops without any significant upward bubble migration. Incomplete drainage of a region leads to incomplete gas release since some gas remains trapped in the remaining liquid-saturated waste. There is often a lag between pumping activities and the corresponding gas release (Hedengren et al. 2001), probably because of the time required for draining liquid to flow within the waste.

As was discussed in Section 3.3, the release of dissolved gases (ammonia in particular) is increased by any waste disturbance that generates a volume of unsaturated but wetted solid surface area in contact with the headspace or in contact with air-filled pores connected to the headspace. Saltwell pumping is the most common such activity.

Percolation is also believed to cause the small spontaneous gas releases observed in gas monitoring data from SSTs, even from some of the tanks that have been saltwell-pumped (Hedengren et al. 2001). However, this percolation is different from saltwell pumping-induced percolation in that the bubbles expand due to accumulation of gases, and not by a decrease in hydrostatic pressure. Most such spontaneous releases occur in the fall and winter because of swings in barometric pressure since any pressure decrease causes the retained gas to expand.

Buoyant-displacement GREs (BDGREs) are an important type of spontaneous event because they are the largest known and more rapid than the spontaneous releases from SSTs. They occur as a result of the continuing accumulation of retained gas generated in a settled solids layer. When the gas fraction becomes large enough to make a region of the waste less dense than the supernatant liquid above it, some buoyant waste rises to the top and releases much (but not all) of its gas. BDGREs have been observed only in DSTs where the relative depths of the supernatant and settled solids layers permit displacements. BDGREs that are about to occur spontaneously can be triggered by atmospheric pressure fluctuations (Hedengren et al. 2000). Because BDGREs release relatively large amounts of retained gas, the composition of the release is generally close to that of the retained gas with less enrichment by soluble species than in slower, smaller GREs.

5.0 Headspace Dynamics

This chapter discusses the mechanisms by which gases and vapors are transported within the headspaces and risers and the relative importance of these mechanisms to different types of gases and vapors. The diffusive and convective mixing of species within the headspaces and risers is discussed, special consideration is given to the mixing of episodic GRE plumes, and the role of vapor condensation is also examined.

5.1 Mixing of Gases and Vapors Within the Headspace

The temperature difference between the waste surface and tank dome produces a corresponding difference in the density of the air, which in turn induces convection within the headspace. The waste itself is heated by radioactive decay, and its surface is warmer than the tank dome. Air near the waste surface is warmed by the waste and rises, displaced by air that has been cooled by contact with the tank dome. This thermally induced convection mixes the gases and vapors both vertically and horizontally throughout the convective zone. Various studies employing numerical modeling and semi-empirical relationships have concluded that transport and mixing of gases and vapors within the convection zone are very rapid compared with their release from the waste surface so concentration gradients within the convection zone are negligible (Claybrook and Wood 1994, Postma et al. 1994, Epstein 1995).

Between the convection zone and the waste surface is a very thin boundary layer region where viscous forces greatly reduce convection velocity. Here, gas and vapor 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; 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 convection-dominated model of the passively ventilated waste tank headspaces is supported by tests performed in tanks C-103 and C-111 (Huckaby and Story 1994, Huckaby 1994). These consisted of collecting samples from different elevations above the waste surface and comparing the measured concentrations of gases and vapors at each elevation. No significant differences in gas and vapor concentrations were observed in the samples. A tracer gas experiment was also conducted to evaluate the speed of mixing (Huckaby et al. 1997a). In this experiment, two tracer gases were released into the headspace of tank S-102 through a riser, and samples were collected from another riser about 4 m away. Analyses of the samples suggested that both tracer gases were at significant concentrations in the samples collected 15 minutes after gas injection and that the concentrations of both species were essentially at their final concentrations within about an hour after they were injected. The experimental results of the tracer study were in good agreement with numerical modeling predictions developed to guide the experimental sample collection schedule(a).

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. The potential for large headspace concentration gradients due to this phenomenon was examined in a study of three particularly cool waste tanks (Huckaby et al. 1997b). Tanks B-103, TY-103, and U-112 were sampled in October, November, and December 1996, respectively, at approximately the time of year when the ground temperature above the tanks is hottest.(b) The study involved collecting samples from two different risers as far apart horizontally as possible, from three different elevations in each riser. Analysis of the data indicated no statistically significant concentration gradients in either the horizontal or the vertical directions to be present in any of the three tanks.

The potential effects of incoming fresh air on the homogeneity of a tank headspace were examined with a numerical model by Antoniak.(c) Antoniak used a time-dependent, three-dimensional model to estimate the fate of 5- and 25-ft^3/min fresh air inflows into a tank headspace. The model assumed the dome was 78°F, the waste surface was 80 °F (to support thermally induced convection), and that 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-ft^3/min) and for incoming air that was 79 °F (neutrally buoyant, at 25-ft^3/min). Convection patterns were significantly affected by the inflowing air in each of these scenarios. At 25-ft^3/min, the inflowing air was predicted to flow directly to the waste surface, and from there the fresh air spread out, warmed, and participated in the thermally driven convection within the headspace. At 5-ft^3/min, the inflowing air was predicted to have negligible effects beyond a small region at the bottom of the riser. Although this modeling did not bound all situations, its results suggest that significant concentration inhomogeneities would be difficult to produce given the limited ventilation rates and tank conditions.

5.2 Buoyant Plume Mixing

Trapped gases can be released in small localized plumes resulting in short-term localized high concentrations. However, plumes are rapidly dispersed into the surrounding ambient headspace by convection, turbulent mixing, and diffusion (Hedengren et al. 2001). High temperature and gas

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(a) Antoniak ZI and KP Recknagle. 1996. *Modeling Tracer Gas Concentrations in Single Shell Tank 241-S-102 Dome*. (PNNL letter report TWSFG96.23 sent to GD Johnson, Westinghouse Hanford Company, cover letter from J Brothers, August 14). Pacific Northwest National Laboratory, Richland, Washington.

(b) There is a lag of 2-4 months between the hottest summer atmospheric temperatures and the hottest ground temperatures at the depth of the tank domes. See Section 7.1.1 and Figure 7-1.

(c) Antoniak ZI. 1997. *Modeling of Breathing Effect on Gas Concentrations in a Single-Shell Tank Dome.* (PNNL letter report to LD Pennington and LL Buckley, Lockheed Martin Hanford Corporation, July 16). Pacific Northwest National Laboratory, Richland, Washington.

composition make the plume buoyant, which produces a negative radial pressure gradient. The resulting inflow causes the plume to entrain surrounding air as it rises and dilutes the gases in the plume. As the plume rises, ambient headspace air is pulled in toward the center of the narrowing column of rising gases, and the plume gases are rapidly diluted as the plume ingests this air. Laboratory experiments where fresh water was forced through a porous plate into a saltwater solution showed that most of the mixing occurred within the mixing layer rather than in the plume itself (Epstein and Burelbach 1998).

The rate and location of the release affects the mixing behavior. Computational modeling using a three-dimensional transient model showed that a uniform tank-wide release became fully mixed within minutes while a large, high-concentration local release was nearly completely mixed within about 2 hours. Plume dispersion was not significantly affected by active or passive ventilation (Antoniak and Recknagle 1997).

5.3 Vapor Condensation in Headspaces

One additional phenomenon with significant impacts on the composition of the air in many tank headspaces and risers is that of vapor condensation. Vapor condensation can reduce or increase the headspace and ventilation system concentrations of the condensing species and all species soluble in the condensate.

The most common and possibly most important vapor subject to condensation in the headspaces is water. The conditions leading to water vapor condensation are a warm, wet waste surface and a dome temperature lower than the dewpoint of the air in contact with the waste. Air warmed and humidified by contact with the wet waste surface rises as it is displaced by cool air from the region near the tank dome. The rising moist air is itself cooled by contact with the tank dome, and if it is cooled below its dew point temperature some of the water vapor will condense on the dome. Condensate accumulates and drains off the curved dome to the walls or risers or may drip directly from the dome itself, returning eventually to the waste.

Water vapor condensation on the dome is inhibited in many saltcake tanks where the partial pressure of water above the salt-laden aqueous waste is below the vapor pressure of water at the dome temperature. The lower salt content of aqueous waste in sludge tanks makes these tanks more prone to water vapor condensation in the headspace. In the hotter sludge tanks condensation of water in the headspaces can be so vigorous that water vapor condenses before reaching the dome and forms a fog in the headspace (Huckaby and Estey 1992). Headspace fogs were apparently more common in the 1970s and 1980s, when the wastes were hotter, as indicated by the need to install exhausters on many tanks before photographing the waste surface.(a) As with condensate forming on the dome, walls, and risers, the condensate in a fog is expected to eventually rain-out and rejoin the waste when the droplets grow too large for air convection to counter their settling velocities.

The importance of water vapor condensation is not associated with the water itself but with the water-soluble gases and vapors that are readily absorbed by the water condensate. For example, the headspace concentration of ammonia in a tank with water vapor condensing on its dome and walls would be expected to be much lower than if the dome and walls were dry. Even larger effects would be expected if the tank supports a fog in its headspace. Seasonal changes, such as the diminished humidity of incoming ambient air in winter or the rise in soil and dome temperatures associated with solar heating of the ground in summer, may be important factors in some tanks and make the headspace concentrations of water-soluble species vary with the time of year.

Vapor condensation in the headspaces is generally limited to water vapor because other vapors (i.e., ammonia and organic vapors) are generally not close enough to their saturation partial pressures for the small headspace temperature gradients to induce condensation. Temperature gradients within risers that extend above the ground can be much larger, however, making the condensation of organic vapors possible. This phenomenon and related phenomena that affect the composition of air in the risers is discussed in Chapter 6.

(a) Personal communication from Dennis Maupin, 1993.

6.0 Ventilation Pathway Dynamics

The concentrations of gases and vapors leaving the headspace of a tank can be affected by conditions in the ventilation pathway and may be different at the point of emission than in the headspace. Mixing within the risers and pits above the tanks is considered in this chapter. Also discussed are three mechanisms to reduce concentrations of gases and vapors and the corresponding mechanisms that would increase concentrations.

