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The objective of this document is to describe the physical mechanisms associated with vapor emissions from tanks, atmospheric dispersion, and receptor impacts within the context of short-duration vapor events reported by tank farm workers. The focus of this document is to present information that is currently known, from either literature or technical reports, and to describe the mechanisms by which workers may experience short-duration vapor concentrations above background in the tank farms environment.

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Short-Duration Vapor Concentrations in Worker Breathing Zones In and Near the Hanford Tank Farms: A Summary of Current Knowledge

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EXECUTIVE SUMMARY

Chemical vapor concerns have been expressed by workers on the Hanford Site for many years. During the spring of 2014, a number of workers reported chemical odors and/or symptoms and sought medical attention, which prompted Washington River Protection Solutions, LLC to pursue efforts to address concerns associated with Hanford tank vapors. Part of this effort included the development of the Savannah River National Laboratory Hanford Tank Vapor Assessment Team (TVAT) to provide an independent assessment and recommendations concerning reported vapors by tank farm workers. The assessment is summarized in a Tank Vapor Assessment Report.¹ Within that report, the team developed a hypothesis that “vapors coming out of tanks in high concentration (bolus²) plumes sporadically intersected with the breathing zones of workers, resulting in brief but intense exposures to some workers.”³ This is aligned with events reported by workers that are often described as lasting just a few seconds, and may include an olfactory response, symptoms, or both, while nearby co-workers may not express any abnormal experience.

The intent of the “bolus” term by TVAT may have been simply to describe short-duration elevated concentrations; however, the term has come to imply that workers were experiencing concentrations nearly as high as the headspace concentration, even if they were located many tens of feet from a tank source. The objective of this document, therefore, is to describe the physical mechanisms associated with vapor emissions from tanks, atmospheric dispersion, and receptor impacts within the context of short-duration vapor events reported by tank farm workers. The focus of this document is to present information that is currently known, from either literature or technical reports, and to describe the mechanisms by which workers may experience short-duration vapor concentrations above background in the tank farms environment.

Sources of tank vapors are both passively ventilated tank penetrations that are primarily passive breather filter risers, typically located 4 to 10 ft above the ground surface, and actively ventilated stacks, which are typically tens of feet above the ground. In the absence of waste disturbances, headspace concentrations are generally consistent over time, although the changing solubility of gas and vapor within the waste, which is driven by seasonal temperature ranges, may contribute to variability over long time periods. For waste-disturbing events, headspace concentrations have been observed to peak relatively quickly and rapidly return to previous levels after the waste-disturbing events are terminated. Physical processes within the tank were not found to drive short-duration emissions because emissions themselves are driven by either environmental conditions (in the case of passively ventilated stacks) or stack ventilation rates (in the case of actively ventilated stacks). This is also true in the case of buoyant displacement gas release

¹ SRNL-RP-2014-00791, 2014, *Hanford Tank Vapor Assessment Report*, Rev. 0, Savannah River National Laboratory, Aiken, South Carolina.

² There has been some confusion concerning the term bolus, in part because the term is primarily used in the medical field to describe a single drug dose administered within a specified time period. The term is not part of the standard language of industrial hygiene or atmospheric dispersion.

³ SRNL-RP-2014-00791, pg. 9.

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events that occur within five double-shell tanks (AN-103,⁴ AN-104, AN-105, AW-101, and SY-103).

Variability in meteorological conditions is the primary reason for the short-duration nature of vapor concentrations above background. When emissions are near the ground surface (e.g., passively ventilated risers), stable atmospheric conditions are expected to result in the highest concentrations in the worker breathing zone due to minimal mixing compared with other atmospheric conditions. At the Hanford Site, stable conditions occur approximately 50% of the time, most often during the winter months or between sunset and an hour after sunrise during all seasons. Recent quantitative risk analysis modeling used a set of six meteorological conditions that were expected to generate the highest concentrations and predicted that breathing-zone concentrations are a tenth or less of the source concentration⁵ within less than 2 m from the source and continue to decrease as the distance increases.

For emissions from elevated stacks, unstable conditions are expected to result in the highest breathing zone concentrations relative to the source concentrations as a result of mixing conditions that bring the plume down toward the ground surface. At the Hanford Site, unstable conditions occur approximately 23% of the time, most often during summer and daytime periods. Modeling has shown that, under conditions expected to produce the highest ground-level concentrations, plume transport from an elevated release to the ground-level worker breathing zone travels many tens of feet, over which a factor of 10 or more reduction of concentration occurs.^{6,7}

Area measurements corroborate the fact that worker breathing zone concentrations are a factor of 10 or more lower than source concentrations. Although the majority of sampling represents time-weighted averages that are minutes to hours in duration rather than short-duration peak concentrations, 98% of the ammonia area sampling measurements were below the detection limit.⁸ Where detections were identified in the area sampling measurements, ammonia concentrations were found to be approximately 10 to 100 times lower than the concentration maxima of the sources.⁹ The results from direct-reading monitoring instruments are consistent with area sampling,¹⁰ indicating that elevated concentrations in the relevant area surveys are rarely detected, often originate from solvent or paint use rather than tank vapors, and represent only 1 to 3% of the total area surveys since 2011.¹¹ Additionally, during March and April of

⁴ All Hanford Site tank and tank farm indicators begin with suffix '241-.' That suffix is omitted in this report to ease readability.

⁵ This paper does not attempt to discuss breathing zone concentrations relative to occupational exposure limits due to the variability of source characteristics (e.g., stack height, flow rates, tank headspace vapor concentrations). Instead, the paper focuses on the reduction in concentrations between the source and worker breathing zone. Examples of quantitative reductions relative to exposure limits and odor thresholds are provided in Section 4.3.

⁶ Kenexis 568.002-024:0, 2017, *Quantitative Risk Analysis, 241-AP*, Kenexis, Columbus, Ohio.

⁷ Kenexis 568.002-020:0, 2017, *Quantitative Risk Analysis, 241-AW*, Kenexis, Columbus, Ohio.

⁸ The detection limit for ammonia averaged less than 0.5 ppm. The maximum detection limit for samples without data quality issues was 2.2 ppm.

⁹ Ammonia concentrations from area sampling were all less than 1 ppm (Table 4-3).

¹⁰ Ammonia concentrations from direct reading instruments ranged from <1 ppm (0 reading) to a maximum of 10.2 ppm (Tables 4-3 and 4-4).

¹¹ Thousands of direct-reading instrument measurements have been recorded that generally support a key conclusion from risk analyses modeling that elevated concentration events in the breathing zone are infrequent. However, monitoring results to date may not adequately address all tank farm locations or meteorological conditions that have been considered through modeling.

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2017, several open-path spectroscopy instruments deployed within the A Tank Farm and around the AP Tank Farm as part of the vapor monitoring and detection system pilot-scale testing, simultaneously detected ammonia at low concentrations on several days for relatively short periods, ranging from 1 to 32 minutes. The concentration maxima, assuming the plume occupied the full 152-m path length of the instrument in the A Tank Farm, ranged from 0.05 to 0.19 ppm.¹²

While most of the historical data that are available for area concentration measurements are time-weighted average values, a mobile laboratory equipped with a proton-transfer-reaction mass spectrometer, CO₂ sensor, and ammonia sensor has been deployed for several measurement campaigns since 2016 and is now regularly deployed to provide continued area monitoring and to evaluate fugitive emissions sources. This new capability collects concentration data for a variety of chemical compounds at 2-second temporal resolution and is an effort to identify short-duration vapor emissions and potential worker exposures.