6.1 Mixing Within Risers and Pits

The risers above a tank are typically 8 to 16 feet long and vary in diameter from 4 (most common) to 42 inches (only one or two per tank). They may extend about a foot above ground level (riser extensions and mounted equipment may increase this height substantially), or may stop several feet below ground level inside a concrete pit. The pits themselves are typically rectangular concrete boxes covered with thick concrete lids or steel plates. Flanged fittings and gaskets are used to seal the risers with blind flanges (in the case of unused risers) or installed equipment. Pits not currently in use are covered with concrete lids and sealed with closed-pore foam. Steel plates are commonly used to cover pits in use. The steel plates may be relatively well sealed at the edges with tape but may also have access holes (e.g., a hole to allow access to a manual valve inside the pit) that allow air exchange between the pit and the atmosphere. Most pits are equipped with a floor drain connected to the headspace that allows headspace air to enter the pit or vice versa.

Although there may be considerable exchange of air between the headspace, risers, and pits, the air within a tank riser or pit is not generally considered representative of the headspace itself. Risers and pits that are not sealed from the atmosphere can be expected to participate in the passive ventilation of the headspace, either allowing ambient air in or headspace air out. Clearly, when serving as an inlet of ambient air the composition of the riser will be at worst a diluted version of the headspace or at best that of the inflowing air. When serving as an outlet of headspace air the composition inside the riser or pit may be affected by vapor condensation and the absorption and adsorption of species due to temperature differences between the headspace and the riser or pit (see Section 4.4).

6.2 Condensation and Evaporation

Headspace vapors that are at (or nearly at) equilibrium with liquids in the tank can condense in the ventilation system if it is cooler than the headspace. The primary example of this is water, which evaporates from the waste and condenses on the tank dome, risers, and in the ventilation pathways, particularly in warm sludge tanks. For example, condensation of water vapor in the HEPA filter housing of tank C-107 was found to be such a problem in the 1980s that heat trace was applied to the filter housing in winter to prevent the condensed vapor from collecting and freezing.

Condensation of organic vapors in the ventilation pathways may also occur for certain low-volatility compounds, particularly in tanks that have a large surface area of organic liquid (e.g., tank C-103). When a small exhaust system was installed on tank C-103 in 1995, an accumulation of “light oil” was noticed on the stack rain-cap, and there was evidence that the HEPA filter was plugging with an organic condensate.(a)

The condensation of vapors in ventilation pathways results in at least a temporary decrease in their concentrations in atmospheric emissions. However, if and when the condensate temperature rises above its dewpoint in the headspace, the condensate will start to evaporate, and the atmospheric emissions may contain higher concentrations of this vapor than present in the headspace.

6.3 Adsorption and Desorption

Even vapors present at low concentrations (low compared to their concentrations above their liquids) may be accumulated within the ventilation system of a tank by adsorption onto solid surfaces. Adsorption is the process by which vapors or gases are bound to a solid surface. It is generally reversible, with adsorption causing more material to be bound when the temperature of the surface is decreased and some of the material to be desorbed when the temperature of the surface is increased.

The potential quantity of material adsorbed by the ventilation system is inherently limited by the surface area of solids present and is generally small. For volatile headspace constituents, particularly those present at relatively high concentrations, adsorption and desorption probably have negligible effects on the concentrations released to the atmosphere. For the less volatile headspace constituents (semivolatile species) the impact of adsorption and desorption processes may be significant to the rate at which a given species is released to the atmosphere. The magnitude of the effect depends heavily on the temperatures, available surface area, the sorbent properties of the solid surface, and the competition between the various species for active sorption sites.

Chemical analyses of HEPA filters from various SSTs indicated the presence of trace levels of tributyl phosphate, semivolatile alkanes, polychlorobiphenyls, and other semivolatile organic compounds. These were presumably present at very low concentrations in the tank headspaces, and gradually adsorbed to measurable levels on the filters.(b)

6.4 Absorption and Evaporation

When a liquid is present in the ventilation system, as from the condensation of water or organic vapors, there is the potential for absorption of gases and vapors by the liquid. Whether the absorption of gases and vapors causes a significant change in the release rate of the absorbed species depends on the ventilation rate, the amount of liquid present and the rate that it is forming, and any change in conditions (e.g., the solubilities of gases and vapors in liquids are generally temperature-dependent). The absorbed species will eventually either be returned to the air exiting the tank or returned to the tank itself.

(a) Personal communication (e-mail of 9/15/1995, 10/4/1995).

(b) See, for example, WSCF Analytical Results Report for CH2MHILL Hanford to Jean Quigley, Report 20030797, dated July 17, 2003.

One scenario leading to the release of the absorbed species to the atmosphere (at potentially higher concentrations than originally present) is that of a warm, humid tank that is slowly exhausted via a HEPA filter mounted above the tank. During a cool night, the HEPA filter housing temperature drops below the dewpoint of the air exiting the tank, and water vapor condenses in the housing. Water-soluble gases and vapors (e.g., ammonia, methanol, acetone, etc.) in the air from the tank are absorbed by the condensate as the tank continues to vent. When the HEPA filter housing temperature rises the next day, condensation of the water vapor ceases, and the condensate begins to evaporate. The increase in condensate temperature and its evaporation cause the absorbed species to also evaporate, raising the concentration of these species in the air released to the atmosphere.

Absorbed species may be returned to the tank if the condensate is drained back into the tank, as in the scenario of condensate forming on the ventilation riser, or if the tank happens to be inhaling via the ventilation pathway when the absorbed species are evaporating. Indeed, the evaporation of condensate and absorbed species is likely any time the ventilation pathway they reside in is the inlet of air to the headspace–ambient air at the Hanford Site is rarely saturated even with water vapor.

7.0 Passive Headspace Ventilation

The quiescent SSTs are passively ventilated with the atmosphere to prevent pressurization of the tanks and accumulation of gases released by the waste. The exchange of air between the tank headspaces and the atmosphere is driven by meteorological conditions. As a result, the tank ventilation rates fluctuate as the weather changes. Passive ventilation rates are much lower than those supplied by mechanical exhausters but are large enough to have a significant effect on headspace conditions. This chapter discusses the phenomena that induce passive ventilation and the available information of passive ventilation rates.

7.1 Passive Air Exchange Motive Forces

Barometric pressure changes, cold ambient air temperatures, and wind provide driving forces that induce passive air exchange between the underground tanks and the atmosphere. It has long been recognized that changes in the barometric pressure create a slight, transient pressure imbalance that either pushes air into the tank or draws it out (Garfield 1975, Crippen 1993). The magnitude of this effect is easily estimated, and it is the best understood of the identified passive ventilation motive forces, as discussed below in Section 7.1.1. Ambient air that is colder than the headspace can cause a convective transport of the cold, dense air down into the headspace, and the warm, less dense headspace air out into the atmosphere. Less easily calculated than barometric pressure fluctuation-induced air exchanges, this phenomenon depends on the number and configuration of ventilation pathways, as discussed n Section 7.1.2. Wind across the tank farm can induce pressure differences between connected tanks and between individual tanks and the atmosphere, which in turn induce air exchanges between tanks and the atmosphere. Wind can also induce a pressure change at an open riser. When the vent is leeward, a venturi effect can draw air out of the tank. When the vent is windward, the air will tend to be compressed into the tank. The pressure drop downwind of an obstruction can also induce flow though a riser from a tank. Largely because of the complex interactions with ambient winds, these are the least well understood and most difficult causes of passive ventilation to evaluate. Section 7.1.3 below discusses the effects of wind.

It is important to note that these three influences, pressure, temperature, and wind act in interdependent ways to drive or impede the ventilation of the tanks. Depending on the ambient conditions, they may act together or in opposing ways.

7.1.1 Barometric Pressure Fluctuations

When the barometric pressure is decreasing, the headspace pressure follows it closely and also falls, causing the headspace gas to expand. The excess volume created by expansion flows out of the headspace. Conversely, when the barometric pressure increases, the headspace pressure also increases and air is drawn in from outside. This effect was commonly considered the only significant cause of passive ventilation in the tanks until the passive ventilation rates of several SSTs were measured using tracer gases in 1997 (Garfield 1975, Crippen 1993, Huckaby et al. 1997a). Ventilation rate estimates are still sometimes conservatively assumed to be no larger than that due to barometric fluctuations (Hu and Zach 2003).

Assuming the headspace temperature is constant, the ideal gas law can be used to estimate the volume of air, ΔV, exhaled by a tank headspace having volume V, when the barometric pressure changes by ΔP is given by

$$\Delta V \quad = \quad -\frac{\Delta P}{P} V \tag{7.1}$$

where P is the final pressure in the headspace. A decrease in barometric pressure causes the headspace to exhale air, and an increase in barometric pressure causes the headspace to inhale air. Larger headspaces result in higher breathing rates.

Garfield (1975) examined the daily barometric pressure changes reported for calendar year 1973 and estimated the breathing rate due to this effect to be 0.667% of the headspace volume per day. Crippen (1993) repeated this using 4 years of hourly barometric pressure data from 1988 through 1991 and estimated the effect to be about 0.46% per day. Given SST headspace volumes range from about 33,000 ft^3 for an SST holding the maximum allowed volume of waste to about 176,000 ft^3 for an empty 1-million-gallon SST, the average ventilation rate due to barometric pressure fluctuations ranges from about 0.11 to 0.56 ft^3/min, depending on the headspace volume.

Crippen pointed out that because the barometric pressure *typically* has a diurnal cycle, the tanks are typically exhaling between about 10 a.m. and 5 p.m. and inhaling between about 6 p.m. and 8 a.m. the following morning. The hourly data used by Crippen indicate the maximum pressure drop likely to be observed during a 1-year period is about 0.11 in. of mercury, which would correspond to the tank exhaling air at about 0.38% of the headspace volume per hour. For a typical SST headspace volume of about 80,000 ft^3, this 0.11 in. of mercury pressure drop would correspond to a ventilation rate of about 5 ft^3/min.