The TVAT concluded that the presence of elevated source concentrations (e.g., headspace) concurrent with abnormal operating procedure AOP-015¹³ events within the tank farm “provide clear testimony that exposures are to acute intense concentration.” It also states:

...while at this point in time there is little direct evidence of this linked temporal occurrence, it is believed that fugitive tank emissions always precede worker inhalation exposures. Lending credence to this temporal relationship is the co-occurrence of exposure events with low air speed on farms.¹⁴

Data from event investigation and earlier injury reports provides evidence that reported events (odor, symptoms, or both) encompass events inside and outside the tank farms, with and without symptoms, and frequently distant or upwind from tank sources. Although earlier events (pre-TVAT) were frequently reported as inside the tank farm, more recent reports are nearly equally split between inside and outside of a tank farm.¹⁵ Symptoms are reported in slightly more than half of the AOP-015 events. While the TVAT does not clearly define “acute intense concentration,” the TVAT does imply relatively high vapor concentrations and resulting symptoms of irritation or other effects.¹⁶

In short, both the empirical air monitoring and sampling data, as well as air modeling results, do not provide information that supports the TVAT hypothesis that have experienced concentrations approaching 80% of the tank headspace up to 10 ft from tank sources. The data indicate that the volume generated by releases within the tanks is not the driving force for flow rates out of the tank. The exhaust flow rates themselves are driven by either environmental conditions (passive-ventilation emissions) or exhauster ventilation rates (actively ventilated stacks). Variability in meteorological conditions is the primary driver for the short-duration nature and infrequency of vapor concentrations above background. Modeling indicates that concentrations are quickly

¹² Because the plumes were measured with multiple instruments, the plumes were likely large. However, if the plumes were narrower, the plume concentration would be higher. For example, the concentrations would range from 0.77 to 2.86 ppm if the plume were just 10 m wide.

¹³ AOP-015, 2017, *Response to Reported Odors or Unexpected Changes to Vapor Conditions*, Washington River Protection Solutions, LLC, Richland, Washington.

¹⁴ SRNL-RP-2014-00791, pg. 84.

¹⁵ Requirements for use of self-contained breathing apparatuses or full-face air purifying respirators within tank farms as well as reporting expectations have changed over time, which may have affected the distribution of AOP-015 events between inside and outside tank farms.

¹⁶ SRNL-RP-2014-00791, pg. 43.

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reduced from the source, and that the greatest upper end predicted concentrations at worker breathing zones are a factor of 10 or more lower than source concentrations. Area measurements corroborate the fact that worker breathing zone concentrations are 10 to 100 times lower than source concentrations, and events with elevated concentrations are rare. These vapor concentrations may still result in detectable odors and possible irritation depending on a worker's specific odor threshold and sensitivity to the chemical species. Short-duration vapor events may be mitigated by evaluating atmospheric conditions in conjunction with tank farm activities on a daily basis. Monitoring changing conditions related to tank vapors concentrations at the source and within worker breathing zone is also an important step to protect workers from short-duration elevated concentration events.

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LIST OF TERMS**Acronyms and Abbreviations**

BDGRE	buoyant displacement gas release event
CFD	computational fluid dynamics
COPC	chemical of potential concern
DAV	tank vapors data analysis and visualization explorer
DRI	direct-reading instrument
DST	double-shell tank
EIR	event investigation report
FDS	Fire Dynamics Simulator
FTIR	Fourier transfer infrared spectrometer
HEPA	high-efficiency particulate air
IH	industrial hygiene
NDMA	N-Nitrosodimethylamine
OEL	occupational exposure level
OP	open path
PBF	passive breather filter
PTRMS	proton-transfer-reaction mass spectrometer
QRA	quantitative risk analysis
RC	risk classification
SST	single-shell tank
SWIHD	Site-Wide Industrial Hygiene Database
TVAT	Tank Vapor Assessment Team
TWA	time-weighted average
TWINS	Tank Waste Information Network System
UV-DOAS	ultraviolet differential optical absorption spectrometer
VCZ	vapor control zone
VMDS	vapor monitoring and detection system
VOC	volatile organic compound
WRPS	Washington River Protection Solutions, LLC

Units

°C	degrees Celsius
°F	degrees Fahrenheit
µm	micrometer
ft	foot
ft ³	cubic feet
hr	hour
km	kilometer
m	meter
m ³	cubic meter

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mg	milligram
min	minute
mph	miles per hour
ppb	parts per billion
ppm	parts per million
sec	second

Note: Values in this report fluctuate between English and International System of Units (SI) units based on source.

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1.0 INTRODUCTION

Chemical vapor concerns have been expressed by workers on the Hanford Site for many years. During the spring of 2014, a number of workers reported chemical odors and/or symptoms and sought medical attention, which prompted Washington River Protection Solutions, LLC (WRPS) to pursue efforts to address the potential for worker exposures related to Hanford tank vapors. Part of this effort included the development of the Savannah River National Laboratory Hanford Tank Vapor Assessment Team (TVAT) to provide an independent analysis and recommendations concerning vapors exposures to tank farm workers. The assessment is summarized in SRNL-RP-2014-00791, *Hanford Tank Vapor Assessment Report*. Within that report, the team postulated:

...that vapors are coming out of the tank in high (bolus¹⁷) concentration plumes that sporadically intersect with the breathing zone of workers, such that the workers receive brief but intense exposures.

The term bolus was introduced to describe relatively high concentration emissions as well as relatively high-concentration, short-duration exposures.¹⁸

The basic description of bolus, as expressed by SRNL-RP-2014-00791, is aligned with worker descriptions of vapor events. These events are often described as lasting just a few seconds; it is sometimes noted that one worker may experience events, either through an olfactory response, symptoms, or both, while nearby co-workers may not express any abnormal experience.

The intent of the “bolus” term by TVAT may have been simply to describe short-duration elevated concentrations; however, the term has come to imply that workers were experiencing concentrations nearly as high as the headspace concentration even if they were located many tens of feet from a tank source. Although reports, analyses, and data collection have been performed to address the sources and concentrations of short-duration events, a summary that addresses these efforts and the current understanding, based on measurements and modeling, has not existed in a single document until now. The objective of this document, therefore, is to describe the physical mechanisms associated with vapor emissions from tanks, atmospheric dispersion, and receptor impacts within the context of short-duration vapor events reported by tank farm workers. The focus of this document is to present information that is currently known from literature or technical reports and to describe the mechanisms by which workers may experience relatively high concentration, short-duration vapor concentrations above background in the tank farm environment.

The TVAT offered four primary observations, summarized in Table 1-1, to support their bolus hypothesis. The table also identifies the sections of this report that specifically address these four observations and provides additional analysis to better inform the bolus hypothesis.

¹⁷ SRNL-RP-2014-00791 defines bolus exposure as: “an acute exposure to a relatively high concentration of airborne contaminants. Where time-weighted average exposures may be measured in tens of minutes to hours, bolus exposures are measured in seconds to tens of seconds. Bolus exposures can also cause an untoward health effect that is different from the effect caused by exposures metered out somewhat evenly over 8 hours.”