7.1.2 Chimney Effect

When the air in a tank headspace is warmer than the ambient air above the tank, a metastable (or unstable) condition exists. Warm, less dense air within the tank is located below cool, denser ambient air.(a) If any perturbation moves a parcel of air up or down, that parcel of air will tend to be accelerated by the thermal structure in the direction of the perturbation. If pathways exist for the convective transport of air, the cooler denser ambient air will enter the headspace, displacing the warmer, less dense headspace air and expelling it out of the tank. This is generally referred to as the "chimney effect" because of its similarity to the air exchange in a house due to hot air rising from a fireplace chimney. The air movements in the vents from barometric pressure and wind effects are likely initiating mechanisms for this overturning of air.

(a) The air density is also be affected by its humidity. At a given temperature, humid air is slightly less dense than dry air, and the headspaces are generally more humid than the ambient air at the Hanford Site. The effect of humidity is small – typically causing about a 10% decrease in density in the summer and less than 1% change in winter.

When the air in a tank headspace is cooler than the ambient air above the tank, a stable vertical thermal structure exists. If any perturbation moves a parcel of air up or down, that parcel of air will tend to be returned to its original location by the thermal structure. The air movements in the vents from barometric pressure and wind effects will thus be impeded by the existence of a stable thermal structure. This reverse “chimney effect” means that lower exchange rates can be expected from all influences when a stable thermal structure exists.

Unlike air exchange due to barometric pressure fluctuations, the chimney effect induces a continuous flow of air and requires both an inlet and an outlet. Under special circumstances a single opening can serve as both the inlet and outlet,(a) but generally it requires two distinct ventilation pathways such as the HEPA-filtered breather riser and the cascade line to an adjacent tank. The number and configuration (i.e., size, shape, temperature profile, etc.) of ventilation pathways strongly affect the magnitude of the chimney effect, and the inherent problems associated with identifying and characterizing all ventilation pathways in the tank farms would make accurate calculation of the chimney effect very difficult.

7.1.3 Wind-Induced Dynamic Pressure Effects

The interaction of wind with the surface protrusions of the tanks (vents, pits, risers, etc.) can cause both spatial and temporal dynamic pressure variations that induce air exchange between the tank headspace and the atmosphere. Dynamic pressure drives passive tank ventilation in two ways: 1) a pressure-driven change in density of the headspace air, and 2) a pressure differential-driven circulation. A tank with only one vent can only respond to pressure changes in terms of changes in density of the headspace; air flows into the tanks when the dynamic pressure increases and out when pressure decreases. A tank with multiple ventilation paths (connections with other tanks, cracks, open access ports, etc.) can respond to pressure differences with a circulation of air; i.e., support the simultaneous flow of air into and out of the tank.

When wind impinges on an object, the dynamic pressure is slightly greater than the static pressure on the upwind side and slightly lower on the leeward side. A similar effect occurs across a surface (or opening) that is oriented perpendicular to the direction of the wind (the venturi or Bernoulli effect). Air flowing across the horizontal tank vent openings will cause a net negative pressure on the vent opening, drawing air out of the tank. Also, the presence of significant flow obstructions directly upwind (e.g., instrument buildings, electrical panels, etc.) can reduce the local wind speed but also generate a local area of negative dynamic pressure in the wake of the obstruction.

The wind-driven dynamic pressure changes affecting ventilation are thus expected to result from a combination of wind effects on 1) the ventilation filter housing as an obstruction in the wind and with corresponding high- and low-pressure zones, and 2) the down-facing vent openings that are typically perpendicular to the direction of the wind. The Bernoulli equation reflects the observation that the static

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(a) If a single opening is large enough to support counter-current flow (without eliminating the temperature difference between incoming and outgoing air) it may be sufficient for the chimney effect. For example, the 12-in. observation riser used to collect liquid samples from tank C-103 in December 1993 was visually observed to support counter-current flow of cold ambient air down the open riser and warm headspace air up and out of the riser. This was evidenced by the formation and vertical motion of wisps of fog in the riser as the warm, humid air rising upward was cooled (unpublished personal observations, JL Huckaby).

pressure difference induced at a surface perpendicular to the wind is a function of the square of the wind velocity. Assuming the air exchange is directly proportional to the dynamic pressure changes, the importance of this means of tank ventilation should vary with the square of the ambient wind speed, making high-wind conditions potentially very important events for tank ventilation.

An additional consideration is that fluctuating dynamic pressures may not induce enough air exchange for an incoming packet of air to reach the headspace before it is drawn back out into the atmosphere. Convective mixing within the ventilation path (i.e., within the filter housing, riser, pit, etc.) due to turbulence and temperature gradients reduces the impact, but small dynamic pressure fluctuations may still have essentially no effect on the ventilation rate.

Based on reported exchange rates of 1 to 10 m^3/h (Huckaby et al. 1997a, Huckaby et al. 1998), passively ventilated tanks have typical exchange rates of headspace air that range from 7×10^{-4} to 1×10^{-2} air exchanges per hour. The potential magnitude of dynamic wind-driven exchange rates for a tank with a single vent can be evaluated by assuming the tank vent acts as a Pitot tube(a) in the wind. Using hour-to-hour wind speed observations from the Hanford Meteorological Station for 1999, potential average and peak ventilation rates(b) of 4×10^{-5} and 1×10^{-3} air exchanges per hour were calculated. These are about one order of magnitude too small to account for the observed rates. Using fifteen-minute changes in mean wind speed, somewhat higher average and peak values of 3×10^{-4} and 1.6×10^{-3} air exchanges per hour were calculated. Using shorter-term variability, the one time rise of wind speed from a minimum to the reported peak within a fifteen minute period, computed exchange rates of 5×10^{-4} and 9×10^{-3} air exchanges per hour were calculated – these are close to the range of typical exchange rates for tanks. The inclusion of the actual variability of wind speeds could easily project air exchanges that are greater than typical tank exchanges. Although based on an upper limit for potential interactions of winds and tank vents, these results indicate that dynamic pressure changes resulting from short-term temporal changes in wind speed do have the potential of being a significant, if not dominant, factor in passive tank ventilation.(c)

7.2 Passive Ventilation Rates

Several studies have been conducted to estimate the passive ventilation rates of the Hanford Site tanks. These have indicated ventilation rates are significantly higher than would be predicted by barometric pressure fluctuations alone and vary appreciably from tank to tank and with time. The following sections discuss the available information on passive ventilation rates.

(a) These dynamic wind pressures are representative values of the magnitude of values that can potentially occur if a vent were a tube oriented into the wind. The pressure values for the Pitot tube tend to be are slightly higher (~30%) than those given in the ASCE building loading guidance (ASCE 7-98, 2000) for windward and lee pressures on structures. Because the vent openings are not perpendicular to the flow, the actual pressure on the vent will be less than predicted, and these estimates are an upper bound for potential flow rates.

(b) In reality, the openings are facing downward and only some fraction of the computed dynamic pressure will occur. Also, different vent structure orientations relative to wind direction can potentially result in positive and negative dynamic pressures.

(c) These estimates of exchange rates only provide a definition of the magnitude of ventilation that the dynamic changes in wind can potentially account. The prediction of relatively large rates is balanced by the expectation that the actual dynamic pressure on the vent exits is expected to be lower than predicted.

7.2.1 Measured Ventilation Rates

Passive ventilation rates have not been measured directly because air flow rates tend to be too low for existing appropriate instrumentation(a) and because some air flow occurs via inaccessible pathways (e.g., buried cascade lines that connect tank headspaces). The best current estimates of passive ventilation rates are based on an indirect method that relates measured changes in concentration of a headspace gas to the ventilation rate. This technique has been applied to headspace gases that are sporadically released by the waste (Wilkins et al. 1996, Sklarew and Huckaby 1998) and to tracer gases injected into the headspace for the purpose of estimating ventilation rates (Huckaby et al. 1997a, 1998).

The calculation of ventilation rates from the change in headspace concentration of a tracer gas (or sporadically released waste gas) is simple if it can be assumed that the gas is well-mixed within the headspace at all times and its concentration is not affected by any creation or depletion mechanisms other than ventilation (i.e., the gas is not being released by nor absorbed by the waste). Under this assumption the change in headspace concentration, C, with time, t, is given by

$$\frac{dC}{dt} = -\frac{Q}{V}C \tag{7.2}$$

where Q is the volumetric air flow rate out of the headspace and V is the headspace volume. This ordinary differential equation is easily solved and rearranged to give

$$Q = -\frac{V}{(t_f - t_i)} ln\left(\frac{C_f}{C_i}\right) \tag{7.3}$$

where subscripts i and f denote initial and final values, respectively. This second equation indicates that the concentration of a gas released into the headspace, given the assumptions discussed above, will decrease exponentially with time. The equation is only slightly complicated by the inclusion of a constant source (or sink) such as a low level of the tracer gas in the atmosphere or the slow constant release of a waste gas. The equation corrected for a constant background level of the gas of interest, C_0, is

$$Q = -\frac{V}{(t_f - t_i)} ln\left(\frac{C_f - C_0}{C_i - C_0}\right). \tag{7.4}$$

The exponential decay of an introduced gas was first applied to estimate ventilation rates from the sporadic release of hydrogen by the waste in selected SSTs (Wilkins et al. 1996). At that time, headspace hydrogen concentrations were being monitored using instrumentation in the Standard Hydrogen Monitoring Systems (SHMSs) mounted on selected tanks. Occasional GREs in these tanks caused the headspace hydrogen concentration to rise rapidly and then exhibit an exponential decrease back to the

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(a) Very low gas flow rates are routinely measured with great accuracy in laboratory settings with inexpensive instruments. However, these instruments require the air flow to pass through small-diameter tubing within the instrument, and introduce a resistance to flow that would effectively alter the measurement of passive ventilation rates.

baseline hydrogen level. Wilkins et al. examined the SHMS data and reported estimated ventilation rates derived from 19 GREs in 7 different passively ventilated SSTs between September 1995 and December 1996. They reported values ranging from 2 to 11 ft^3/min.

Sklarew and Huckaby (1998) reexamined the SHMS data considered by Wilkins et al. (1996) and extended the technique to other tanks and more recent data. They analyzed over 80 GREs in passively ventilated tanks and calculated lower bound, upper bound, and best estimate ventilation rate values from the hydrogen concentration decay following each GRE. Their analyses indicate relatively high ventilation rates in 241-A, 241-AX, and 241-BY tank farms, which had best-estimate ventilation rates ranging from 3.5 to 42 ft^3/min. Generally lower ventilation rates were observed for tanks in 241-S and 241-U tank farms. While of value, many of the results presented by Sklarew and Huckaby (1998) were based on relatively inaccurate hydrogen concentrations (prone both to drift and noise) and a subjective determination of the background level of hydrogen in the headspace (C_0).

Better passive ventilation rate estimates were established by Huckaby et al. (1997a, 1998) by releasing tracer gases into the tank headspaces and collecting headspace air samples periodically until the tracer gas was essentially gone. Depending on the ventilation rate and the amount of tracer gas released in the headspace, the tracer gas method can provide rate measurements for periods ranging from several days (if the ventilation rate is high) to several months (if the ventilation rate is low). The first tank into which tracer gases were injected was also the subject of a simple headspace mixing experiment, which indicated the assumption of a well-mixed headspace was reasonable.

Initial tests of the method involved helium (He) and sulfur hexafluoride (SF_6) as tracer gases. Because He is present in the atmosphere at a concentration of about 5 ppmv, relatively large volumes of He had to be released to provide the necessary resolution to monitor its depletion from the headspace. In contrast, atmospheric background levels of SF_6 are much lower (in the single parts per trillion by volume level, pptv), and SF_6 is readily measured at very low concentrations by available instrumentation, providing a much larger dynamic range and allowing much less gas to be used as a tracer. However, it was found that SF_6 was not stable in all the tank headspaces; it was either absorbed by waste liquids or destroyed after absorption of beta radiation, and its use was discontinued (Huckaby et al. 1997a). Instrumentation in the SHMS E+ monitor installed on tank S-106 allowed almost continuous measurement of the headspace He concentration giving additional information about the variability of the ventilation rate in that tank (Huckaby et al. 1999).

Table 7.1 lists the measured average ventilation rates calculated using the tracer gas method. Consistent with the analyses of the exponential hydrogen concentration decreases after GREs conducted by Sklarew and Huckaby (1998), the 241-A, 241-AX, and 241-BY tank farms were found to have relatively high passive ventilation rates. Also consistent with the analyses of GREs by Wilkins et al. (1996) and Sklarew and Huckaby (1998), the measured ventilation rates are significantly higher than that expected from barometric pressure fluctuations alone. Passive ventilation rate variability from tank to tank and variability with time are discussed in Sections 7.2.3 and 7.2.4, respectively.

Table 7.1. Passive Ventilation Rates Measured with Tracer Gas Method

Tank	Tracer Gas	Time Period	Reference	Ventilation Rate	
				(m^3/h)	(ft^3/min)
A-101	He	July 9 – July 15, 1997	(2)	17	10
AX-102	He	August 8 – September 8, 1997	(2)	28	16
AX-103(1)	He	February 25 – March 3, 1997	(2)	42	25
BY-105	He	April 17 – April 23, 1997	(2)	36	21
	SF_6	April 17 – May 8, 1997	(2)	26	15
C-107(1)	He	February 21 – March 21, 1997	(2)	1.9	1.1
S-102	He	September 24 – October 11, 1996	(2)	3.3	1.9
	SF_6	September 24, 1996 – February 11, 1997	(2)	3.8	2.2
S-106	He	April 16 – May 6, 1999	(4)	17	9.9
		May 19 – June 13, 1999	(4)	15	8.6
TX-104	He	January 14 – February 12, 1998	(3)	5.9	3.5
U-102	He	January 9 – March 24, 1998	(3)	3.5	2.1
U-103	He	February 27 – April 9, 1997	(2)	4.3	2.5
		July 15 – August 13, 1997	(2)	2.6	1.5
		November 18, 1997 – January 8, 1998	(3)	4.0	2.3
	SF_6	February 27 – July 22, 1997	(2)	2.9	1.7
U-105	He	July 18 – August 15, 1997	(2)	8.6	5.1
U-106	He	January 9 – March 24, 1998	(3)	2.2	1.3
U-111	He	January 9 – March 24, 1998	(3)	3.2	1.9

(1) Ventilation rates calculated from SF_6 data for tanks AX-103 and C-107 are not included because of apparent absorption or chemical degradation of SF_6.
(2) Huckaby et al. 1997a.
(3) Huckaby et al. 1998.
(4) Huckaby et al. 1999.

7.2.2 Ventilation Pathways

Each of the SSTs is equipped with a filtered opening to the atmosphere to allow ventilation of waste gases and pressure equilibration between the tank headspace and the atmosphere. Any unsealed tank penetration is also a potential ventilation pathway, including risers that extend above ground level, instrumentation mounted on risers, and the various concrete pits installed on many of the tanks. The pits are generally designed with an open floor drain that allows air exchange between the headspace and the pit via a 2-in.-diameter drain pipe, so openings or penetrations into the pits may serve as headspace ventilation pathways as well.

The headspaces of most SSTs are also connected to the headspaces of adjacent tanks via underground cascade lines. Typically these are 3-in.-diameter pipes that connect sets of three tanks in series; e.g., tank C-101 is connected to tank C-102, which in turn is connected to tank C-103. The cascade lines are just over 25-ft long, joining tanks that are 25-ft apart and extending a short way into each headspace. There are 4-in. cascade lines (in 241-SX and 241-TY tank farms), 6-in. cascade lines (in 241-A tank farm), and cascades that include only two tanks (241-T tank farm and parts of 241-U tank farm), four tanks (in 241-TX tank farm), and even six tanks (each three-tank cascade in 241-BX tank farm is cascaded to a corresponding three-tank cascade in 241-BY tank farm). None of the tanks in 241-AX tank farm nor any of the 200-series SSTs are connected via cascade lines, and the cascade lines to certain tanks have been cut and capped to isolate the tanks (i.e., SX-113, SX-114, SX-115, U-101, U-104, and U-112). It is thought that most cascade lines are open, but there is evidence that some are essentially clogged, presumably with waste.(a)

In addition to cascade lines, various small piping systems connect tank headspaces to valve pits and pits on other tanks. Power and instrument wire conduits leading out of the pits, valve pit drains, etc., can all contribute to ventilation of a tank. Both 241-A and 241-AX tank farms were constructed with 20-in. underground vent headers that connect the headspaces of the tanks in each farm. While the mechanical exhauster originally installed on these farms has been removed and the outlet of the vent headers sealed, the ventilation headers and lines to individual tanks are still open and allow air to pass freely between the tanks.

Ventilation pathways in addition to the filtered pathway appear to be important factors to the passive ventilation rate. Three of four tanks with the highest measured passive ventilation rates in Table 5.1, A-101, AX-102 and AX-103, are in tank farms with large underground ventilation headers. The relatively high ventilation rate observed for tank BY-105 may be due to the poor seals of instrument and blanked risers on that tank and adjacent tanks. The relatively low ventilation rate of tank C-107 has been associated with its well-sealed risers, lack of pits, and the possibility that the cascade line connecting it to tank C-108 may be blocked.(b)

7.2.3 Variability With Time

Passive ventilation rates are expected to vary with time because the forces that drive passive ventilation vary with time. This was confirmed by results from the tracer gas ventilation rate measurements conducted in the 1990s (Huckaby et al. 1997a, 1998). The ventilation rate measurements reported by Huckaby et al. (1997a, 1998) for several tanks are plotted in Figure 7.1 as a function of date for the various passively ventilated tanks studied. The rates shown were calculated from headspace tracer gas concentrations determined by periodic sampling, and are illustrated as flat lines over the period between sampling events (vertical lines are included to provide visual continuity). Rates for several tanks are nearly constant over separate periods (e.g., S-102, TX-104, U-106), but others fluctuate significantly, especially when the period is short.

The tracer gas method was also applied in one tank, S-106, which was equipped with a gas chromatograph that performed nearly continuous monitoring of the tracer gas (helium) concentration. This allowed the ventilation rate of the tank to be estimated over shorter time periods, and the daily ventilation rate estimates are plotted in Figure 7.2 (Huckaby et al. 1999). As indicated in Figure 7.2, the daily averaged S-106 ventilation rate varied from over 14 m^3/h (24 ft^3/min) to about 0.1 m^3/h

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(a) For example, the portable exhauster used on tank S-112 during waste retrieval had no apparent affect on the headspace vapor concentrations in tank S-111, suggesting that the cascade line between these two tanks is effectively blocked with waste.

(b) Headspace concentrations of waste gases and vapors measured in tanks C-107 and C-108 (the only tank C-107 is connected to) are consistent with little or no air exchange occurring between these tanks (Huckaby and Bratzel 1995).