¹⁸ There has been some confusion concerning the term bolus, in part because the term is primarily used in the medical field to describe a single drug dose administered within a specified time period. The term is not part of the standard language of industrial hygiene or atmospheric dispersion.

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Table 1-1. Summary of TVAT Basis for Bolus Hypothesis and Section of this Report Addressing Each Basis.

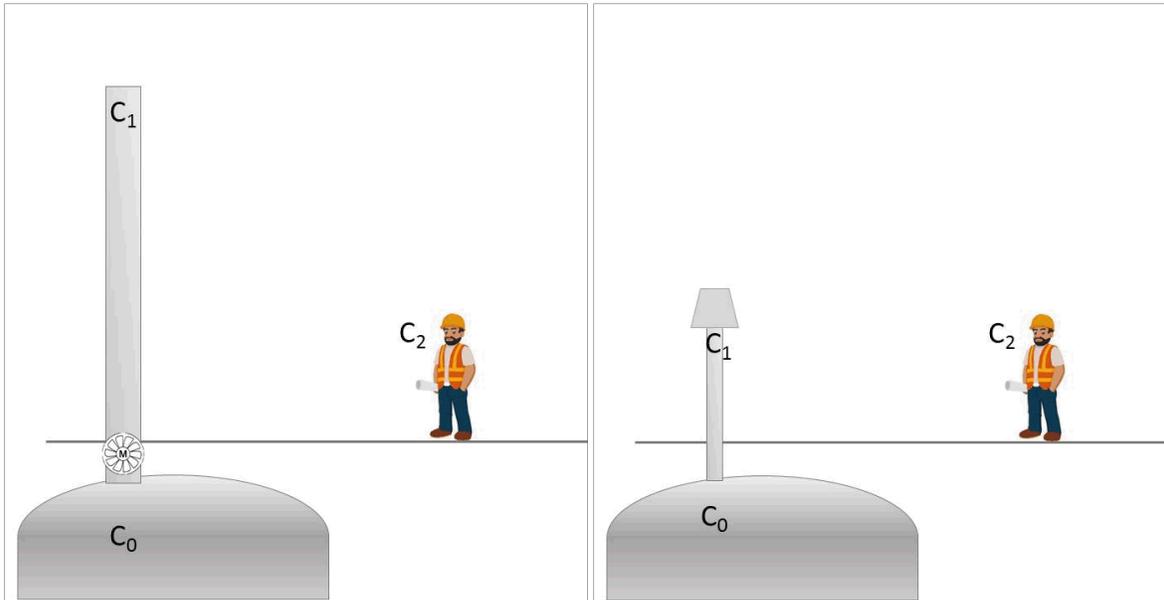
TVAT Basis	TVAT Report Excerpt	Section Addressed
Model results predicting elevated concentrations in breathing zone	“The hypothesis was substantiated by computer modeling, which indicated that under certain weather conditions, concentrations approaching 80% of the headspace concentration could exist 10 feet downwind from the release point and potentially in workers’ breathing zones.” (App. C, pg. 87)	Section 3.0 Limitations of the modeling referenced by TVAT are described. Additional risk assessment modeling that has been performed since 2014 demonstrated 10× to 100× reduction in concentrations from the source within several feet from the source.
Proximity and correlation of elevated irritant source concentrations with reported personnel exposures	Elevated direct-reading instrument source readings of ammonia and volatile organic compounds reported concurrent with AOP-015 reported symptoms of workers: “symptoms and signs reported only during times workers are physically on the tank farm.” (App. C, pg. 84) “...there is essentially a perfect correlation between the workers having an adverse acute inhalation health effect and being physically present on a tank farm.” (App. C, pgs. 84-85) “provide clear testimony that exposures are to acute intense concentration.” (Sect. 6, pg. 43)	Section 2.0 Section 4.0 The range of source concentrations, as well as the mechanisms for emissions from tanks are described along with analysis of available area measurement data. AOP-015 events with reported symptoms occurred equally inside and outside of the tank farms.
Fugitive tank emissions precede worker exposure	“Thus, while at this point in time there is little direct evidence of this linked temporal occurrence, it is believed that fugitive tank emissions always precede worker inhalation exposures. Lending credence to this temporal relationship is the co-occurrence of exposure events with low air speed on farms.” (App. C, pg. 84)	Section 4.0 Analysis of a wide range of exposure events and extensive monitoring data collected over decades provides evidence of tank and non-tank sources.
Correlation between exposures and tank farm presence	“symptoms and signs reported only during times workers are physically on the tank farm.” (App. C, pg. 84) “...there is essentially a perfect correlation between the workers having an adverse acute inhalation health effect and being physically present on a tank farm.” (App. C, pgs. 84-85)	Section 4.0 Analysis of two decades of vapor events provides evidence of odors and symptoms inside and outside of tank farms.

AOP-015, 2017, *Response to Reported Odors or Unexpected Changes to Vapor Conditions*.

The following sections describe the tank farm emission sources, including drivers for emissions and measured source concentrations as well as provide a discussion of the atmospheric dispersion mechanisms that may lead to instantaneous concentration levels that may be noticeable to workers. Additional discussion of measurements made in and around the tank farms is included. Left: Typically actively ventilated. Right: Typically passively ventilated.

Figure 1-1 presents a representation of the relevant concentrations that are considered in the context of these short-term elevated vapor concentration reports.

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Left: Typically actively ventilated. Right: Typically passively ventilated.

Figure 1-1. Illustration of Relevant Concentration Positions for an Elevated Emission Point and a Near-Surface Emission Point.

The objective of the discussions presented in Sections 2.0 through 4.0 is to explore typical and elevated concentrations at each of C0, C1, and C2 locations (from Left: Typically actively ventilated. Right: Typically passively ventilated).

Figure 1-1) to determine the range and frequency of concentrations, with the overall aim of understanding the conditions under which worker breathing zone concentrations (C2) may be elevated such that operational controls may be implemented. C2 may be within the bounds of a tank farm, adjacent to a tank farm, or within a neighboring tank farm. Finally, Section 5.0 presents a discussion to summarize our state of knowledge on this topic.

This document seeks to address the current understanding of tank and headspace chemistry, meteorological conditions that affect emissions, and the effect of emissions on the surrounding environment in which tank farm workers conduct their work. The ability to monitor for changing conditions related to tank vapor concentrations at the source and within worker breathing zones is also important to protect workers from short-duration elevated concentration events. Efforts at the tank farms are underway to address this, including monitoring for a sentinel chemical (e.g., ammonia) using direct-reading instruments to recognize concentration increases before tank vapors concentration levels reach harmful levels. Testing and evaluation of respirator cartridges on tank vapor mixtures has identified the key factors needed to appropriately select respirators and determine the service life of cartridges for specific applications. Additionally, coupling measurement data with meteorological measurements may allow Operations staff to take proactive steps to further protect workers. These protective measures are established through the Industrial Hygiene program exposure assessment process. Continued insight into tank dynamics, emissions, and potential impacts to workers will be gleaned as more measurements are made, both in continuous monitoring and measurement campaign modes. While focus is placed on characterizing tank emissions, additional efforts to

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understand locations, chemical identifications, and emission rates of fugitive emissions (e.g., sewers, diesel generators) are also underway.

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2.0 SOURCE CHARACTERISTICS

The Hanford tank farms have numerous atmospheric emissions sources, ranging from septic system vents and diesel generators to waste transfer structures and tank stacks. However, this report focuses specifically on tank vapors generated by tank waste. This section describes the sources of tank waste gases and vapors within the waste, their release from the waste into the tank headspace, and the mechanisms by which the headspace vents into the atmosphere.

The discussion is based on gas and vapor source data collection that began in the early 1990s. No new substantive chemical processes have been introduced into tank farms since the 1970s and the effect from ongoing operations (e.g., storage, evaporator campaigns, retrievals, waste transfers, chemical additions) are understood (RPP-21854, *Occurrence and Chemistry of Organic Compounds in Hanford Site Waste Tanks*). The data collected over the past decades reflect the effect of these operations and can be used to understand source characteristics. The chemical reactions creating the gases and vapors are slow, and the same compounds will continue to be produced until final waste disposal (RPP-21854). Headspace and ventilation stack source sampling over the last three decades corroborate waste chemistry, and the chemical vapors observed in the 1990s are the same compounds observed in the 2000s and 2010s (PNNL-25880, *Hanford Tank Vapors COPCs Update*; PNNL-26820, *Hanford Tank Vapor FY 2017 Chemicals of Potential Concern Update*).

Examples presented in this section represent the highest measurements made in quiescent tank headspaces or during a specific type of waste-disturbing event and should not be interpreted as typical results. Large gas and vapor releases during waste-disturbing activities depend on the quantity stored, the volume of waste disturbed, how rapid the waste is stirred or mixed, and whether the tank headspace is actively or passively ventilated. A separate report is being drafted to summarize the available vapor and gas data recorded during waste-disturbing activities.

2.1 GAS AND VAPOR RELEASE FROM WASTE

2.1.1 Gas and Vapor Storage

Within tanks, waste gases and vapor species are found in three forms: (1) dissolved in the aqueous waste, (2) retained in the settled solids as gas bubbles, or (3) organic hydrocarbon droplets adsorbed onto settled solids (PNNL-14831, *Overview of Hanford Site High-Level Waste Tank Gas and Vapor Dynamics*).

Most of the gas and vapor inventory within the tanks is found in solution in the aqueous liquid waste. The amount of any given species dissolved in the aqueous liquids depends heavily on its solubility in water. Ammonia is very water soluble. Retained gas sampling has shown that more than 97% of ammonia is stored in the liquid phase in tanks (PNNL-13000, *Retained Gas Sampling Results for the Flammable Gas Program*). Work in PNNL-14831 with tank SY-101 waste indicated that, for water-soluble organic compounds, only a small fraction of the total mass present in the waste was found in the retained gas; most of the mass was dissolved in waste liquid.

Gas species that are not water-soluble are predominantly found in the retained gas bubbles. For example, more than 99% of hydrogen and nitrogen was stored in the gas phase because gases

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generated in the liquid waste form bubbles when concentrations exceed the saturation limit. As more gas is generated, dissolved gas species diffuse to existing bubbles and cause them to expand existing bubbles or nucleate additional bubbles. Bubbles formed in the supernatant liquid are free to rise to the surface, producing a continuous release into the headspace. However, the gas bubbles that are formed in the interstitial liquid, in the pores of the settled solids, are constrained by the strength or pore structure of the surrounding material and may be retained for an indefinite period within the settled solids.

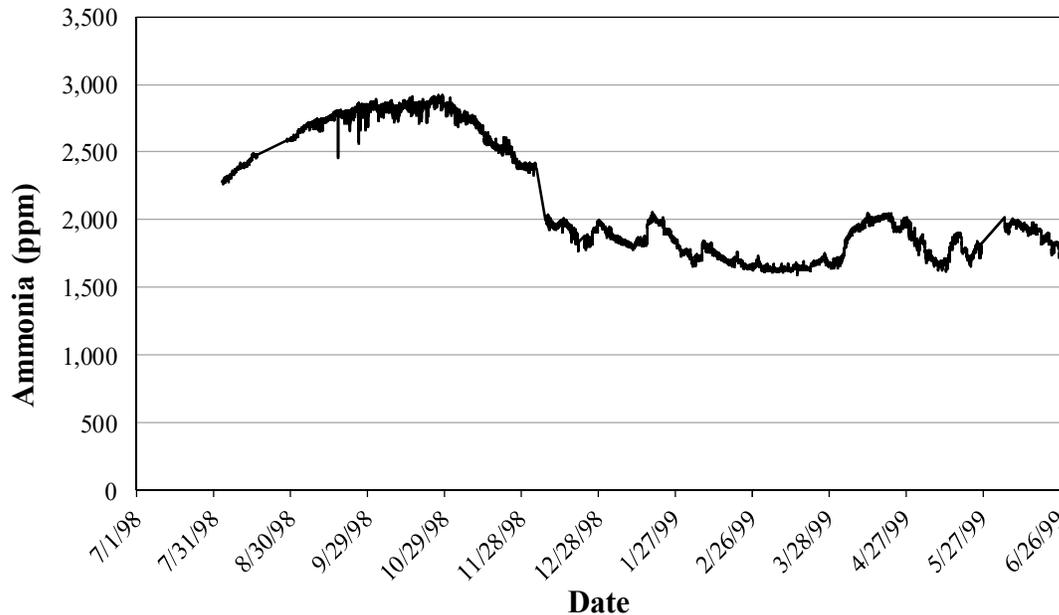
Residual organic liquid wastes from various Hanford separations processes exist in the tanks. Waste samples contain solvents that were used in processing, notably tributyl phosphate and the semi-volatile normal paraffinic hydrocarbon diluents as a separated organic liquid phase (PNNL-14831). In general, the organic liquid wastes are solutions of nonpolar species that tend to store nonpolar (hydrophobic) species better than the aqueous wastes. Nonpolar organic species that have exceeded their solubility in the aqueous phase will form a separate organic liquid phase and may take the form of a continuous layer on the surface of the supernatant, a coating on settled solids, or droplets attached to the solids.

2.1.2 Semi-Continuous Gas and Vapor Release

Rates at which gases and vapors are transferred to tank headspaces depend on where they originate and the configuration of waste between their origin and the headspace. Gases and vapors dissolved in liquid waste are transferred to the headspace via diffusion or convection to the supernatant/headspace interface, from which they enter the headspace by degassing. In settled solids layers, dissolved gases and vapors diffuse through the interstitial liquid from lower regions to the upper surface layer. Liquid-phase diffusion is relatively slow and settled solids make the diffusion path tortuous. The settled solid matrix decreases the cross-sectional area available for diffusive transport. Because the diffusing molecules must circumnavigate the solid particles and blocked pores, it effectively increases the distance that the diffusing molecules must travel. Soluble species release continuously from the waste surface; however, concentrations in interstitial liquid of the settled solids and any regions of non-convectively mixed supernatant liquid increase over time.

The headspace concentrations of species that are primarily present in solution (e.g., ammonia) vary over time as a result of changes in rates of release from the waste liquid and headspace ventilation rates. Seasonal changes in waste temperature change the solubility of species and affect releases to the headspace. Ventilation rates can vary because of operational changes (in actively ventilated tanks) or variation in meteorological conditions (for passively ventilated tanks). Gas and vapor data from passively ventilated tank headspaces, with quiescent waste, indicate less than factor of 10 change in concentration over time (RPP-22491, *Industrial Hygiene Chemical Vapor Technical Basis*). Figure 2-1 shows 1 year of continuous ammonia monitoring in the headspace of tank U-105 (a passively-ventilated, single-shell tank [SST]) during quiescent waste storage (HNF-SD-WM-TI-797, *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks*, Rev. 4). Ammonia concentration over the entire year varied by less than 40% from the mean.