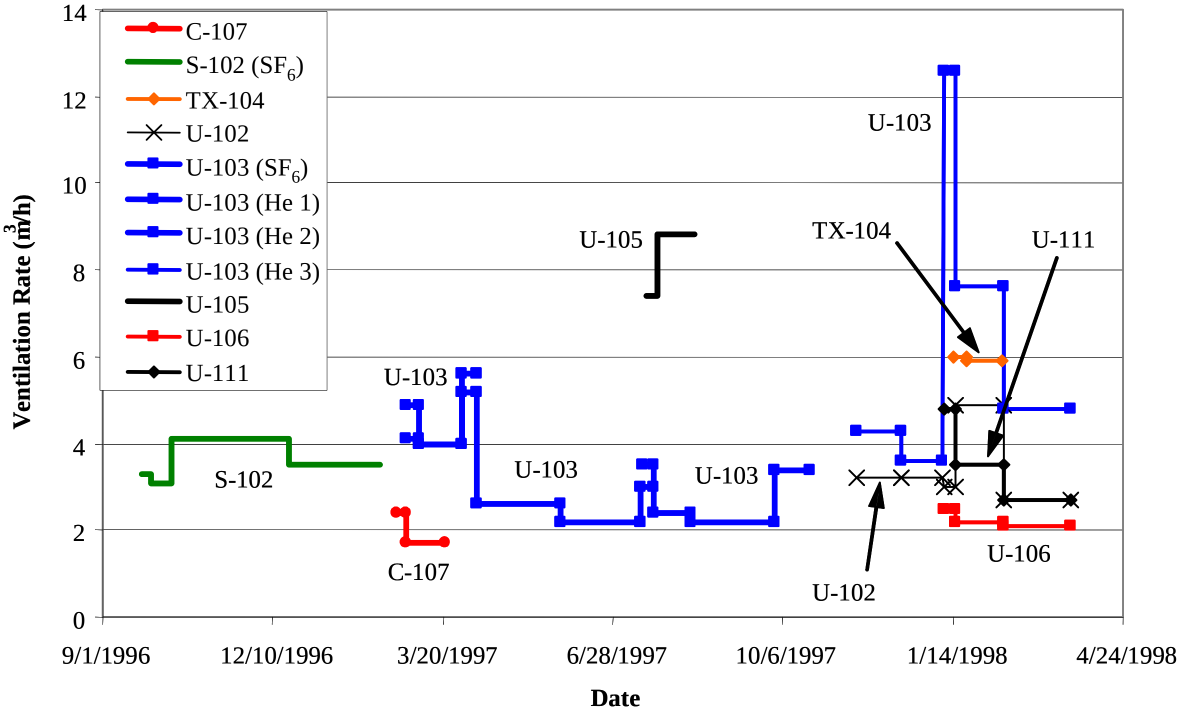

Figure 7.1. Passive Ventilation Rates Reported by Huckaby et al. (1997a, 1998)

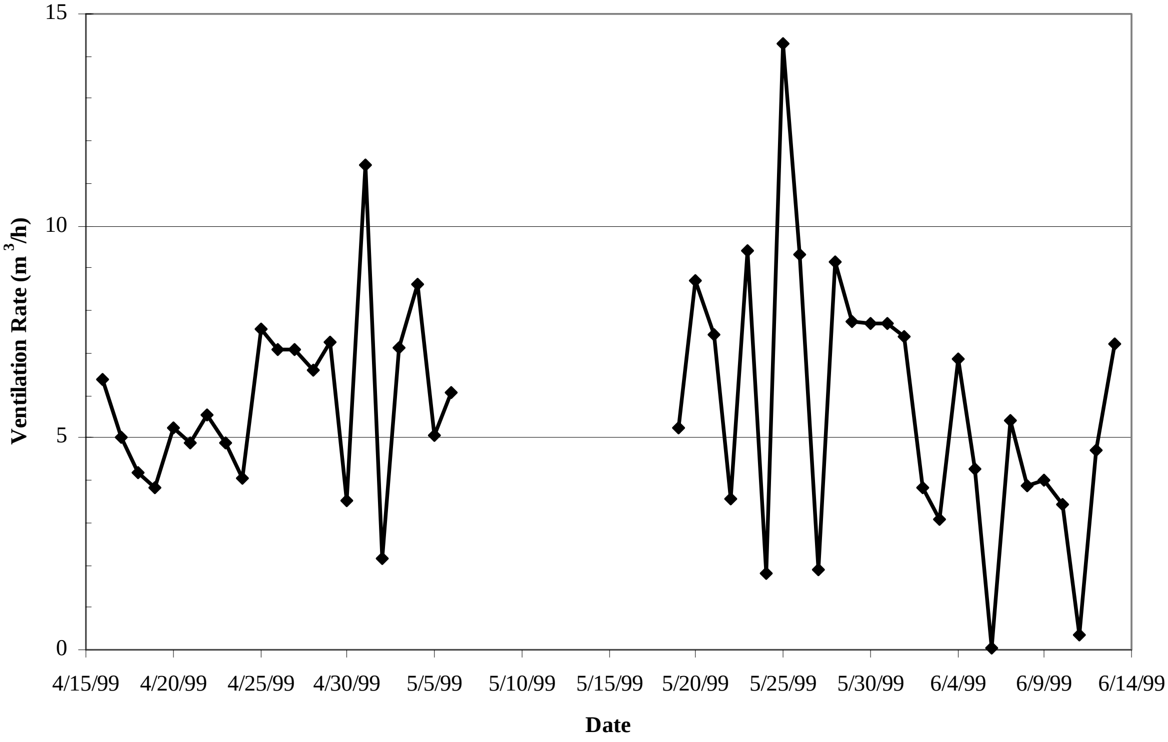

Figure 7.2. Tank S-106 1-Day Average Ventilation Rates

($0.1\ ft^3$/min). While this range may be exaggerated by inaccuracies in the tracer gas concentration measurements and the possible return of tracer from an adjacent tank,(a) this relatively large variability in the average daily ventilation rate suggests that ventilation rates may vary even more dramatically over shorter periods during a day.

The passive ventilation rates measured in tracer tests for tank U-103 (Huckaby et al. 1997a, Huckaby et al. 1998) were analyzed in terms of ventilation influences by Droppo (2004b). As indicated in Figure 7.1, the U-103 tracer tests provide average ventilation rates for time periods varying from a week to a month spanning the four seasons. The average contribution of barometric pressure changes over the test periods was computed based on hourly observations during the test periods and found to be consistently on the order of 0.18 ft^3/min (0.3 m^3/hr). This accounts for less than 10% of the observed winter ventilation rate and about 15% of the observed summer ventilation rate. Droppo (2004b) applied a simple model to the data and concluded that the chimney effect accounted for about 50% and 15% of the observed ventilation rates in the winter and summer, respectively. The model also indicated that energy in the winds account for about 40% and 70% of the observed ventilation rates in the winter and summer, respectively. These results for tank U-103 match expected roles of pressure, temperature, and wind influences on tank ventilation rates.

There is little information on short-term (i.e., less than 1 day) variability of tank ventilation rates. The barometric pressure has a small diurnal influence and will be important during short time periods of rapid pressure change when weather fronts pass through. The Hanford Site experiences large, diurnal ambient-air temperature fluctuations that may result in corresponding diurnal changes in the exchange of air due to the chimney effect. Specifically, the chimney effect will tend to be strongest at night when ambient air temperatures are typically their lowest. Short-term variability from winds is expected to occur in time periods of 1 hour or less. As wind speeds rise and fall, and as wind directions shift, the dynamic pressures and pressure differences will change.

The hourly contributions from wind, temperature, and pressure influences were projected for summer and winter time periods of 1 week duration by Droppo (2004b). The analysis is on a least square fit to the observed tank ventilation rates for tank U-103. These data show large hour-to hour changes in the rates (wind influences) and smaller diurnal changes (temperature and pressure influences).

7.2.4 Variability Between Tanks

As discussed in previous sections, the passive ventilation rate of any given tank appears to depend on the micrometeorology above the tank, tank headspace volume, temperature, and humidity, as well as the number and configuration of ventilation pathways connecting the tank headspace with the atmosphere and other tanks. While the tanks do have many similarities, the many differences between them give no two tanks predictably the same passive ventilation rates.

(a) Transfer of headspace air from S-106 to S-105 (via their cascade line) for a period would build an inventory of tracer in S-105. Subsequent exchange of air from S-105 to S-106, transferring the tracer back into S-106, would reduce the apparent ventilation rate of S-106.

To illustrate the variability of passive ventilation rates of different tanks, ventilation rates determined by tracer gas studies are plotted in Figure 7.3 for each of the tanks studied. Eight of the 12 tanks studied had ventilation rates below 10 m^3/h (15 ft^3/min), with the remaining four tanks exhibiting significantly higher rates. Although this type of passive ventilation rate measurement is available for only about 8% of the SSTs, available data suggest unless a tank has a large or multiple ventilation pathways (as is the case for the 241-A and 241-AX farm tanks), its average ventilation rate is probably in the 2 to 10 m^3/h (about 3 to 15 ft^3/min) range.