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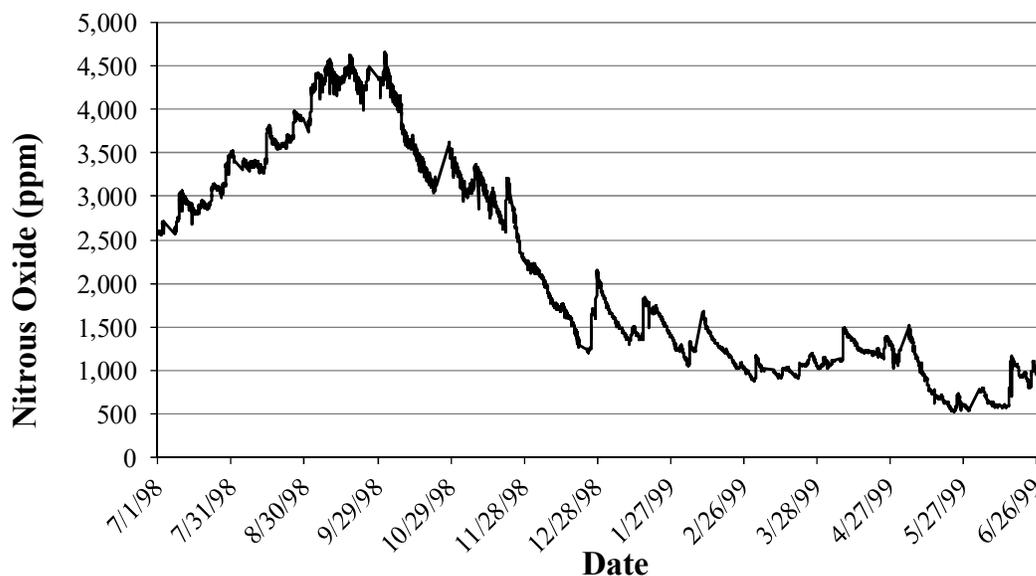
Data from HNF-SD-WM-TI-797, *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks*, Rev. 4.

Figure 2-1. Tank U-105 Ammonia Headspace Concentrations during Quiescent Waste Storage.

In the case of species that are not water soluble, releases to the headspace come not only from diffusion in the liquid, followed by evaporation, but from the escape of retained gas bubbles. One form of release is the free rise of bubbles generated within bulk liquid that has a surface open to the headspace, such as a supernatant layer. Bubbles also come from retained gas in the settled solids layers, most of which have reached a balance between non-soluble gas generation, gas retention, and gas release (RPP-10006, *Methodology and Calculations for the Assignment of Waste Groups for the Large Underground Waste Storage Tanks at the Hanford Site*). Bubble percolation is the dominant mechanism for gas transfer through the liquid-filled pores of the settled solids. Laboratory experiments and tank headspace continuous monitoring show gas percolation through settled solids is semi-continuous, which can cause day-to-day variations in headspace concentrations. Bubble percolation releases can be stimulated by decreases in barometric pressure, which cause the retained gas bubbles to expand in the pores.

Headspace monitoring data that were collected in the 1990s indicated that periodic small gas releases occur in tanks (HNF-SD-WM-TI-797, Rev. 2). Monitoring data indicated that these small gas releases typically increased the headspace concentration by less than a factor of 10 in SSTs. Figure 2-2 shows one year of continuous nitrous oxide monitoring in the SST U-105 headspace during quiescent waste storage. The maximum concentration (approximately 4,500 ppm) is approximately 9× that of the minimum (approximately 500 ppm) for the year.

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Data from HNF-SD-WM-TI-797, *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks*, Rev. 4.

Figure 2-2. Tank U-105 Nitrous Oxide Headspace Concentration during Quiescent Waste Storage.

2.1.3 Waste-Disturbing Activities and Gas Releases

Planned waste-disturbing activities currently performed in the tank farms include liquid waste transfers (both sending and receiving tanks), operating air lift circulators, solid waste retrievals (sluicing and dissolution), large water additions,¹⁹ and transfer pump recirculation. Five double-shell tanks (DST) (AN-103, AN-104, AN-105, AW-101 and SY-103) experience buoyant displacement gas release events (BDGRE), which are waste-disturbing activities that occur spontaneously (to be discussed further below within this section). Waste-disturbing activities can have significant temporary effects on headspace gas and vapor concentrations. Compounds that are present below detection limits in headspace samples during quiescent periods may be observed at elevated concentrations during waste-disturbing activities.²⁰

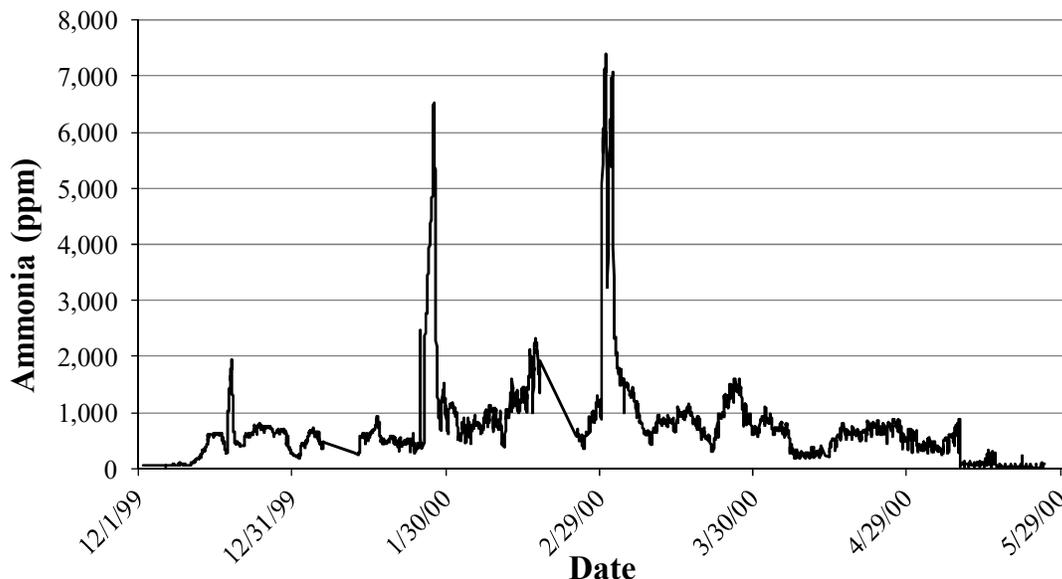
Large increases in headspace concentrations have been observed during liquid waste transfers. The highest ammonia concentration measured within tank farms headspaces was 7,400 ppm in the tank SY-102 headspace (an actively-ventilated DST) during a transfer from tank SY-101 (another actively-ventilated DST) in March 2000 (PNNL-13933, *Review of the Technical Basis of the Hydrogen Control Limit for Operations in Hanford Tank Farms*). Ammonia concentrations in the tank SY-102 headspace in early December 1999 had been between 50 and 70 ppm (see Figure 2-3). Liquid waste containing entrained air (from the siphon break in the tank SY-102 drop leg) was injected into the tank SY-102 supernatant layer in both late January and early March 2000. The relatively high ammonia concentration of 7,400 ppm was a result of mixing and stripping by these entrained air bubbles. This peak quickly dropped to about 3,500 ppm after 24 hours. The ammonia concentration in the headspace of the source tank,

¹⁹ Large water additions represent volumes that may cause a material increase in the concentrations of tank headspace gases and vapors.