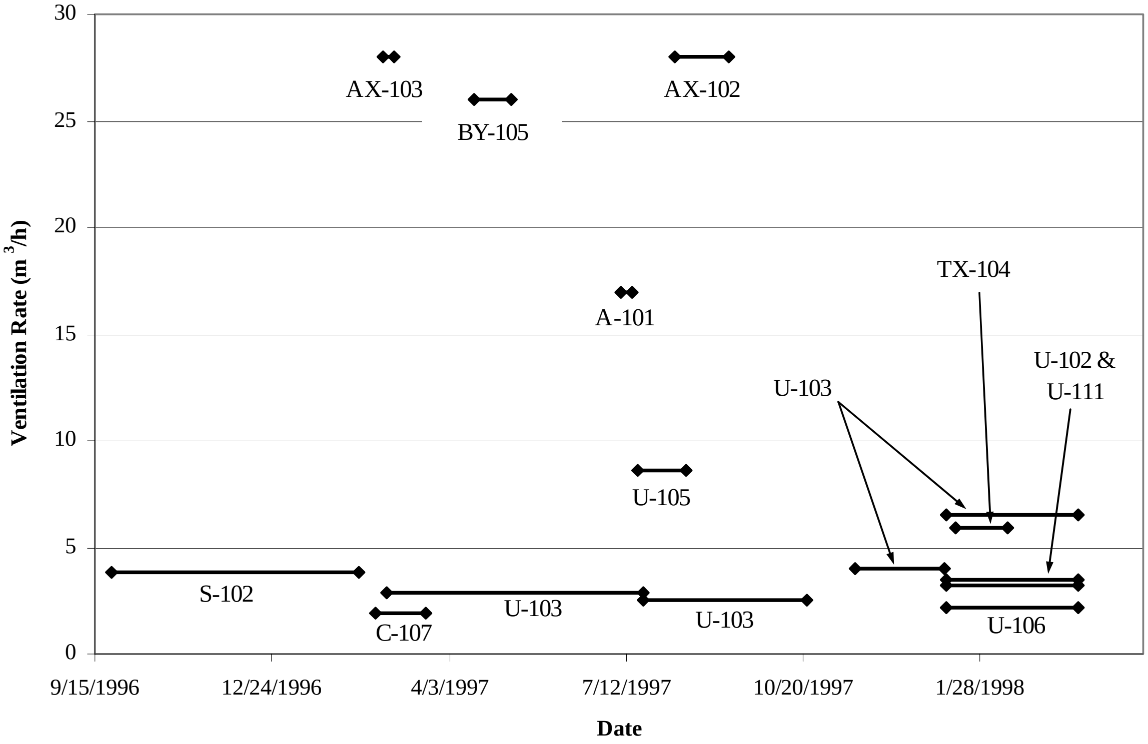

Figure 7.3. Average Passive Ventilation Rates for Various Tanks

8.0 Headspace Composition Variability

Headspace gas and vapor concentrations exhibit both seasonal and sporadic variation. Although these variations cannot be quantitatively predicted, they can largely be explained as the result of climatological conditions or operational activities. This chapter discusses the causes of variation in headspace composition.

8.1 Changes in Gas and Vapor Release Rates from Waste

Chapters 2 and 3 of this report identified the mechanisms by which gases and vapors are generated, stored, and released into the headspaces. This section considers the previously presented information in terms of the conditions or activities that affect the headspace composition.

8.1.1 Temperature Changes

The rates that gases and vapors are released from the waste depend on the temperature of the waste, which is itself a function of time. Waste and headspace temperatures are gradually decreasing as waste radiation levels decline and the rate of heat generation by the waste decreases. Imposed on top of that gradual decline in temperatures is a seasonal fluctuation associated with ambient conditions. These are both evident in Figure 8.1, where measured waste and headspace temperatures for tank C-103 have been plotted for the previous 10 years. Thermocouples 1, 2, and 3 are about 15 in., 39 in., and 63 in. above the tank floor, respectively, and thermocouple 6 is about 16 ft above the tank floor. Thermocouple 1 apparently failed in September 2002. Until the supernatant liquid was pumped from tank C-103 in

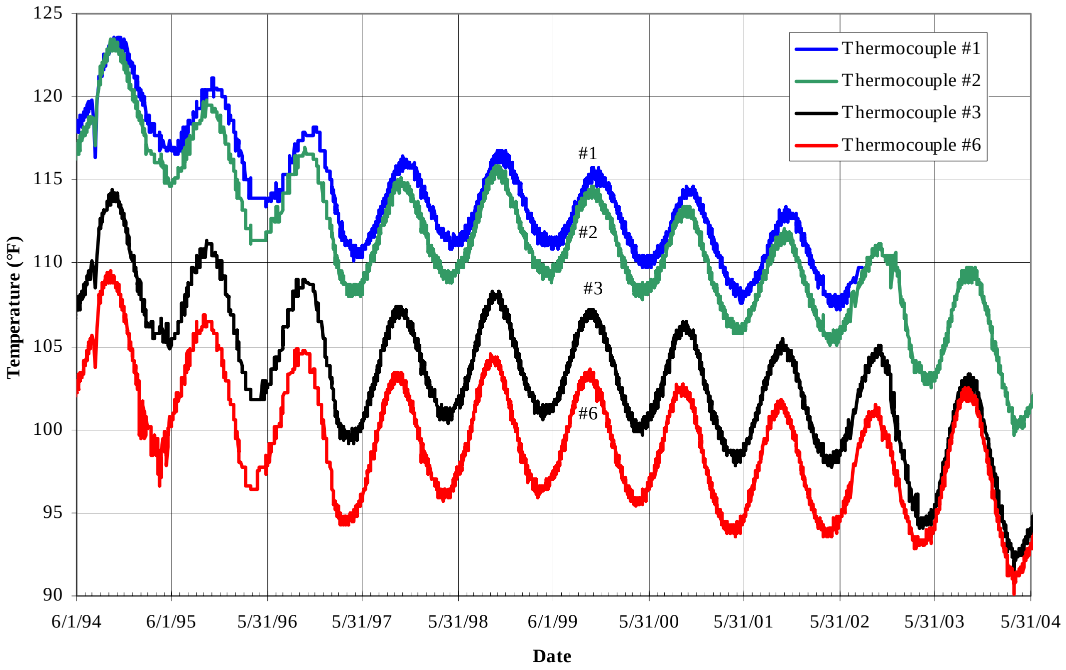

Figure 8.1. Waste and Headspace Temperatures for Tank C-103

December 2002, thermocouples 1, 2, and 3 were below the waste surface, with thermocouple 3 in the convectively mixed supernate (and indicative of the waste surface temperature) and thermocouple 6 in the headspace. Thermocouple 3 has been in the headspace since the supernate was pumped and has agreed quite well with thermocouple 6 since that time. Thermocouple 2 is currently several inches above the actual waste surface, but conduction of heat through the thermocouple tree itself is keeping its temperature about 7 °F above that of the headspace.

The sinusoidal behavior of the temperature curves given in Figure 8.1 is clearly associated with the seasonal change in the temperature of the ground above the tank. The annual temperature maxima and minima lag those of ambient temperature by several months, owing to the thermal inertia of the soil above the tank. The maximum waste temperatures are typically observed in October or November, and the minimum waste temperatures are observed in April or May.

Waste temperature changes affect the continuous release of gas and vapor into the headspace through a variety of mechanisms:

- The generation rates of gases and vapors of concern generally increase as the waste temperature increases. Increases in generation rates, particularly of species generated near the waste surface, cause a corresponding increase in their release rates. Increased gas production rates lead to increased gas bubble migration and release; increased vapor generation rates (e.g., hydrolysis of TBP to form butanol) lead to higher concentration gradients within the waste, higher mass transfer rates, and higher release rates. Similar to the lag between the seasonal waste and ambient temperatures, the seasonal maxima and minima of gas and vapor release rates may lag behind the waste temperature maxima and minima.

- The solubility of gases and vapors in the aqueous waste liquid generally decreases as temperature increases, leading to their enhanced release from solution. In addition, the solubility of most salts increases as temperature increases; the increased salt concentration causes a decrease in gas and vapor solubility, increasing the release. This type of release is most marked in tanks with supernatant layers and no crust and has a larger effect on the release of water-soluble gases and vapors than on species that are not soluble in the aqueous waste.

- The diffusivities of gases and vapors in both the liquid and gas phase increase with temperature. As a result, diffusion of species through the gas and liquid in the tank is enhanced, affecting both soluble and sparingly soluble species.

Changes in ambient temperature can also affect releases by changing the headspace temperature. Though air exchange between the headspace and the atmosphere of a passively ventilated tank does not strongly affect waste temperatures, it does affect the temperatures of risers extending into the headspace and the headspace air. Cooler headspace temperatures may cause condensation of low-volatility organic vapors, and the cyclic cooling and warming of the headspace may cause a corresponding cyclic character in their concentrations. Cooler headspace temperatures may also induce or enhance the condensation of water vapor. The presence of water condensate in turn affects the headspace concentrations of water-soluble gases and vapors (see Section 4.4.1).

8.1.2 Barometric Pressure Changes

The filtered ventilation risers ensure that the headspace pressure is always very nearly equal to the ambient barometric pressure, and changes in the barometric pressure are rapidly felt in the tank headspaces. The pressure on bubbles in the waste changes correspondingly as the headspace pressure is transmitted through the liquid in the waste pores. When the barometric pressure decreases, the bubbles of retained gas in the waste expand and tend to migrate faster. If the solid waste is already very nearly saturated with retained gas, bubble expansion may induce a GRE producing concentration spikes in the headspace gas. McCain (1999) discusses the observed correlation between barometric pressure lows and the incidence of GREs. For reasons described in Section 3.3, GREs tend to cause greater increases in the headspace concentrations of those species that are relatively insoluble in the aqueous waste. In BDGREs, the convective mixing of the supernate and refreshing of the waste surface also temporarily enhance the release of soluble species.

8.1.3 Waste Disturbances

Operational activities such as waste retrievals, supernatant and interstitial liquid pumping, core sampling, and water lancing are known to enhance gas and vapor releases. The mechanisms that affect releases can be broadly described as follows (Stewart et al. 2003).

- *Removal or disturbance of the waste containing trapped bubbles.* This directly allows the escape of previously trapped bubble gases, whether the removal is caused by drainage of the interstitial liquid that traps the bubble, an intrusion (as in core sampling), the impact of a water jet (sluicing and water lancing), or the dissolution of salt matrix (saltcake retrieval).

- *Removal of the waste above bubbles.* When the liquid above a bubble is removed (e.g., by saltwell pumping) the hydrostatic pressure on the bubble is decreased and the bubble expands. Bubble expansion enhances upward bubble migration, which in turn enhances the release of the gases trapped in the bubbles.

- *Creation of wetted surface area.* The liquid that remains behind in a drained region of waste is in contact with the headspace through freshly opened pores. The soluble species contained in this exposed liquid are released over time. In addition, the undrained liquid may act to reduce the amount of soluble gas released by bubbles originating beneath the drained region, as was observed in tank S-106 during and after saltwell pumping.(a)

- *Capture of gases and vapors by added water.* Ammonia releases have been observed to be considerably decreased by water added on top of the waste during retrieval (Mahoney et al. 2000). The same reduction in release would occur for any soluble gas or vapor; to some extent, even sparingly soluble species would be taken up by the water. Some of the freshly dissolved species would be re-released later as salt dissolved in the water and reduce the solubility of gases and vapors.