²⁰ Tank farms workers employ respiratory protection during planned waste-disturbing activities.

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tank SY-101, peaked at 2,000 ppm during this transfer and quickly dropped to about 100 ppm after 24 hours (not shown).



Data from HNF-SD-WM-TI-797, *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks*, Rev. 5.

Figure 2-3. Tank SY-102 Headspace Ammonia Concentrations during Tank SY-101 Remediation.

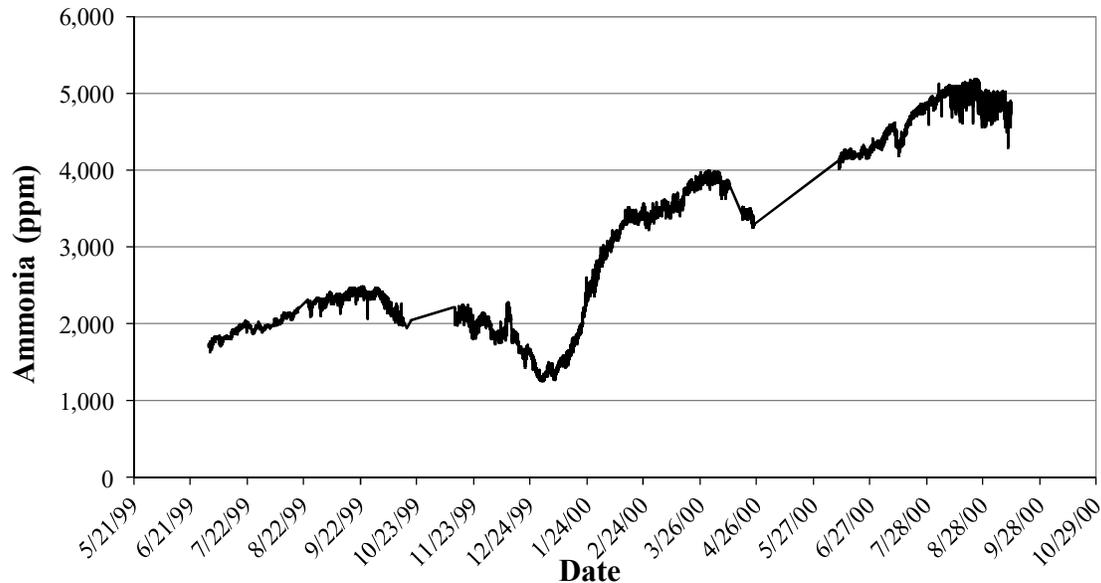
The next highest ammonia measurement in tank farms headspaces was 5,200 ppm after liquid waste transfers from tank U-105 (see Figure 2-4). Ammonia headspace concentrations slowly increased from a baseline of about 2,000 ppm to about 5,200 ppm from January to August 2000 as the higher concentration ammonia solution near the bottom of the tank was exposed to the headspace. Tank U-105 ammonia headspace concentration was about 2,600 ppm in December 2004 (not shown), a slightly higher quiescent concentration than before saltwell pumping. The return to a new baseline concentration after waste-disturbing activities appears to be more rapid in actively ventilated tank headspaces (see tank SY-102 data in Figure 2-3) than in the passively ventilated headspaces.

When organic liquid wastes such as extractants and their diluents are retained in the solid layers, their volatile decomposition products may be trapped within the solid matrix. This is important because intrusive operations (e.g., waste retrieval via sluicing) that mobilize settled solids can release significant quantities of trapped volatile species. This was demonstrated during tank C-106 waste retrieval when sluicing caused organic vapor concentrations to increase by a factor of 1,000 in some cases. Tank C-106 contained organic wash waste that was adsorbed onto the sludge waste solids. Organic vapor concentrations in the actively ventilated tank were low before retrieval; however, measurements made during sluicing showed increases of a factor of 1,000 in some chemical concentrations. For example, the nonpolar organic undecane was 0.00034 ppm on February 15, 1994 before retrieval activities began (Tank Waste Information Network System [TWINS]²¹), and the concentration peaked at 6.3 ppm on March 7, 1999 during

²¹ Accessible at <https://twins.labworks.org/twinsdata/Forms/About.aspx?subject=TWINS>.

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active sluicing (HNF-4261, *Origins of Volatile Organic Compounds Emerging from Tank 241-C-106 during Sluicing*).



Data from HNF-SD-WM-TI-797, *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks*, Rev.5.

Figure 2-4. Tank U-105 Headspace Ammonia Concentrations During Saltwell Pumping.

An example of increased gas release during recirculation is shown in Figure 2-5. The AP Tank Farm stack monitor detected increased nitrous oxide during recirculation in tank AP-107. The recirculation pump was operated for three consecutive days during off-shift hours beginning at 16:30 and stopping at 04:30 the next morning. From Figure 2-5, nitrous oxide concentrations increased for about 4 hours after the start of each recirculation activity, and then stayed relatively steady at 8 to 9 ppm²² until recirculation ended at 04:30. Concentrations started returning to baseline after 04:30 at a rate consistent with the tank AP-107 headspace ventilation rate. Ammonia stack concentrations also showed a similar response to the waste-disturbing activities, though on a much smaller scale. Ammonia stack concentrations increased from about 27 to 29 ppm during recirculation and returned to 27 ppm when the waste-disturbing activity ended (not shown). Tank AP-107 has negligible mercury inventory and there was no change in AP Tank Farm stack mercury concentrations during the recirculation.

²² The absolute concentration may not be accurate due to lack of calibration, but the timing and relative concentrations trends are representative of headspace response to the waste-disturbing activities under discussion.

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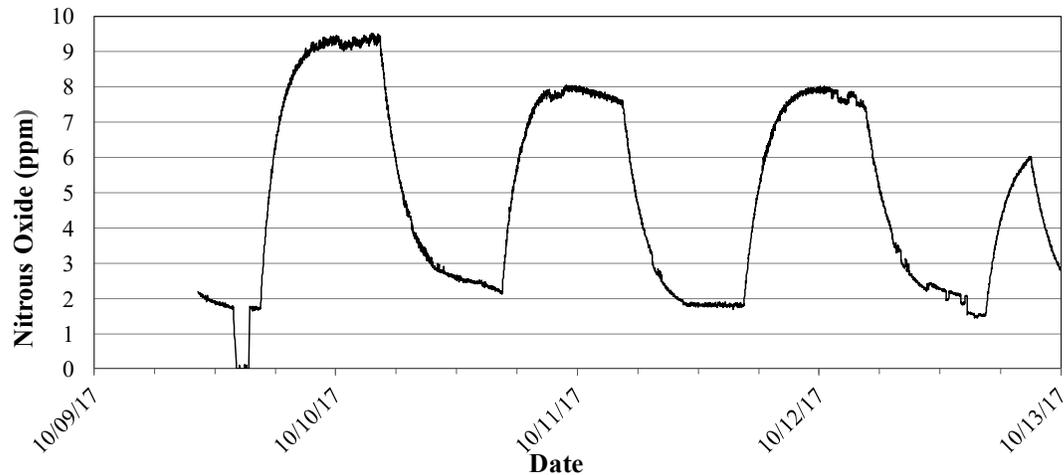
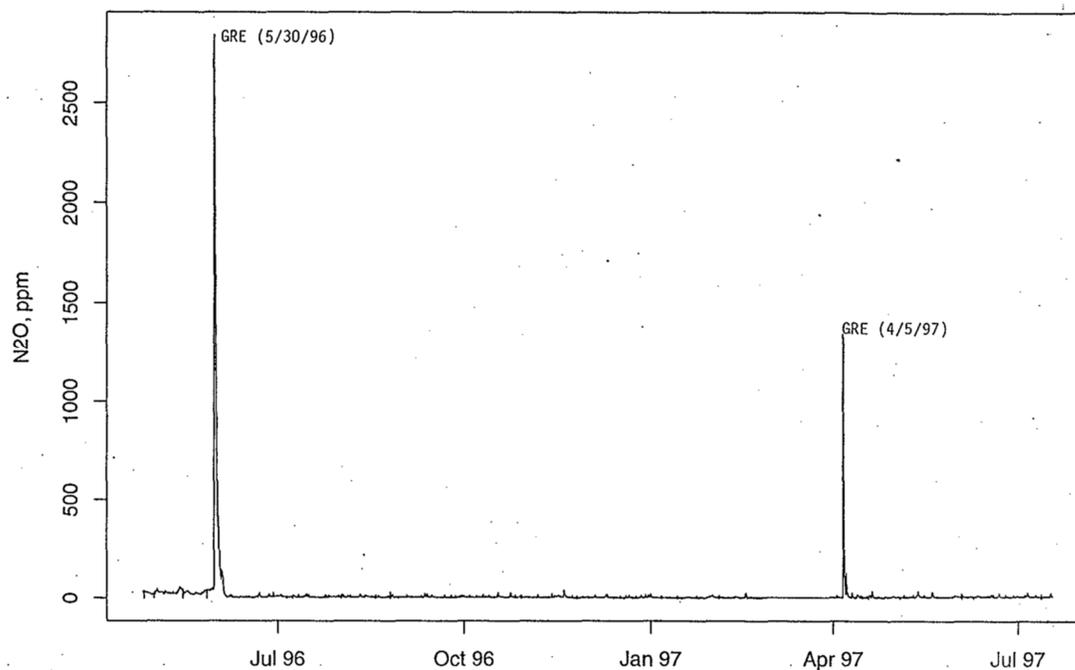


Figure 2-5. AP Tank Farm Stack Nitrous Oxide Concentration During Tank AP-107 Recirculation.

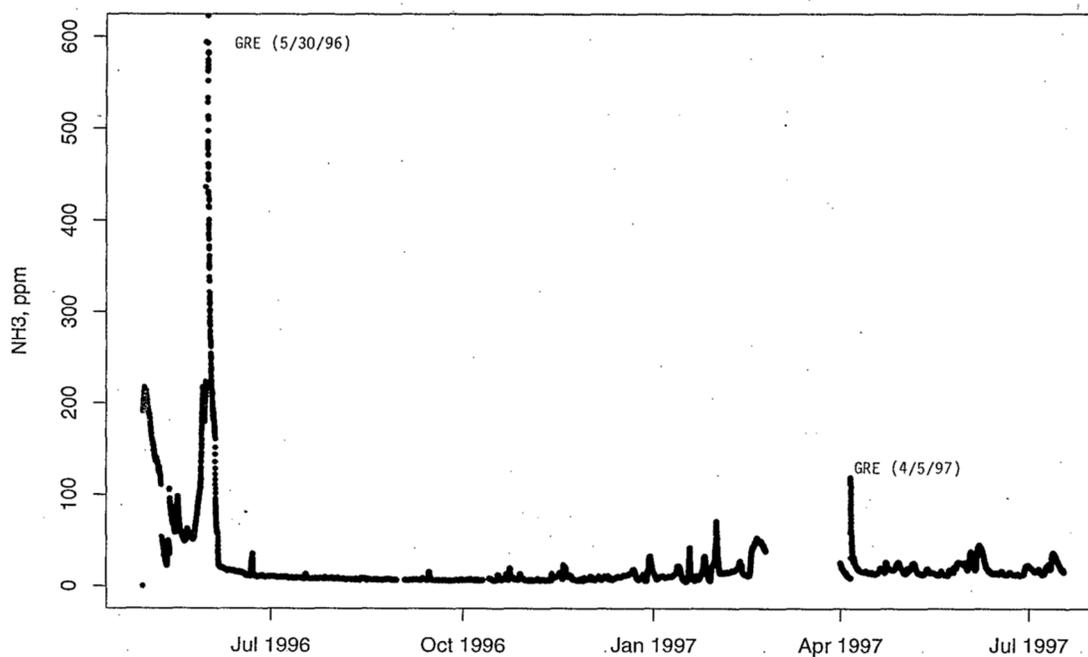
BDGREs are a form of waste-disturbing activity that may occur spontaneously within a limited number of waste tanks. BDGREs occur when a region of waste, which has been called a “gob” in past work, accumulates sufficient gas that it dislodges from the settled solids and breaks apart as it reaches the waste surface (RPP-10006). Nitrous oxide and other lower-solubility chemical species in the gas bubbles are released when the gob breaks apart. BDGREs cause vigorous mixing and release soluble species (e.g., ammonia) at the same time during this spontaneous waste-disturbing activity. BDGREs occur one to three times per year in five Hanford Site DSTs and do not occur in SSTs (RPP-10006). Figure 2-6 shows tank AN-105 headspace nitrous oxide concentrations after two BDGREs. Figure 2-7 shows ammonia headspace concentrations for the same two BDGREs. Figure 2-8 shows AN Tank Farm stack ammonia concentrations during approximately the same time span. The AN Tank Farm stack standard hydrogen monitoring system did not operate throughout the entire period shown but was operating in May 1996 and April 1997 during the BDGREs. The highest ammonia stack concentration measured over that year was 183 ppm (HNF-SD-WM-TI-797, Rev. 2) and did not approach the individual tank headspace maxima due to dilution with six other tank headspace concentrations.

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From HNF-SD-WM-TI-797, *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks*, Rev. 2.