(a) Huckaby JL, LA Mahoney, and ER Siciliano. 2001. *Waste Gas Releases Associated with Recent Saltwell Pumping of Single-Shell Tanks.* Letter report TWS01.36, Pacific Northwest National Laboratory, Richland, Washington.

8.1.4 Ventilation

Ventilation with ambient air reduces the concentration of a species in the tank headspace. On the other hand, it can increase the concentration of waste gases and vapors if the incoming air is coming from another tank headspace (e.g., via the cascade line) in which the concentrations are greater.

In the case of a relatively clean air source, an increase in ventilation causes a proportional increase in evaporation of species that make up much or nearly all of a liquid phase, such as water in most tanks, or the semivolatile organic liquid in tank C-103. Ventilation has very little effect on change in evaporation of most dissolved species. The latter “trace solute” species have to be replenished at the surface by mass transfer from the depths; this slow transfer process is the rate-limiting step for evaporation so changes in airflow have little effect on the evaporation rate. The solvent species, most commonly water, is constantly present at the surface and make up a large proportion of it and hence do not need to be replenished. As a result, mass-transfer on the gas side of the liquid-gas interface is the controlling step, and a change in airflow rate does increase the overall evaporation rate.

8.2 Changes in Ventilation Rate

The steady-state headspace concentration of a gas or vapor is reached when the amount of a species removed by ventilation equals the amount released from the waste in the same period of time. Given a constant release rate, the steady-state concentration is inversely proportional to the ventilation rate.

Actual headspace gas and vapor concentrations reflect a continuing approach to the steady-state concentrations, which do not remain constant because of continuing changes in release rates and ventilation rates. This section draws together information on conditions that influence ventilation rates.

8.2.1 Ventilation Pathway Changes

Ventilation pathway changes can be caused by an engineered tank configuration change, such as changes in the location or orientation of the filtered breathing pathway, or by environmental changes, such as the gradual loading of the HEPA filters or the weather-related failure of a riser seal. They may cause a temporary change in passive ventilation rates, such as when a pit cover block is temporarily replaced by a steel plate with access holes, or a more permanent change, such as the permanent addition of instrumentation in the breather riser.

8.2.2 Air Exchange Impetus Changes

In actively ventilated tanks, the predominant impetus for air exchange is the exhauster. In passively ventilated tanks, local micrometeorology provides the impetus through barometric pressure changes, ambient temperature, and wind.

As discussed in Chapter 5, barometric pressure fluctuations induce a relatively low level of air exchange between the tank headspaces and the atmosphere causing an average ventilation rate of about 0.46% of the headspace volume per day (Crippen 1993). At this low rate, assuming all gas and vapor releases from the waste were stopped, it would require about 150 days to reduce the concentrations of species in the headspace by a factor of two. Furthermore, though there are some small seasonal effects (barometric pressure fluctuations tend to be slightly greater in winter), the amount of air exchanged due to barometric pressure fluctuations is relatively constant from day to day. Crippen (1993) points out that the barometric pressure is almost constantly changing and remains constant over an 8-hour work shift only once during a period of about 2 months.[a] Because barometric pressure fluctuations cause relatively little ventilation and tend to be relatively constant from day to day and even season to season, they do not cause significant day to day or even seasonal variations in the headspace gas and vapor concentrations.

Passive ventilation induced by temperature differences between the headspace and the atmosphere (the chimney effect; see Section 5.1.2) is expected to be significantly higher in winter than in summer. In tanks for which the chimney effect is an important impetus for ventilation (i.e., hot tanks which are minimally affected by the wind) headspace concentrations are expected to be lower in spring (after a period of relatively high ventilation rates in winter) and higher in fall.

The wind-induced dynamic pressure changes that drive air exchange between the tank headspaces and the atmosphere vary with the square of wind speed making higher winds potentially very important in the passive tank ventilation processes. Based on the Hanford Site climatology reported by Hoitink et al. (2004), the winter and early spring have on average 2 to 3 days with peak gusts of 40 mph or greater. All months of the year have peak gusts of 40 mph typically at least once per month. This only implies the largest wind-driven ventilation events will occur more often in the winter and early spring. It does not reflect the distribution of wind speeds with seasons, which will cause total ventilation of the tanks by wind-induced pressures. At Hanford, average wind speeds tend to be higher in the summer than in the winter. The energy available in the wind (based on the square of the wind speed) peaks in the summer months and is estimated to be about 40% less during winter months.[b] This would suggest higher passive ventilation rates occur in the summer months, and this in turn would lead to lower headspace concentrations in late summer and fall (contrary to the expected seasonal behavior of the chimney effect).

8.3 Observed Headspace Composition Variability

Of the 110 SST headspaces that have been sampled and characterized, 33 have been sampled more than once. The discussion of headspace composition variability is divided here into short-term, seasonal, and long-term variability.

8.3.1 Short-Term Headspace Composition Variability

Of the SSTs that have been sampled more than once, none were re-sampled at an interval of fewer than 48 days, and there are essentially no ammonia or organic vapor concentration data for shorter

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(a) By “constant” Crippen is apparently referring to no change between successive hourly barometric pressure readings recorded to 0.01 in. of mercury. For comparison, only about 4 hourly changes of more than 0.10 in. of mercury are recorded per year (Crippen 1993).

(b) The estimate is based on an analysis of the 50-ft wind observations at the Hanford Meteorological Station for three years of data (1997-1999).

periods[(a)]. Headspace composition fluctuations over shorter periods are consequently not well documented by sampling events. However, monitoring instruments installed on selected tanks to monitor flammable gases have indicated that the passively ventilated SST headspaces do not change drastically from day to day.

Data from the SHMS from their initial application on SSTs in March 1995 through June 2001 are summarized in annual reports (Wilkins et al. 1996, McCain and Bauer 1998, McCain 1999, 2000, 2001). After instrument noise and spikes associated with periodic instrument calibration have been accounted for, the data indicate that GREs in the SSTs are relatively small. The largest GRE in an SST reported during the period from the installation of the SHMS through June 1999 was estimated to release a hydrogen volume of less than 5 m^3 over a period of about 6 days, raising the hydrogen concentration in tank U-103 from its background level of 890 ppmv to a peak of 1,260 ppmv (McCain 1999). More dramatic increases in the headspace hydrogen concentrations were reported, but typically GREs in the passively ventilated SSTs caused increases of less than a factor of two above background levels. GREs certainly can occur in tanks other than those monitored, but the SHMS were installed on those SSTs considered most likely to exhibit GREs (Wilkins et al. 1996).

GREs would be expected to have little effect on the headspace concentrations of the water-soluble species (e.g., ammonia, methanol, 2-propanone) because these are not stored in large quantities in the trapped gas (they partition to the aqueous phase) and are more readily transferred to the headspace via the aqueous waste liquids. The headspace concentrations of nonpolar organic vapors that do accumulate in the retained gas bubbles would be expected to increase in proportion to the increases in hydrogen, assuming the release of trapped gas bubbles to be their primary mechanism for transport to the headspace.

8.3.2 Seasonal Headspace Composition Variability

In 1996 and 1997, the headspaces of four passively ventilated SSTs were sampled five times over a 1-year period to evaluate seasonal changes in composition (Huckaby et al. 1997b). Tanks BX-104, BY-108, C-107, and S-102 were selected for the study on the basis that they had widely varying headspace compositions, waste types, and physical headspace conditions. To the extent practicable, sampling methods for each tank were consistent from event to event, and to reduce analytical variability, the raw mass spectral data for organic vapor concentrations from all 20 sampling events were reprocessed by a single analyst. Temporal variations in headspace concentrations were reported in terms of relative standard deviations (RSDs) of the event-average concentrations for each species and seasonal effects were studied.

The principal waste gases and vapors, i.e., ammonia, hydrogen, nitrous oxide, and water, were found to remain within a relatively narrow range over the 1-year study. Water and ammonia vapors had RSDs of less than 20% in each tank over the five sampling events. Both of these vapors are expected to be present in abundance at or near the waste surface in all five tanks, and the rates that they are released into the headspace are not liquid-phase mass transfer dependent (see Chapter 4). Their headspace

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(a) Tank C-103 was excluded from consideration here because C-103 was sampled repeatedly at the very start of the headspace characterization program, in part to provide practice samples for the analytical laboratories to develop methods.

concentrations are less affected by ventilation rate fluctuations than most other volatile species. Hydrogen and nitrous oxide were found to be more variable. Headspace hydrogen concentration may be the best indicator of headspace ventilation fluctuations, because its rate of release from the waste would be expected to be relatively constant in this particular set of SSTs.(a) Temporal RSDs for both hydrogen and nitrous oxide remained below 40% for three of the tanks. Both hydrogen and nitrous oxide concentrations in the fourth tank, C-107, rose significantly between the March 1996 and February 1997 sampling events, suggesting the ventilation rate of this tank was lower during that period than the period prior to the March 1996 sampling event.

Temporal variations in individual organic vapor concentrations were not generally consistent nor did total nonmethane hydrocarbon (TNMHC) concentration changes tend to be consistent with inorganic gases and vapors concentration changes. The TNMHC concentration in tank BX-104, for example, was observed at elevated levels in the August 1996 samples, while hydrogen and nitrous oxide were not. While the concentrations of some organic species rose significantly during the study, others of similar chemical nature fell. This is most likely attributable to changes in the exchange of air with adjacent tanks via cascade lines.

8.3.3 Long-Term Headspace Composition Variability

Twenty of the passively ventilated SSTs have been resampled at intervals of more than 1 year. Headspace characterization data for selected analytes for these tanks are given in Table 8.1. Examination of the table suggests that headspace concentrations are variable but that the concentrations of the analytes listed tend to stay within a relatively narrow range. Exceptions can typically be explained by identifiable changes in the tank conditions. The large increase in organic vapors observed in September 2002, for example, is attributable to an increase in wetted surface area in this tank because it was being saltwell pumped at that time.(b)

Burrup et al. (2004) examined the available data assuming the replicate sampling dates were random and observed that, on average, some species were more apt to change with time than others. For example, Burrup et al. (2004) considered 29 passively ventilated tanks that had been sampled on more than one occasion and found that the average inter-sampling event RSDs for ammonia were less than half (17%) of the RSDs for hydrogen (38%) and nitrous oxide (45%).(c) In other words, ammonia concentrations varied significantly less than hydrogen or nitrous oxide concentrations in the tanks considered. This may in part be attributed to the general availability of ammonia dissolved in aqueous wastes near the waste surface and may imply the ammonia (like water) has a partial pressure in the headspace near its equilibrium partial pressure above the aqueous waste. The same behavior would be expected for semivolatile organic vapors in tanks that are known to have significant surface areas of these organic liquids, such as tanks C-102, C-103, and C-104.

(a) Prolonged decreases in barometric pressure do tend to induce upward gas bubble migration within the waste and increased release rates.

(b) See discussion of enhanced ammonia releases during saltwell pumping in Section 4.3 and references therein.

(c) These values directly from Burrup et al. (2004), but not all of the 17 tanks had ammonia, hydrogen, and nitrous oxide results. When only tanks that had data for all three species were considered, the RSDs were 21%, 38%, and 45% for ammonia, hydrogen, and nitrous oxide, respectively.

Tank S-102 is typical of the tanks for which headspace data are available both from the mid-1990s and the last 2 years. Containing moderate levels of organic vapors, this tank was sampled in March 1995, five more times between January 1996 and February 1997 as part of the seasonal temporal study, and again in August 2002 and January 2004. The sampling events in 2002 and 2004 involved only one SUMMA sample per event and it was only analyzed for organic vapors (no ammonia samples were collected and the SUMMA samples were not analyzed for hydrogen, nitrous oxide, etc.). Headspace concentrations of 1-butanol, 2-propanone (acetone), and ethanol in tank S-102 are plotted in Figure 8.2 as functions of time. As shown, there appears to be as much variability among the 1995 – 1997 samples as between the samples from that period and the 2002 and 2004 samples. Although about 61 kgal of waste liquids were removed from tank S-102 during the 1999–2002 time period, much of this was supernate, and the 2002 and 2004 headspace samples do not appear to have been strongly influenced by the liquid removal (i.e., the effects of increased wetted surface area and other changes were not significant in this tank). Based on this type of analysis of S-102 and several other tanks, Meacham and Huckaby (2004) concluded the long-term differences between recent headspace samples and samples from the mid-1990s were either small or explainable in terms of activities in the tanks.

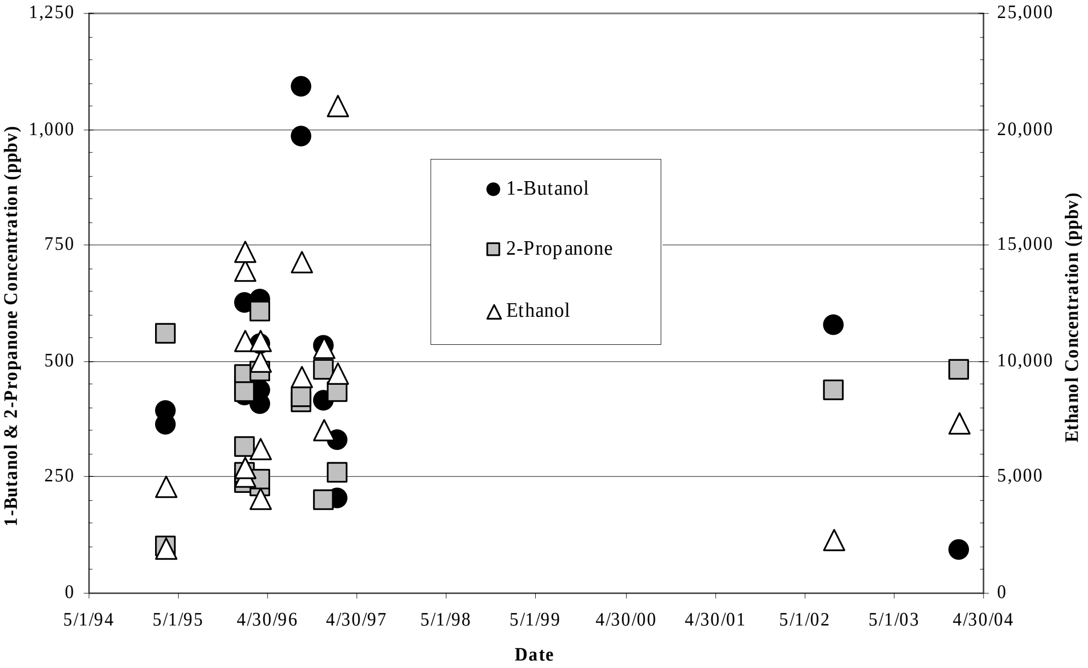

Figure 8.2. Selected Headspace Concentrations in Tank S-102

9.0 Conclusions

The physical and chemical phenomena that cause and influence the transport of gases and vapors from within the waste to the tank headspaces have been described, and available supporting evidence from tank observations has been given, as available. The key conclusions, many of which are not novel to this report, are as follows:

- The rate that volatile species from within the waste are transported to the tank headspaces is typically limited by its transport through the interstitial liquid. Transport through convective liquids (e.g., a liquid pool), through drained porous solids, and through the boundary layer of the headspace itself is relatively rapid compared to the rate that species migrate through interstitial liquids.

- The transport of nonpolar organic compounds trapped within the waste to the headspace is slow compared to that of polar organic compounds. Because of their low solubility and correspondingly low concentration gradients in an aqueous liquid, nonpolar organic compounds do not diffuse through aqueous wastes as rapidly as polar species, and their transport may be governed by the rate they are carried to the surface with rising gas bubbles. This implies that the quiescent headspace concentrations of nonpolar species may not represent the inventory of these species in the waste. Waste-disturbing activities, in particular waste retrieval, can be expected to significantly alter the headspace composition, both the absolute concentrations and the ratios of one species to another.

- Headspace concentrations for most species are determined by the balance between the rate they are released by the waste and the rate they are removed via the ventilation system. Other factors may be important in select tanks, such as the absorption of ammonia by water condensate on the dome and walls of the tank (a sink, in this case, for ammonia), but the concentration of most waste species in the headspace would roughly be halved if the ventilation rate were doubled.

- The inventory of waste in trapped gas bubbles is probably only important for hydrogen, nitrous oxide, and methane. Most other gases and vapors are dissolved in aqueous or organic liquids. The solubility of certain nonpolar species (e.g., n-dodecane) is so low in aqueous solutions that their presence at detectable concentrations in a tank headspace implies the presence of an organic liquid phase source (although the source may actually be in a tank that is exchanging air with the tank sampled).

- It is impossible to estimate amounts of organic liquids from vapor concentrations. Evaporation rates can and have been used to estimate organic waste liquid surface areas (Huckaby and Sklarew 1997) but cannot be used to estimate inventories otherwise.

- Headspaces are convectively mixed by temperature differences between the waste surface and the tank dome. Heat evolved by the radioactive decay of waste in the tanks makes the waste surface hotter than the dome and results in continuous convective mixing within the headspace. Air warmed by the waste surface rises, is cooled by the dome, and sinks. This same phenomenon occurs in tank risers, but it can be defeated when the top of the riser is heated by hot ambient air or solar radiation.

- Vapor condensation in the headspace, either on the dome and walls or as an aerosol, can cause the absorption of soluble species (e.g., ammonia in water condensate) diminishing the concentrations of soluble species both in the headspace and in air released to the atmosphere. Similarly, vapor condensation in a ventilation pathway can cause temporary decrease in the release of any condensing species and any species soluble in the condensate, and a corresponding increase in releases when conditions change. For example, water condensate and ammonia may accumulate in a ventilation filter housing during a cool night and release ammonia concentrations that are higher than those seen in the headspace when the filter housing is warmed the following morning. Similarly, semivolatile organic compounds may accumulate during cold months in the filter itself and then may be released at relatively high concentrations when the filter is warmed in the spring and summer.

- Passive ventilation is thought to be due to barometric pressure fluctuations, a difference between temperature of the ambient air and the headspace (the chimney effect), and the effects of wind on risers, pits, and instruments that are connected to the tank headspace (or to connected tanks). Barometric pressure fluctuations appear to have the smallest overall impact on ventilation rates. The magnitude of the chimney effect depends heavily on the headspace temperature but is typically not important to the passive ventilation rates of most tanks in the warmer summer months. Wind effects appear to be the most important driver for passive ventilation in the tanks. Wind effects are also believed to cause the greatest fluctuations in ventilation rates and are the most difficult to quantify or predict.

- Passive ventilation rates vary significantly from tank to tank and from one time period to another. Average passive ventilation rates measured at selected tanks range from about 2 to 40 m^3/h (about 1 to 25 ft^3/min) over time periods of about 1 week and longer. Short-term passive ventilation rates (for periods of less than 1 day) have not been established but are thought to be significantly more variable than the measured average rates.

- Higher passive ventilation rates appear to be associated with multiple and larger ventilation pathways. This implies that adding an additional filtered ventilation pathway would promote ventilation and decrease waste species concentrations in the headspace.

- Headspace composition varies with a variety of factors that tend to be tank-specific, and no simple relationship between seasonal changes in the tank conditions and headspace compositions has been identified. Variations in headspace composition are also frequently compound-specific so concentrations of some species are decreasing while others are increasing. The complex effects of varying ventilation rates, air exchanges with connected tank headspaces, temperature-related effects on the rates of generation and release of volatile species, and other minor effects result in a moderate uncertainty in the headspace composition at any time.

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