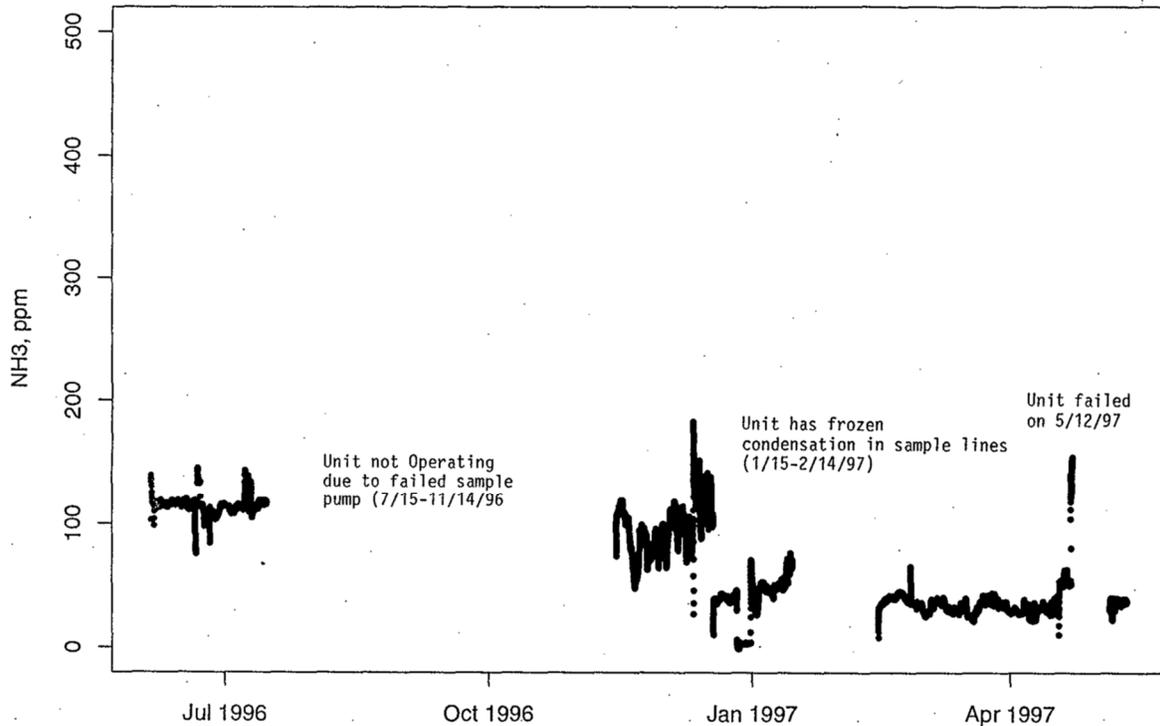
Figure 2-6. Tank AN-105 Headspace Nitrous Oxide after BDGREs.



From HNF-SD-WM-TI-797, *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks*, Rev. 2.

Figure 2-7. Tank AN-105 Headspace Ammonia Concentrations after BDGREs.

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From HNF-SD-WM-TI-797, *Results of Vapor Space Monitoring of Flammable Gas Watch List Tanks*, Rev. 2.

Figure 2-8. AN Tank Farm Stack Ammonia Concentrations after BDGRes.

2.2 PASSIVE VENTILATION

On each of the 149 SSTs, the primary point of release is the ventilation riser that allows air exchange between the tank headspace and the atmosphere. The filters on these risers are referred to as passive breather filters (PBF). Other points of near-ground-level passive release also exist; these include but are not limited to flanges, pits, and instrument cabinets.

Figure 2-9 shows an example of both the riser design with radial PBFs (on 142 tanks) and the older-style G-1 PBFs (on seven tanks). Most ventilation risers are between 2 and 6 ft in height, but some are as high as 19 ft. Ventilation risers serve two purposes: (1) ensuring that the tanks do not pressurize and (2) allowing passive air exchange that effectively purges the headspaces and limits flammable gas concentrations. In addition to the filtered ventilation riser, most SSTs are connected via underground pipes to other SSTs. These connections are typically 3- or 4-in.-diameter cascade lines, but in some tank farms there are also large underground ventilation systems that facilitate air exchanges between tanks (e.g., SSTs in the A Tank Farm are each connected to a 20-in.-diameter underground ventilation manifold). Where interconnections are present, air exchanges occur between one tank headspace and another as well as between the headspace and the atmosphere.

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Left: With attached breather filter and weather protection hood. Right: Older-style riser with filter.

Figure 2-9. Typical Single-Shell Tank Riser.

Tank headspace passive ventilation is governed by three general driving forces (PNNL-14831):

- **Barometric pressure changes** – Changes in static barometric pressures create slight, transient pressure imbalances that either push air into the tank or draw it out (ARH-CD-256, *Anticipated Natural Air Breathing Rates for Underground Tanks*; WHC-EP-0651, *Barometric Pressure Variations*). A tank with only one vent can respond to barometric pressure increases with an inflow of air, and to decreases with an outflow of headspace gas. The magnitude of this effect is easily estimated, and it is the best understood of the identified passive ventilation motive forces.
- **Buoyancy forces** – Ambient air that is colder than the headspace can cause convective transport of the cold, dense air down into the headspace, and the warm, less dense headspace air out into the atmosphere. This “chimney effect” depends on the number and configuration of ventilation pathways and is less easily calculated than barometric pressure-driven air exchange. Additionally, buoyant gas (e.g., hydrogen) may also result in emissions through a riser, though this is not a dominant effect on buoyancy. Given two independent air pathways into a headspace (e.g., the filtered ventilation riser and an open cascade line to another tank headspace), differences between headspace and external buoyancy can sustain simultaneous air flow into and gas flow out of the headspace.

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- **Wind-generated pressures** – The interaction of wind with the vents, pits, risers, etc. of the tanks 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 that can lead to headspace gas releases even from single-vented tanks, and (2) a pressure differential-driven circulation that requires multiple ventilation paths (e.g., connections with other tanks, cracks, open access ports) and supports simultaneous air flow into and gas flow out of the headspace. When wind impinges on an obstruction, 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. 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 (2) the down-facing vent openings that are typically perpendicular to the direction of the wind. Also, the presence of significant flow obstructions directly upwind (e.g., instrument buildings, electrical panels) can reduce the local wind speed but also generate a local area of negative dynamic pressure in the wake of the obstruction. The venturi effect on passive ventilation is not easily calculated because it depends on the wind direction and the nature of upwind structures as well as wind speed.

These driving forces act in interdependent ways to drive or impede passive tank ventilation. Depending on ambient conditions, the forces can act together or in opposing ways, causing each tank to alternately inhale and exhale air or induce continuous airflows between two or more tanks. Note also that barometric pressure fluctuations cannot by themselves sustain air flow in or out of the tank because the magnitude of the barometric pressure induced flow is often quite small. However, given two independent air pathways into a headspace (e.g., the filtered ventilation riser and an open cascade line to another tank headspace), the chimney effect can sustain simultaneous airflows into and out of the headspace as long as the ambient air is cooler than the headspace.

The behavior of passive ventilation was analyzed using ammonia concentration data collected for other purposes from May through July 2018 at the PBF on tank A-103. These data had not been collected for monitoring purposes and the experimental design did not allow for an evaluation of the way in which meteorological conditions correlated with the magnitudes of observed peaks. In addition, the size of the volumetric release rate could not be inferred. However, the presence and timing of concentration peaks at the PBF could be used as evidence of whether headspace gases were flowing out through the tank A-103 PBF, and of what conditions were associated with the peaks.

The details of the data collection and analysis are given in Section A2.0 of Appendix A. In summary, the most readily observed relationship between gas outflow through the PBF and meteorological conditions was associated with decreases in barometric pressure. Figure 2-10 shows ammonia concentration measured at the tank A-103 PBF and the corresponding barometric pressure data during the test period. The light red (lighter) shaded areas are periods when the barometric pressure was falling, and the blue (darker) shaded areas are periods when

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the barometric pressure was increasing or flat.²³ For most cases, the ammonia concentration peaked within the red shaded area and was declining or zero in the blue shaded area with an increase in barometric pressure. Barometric pressure reductions, which are also typically accompanied by wind speed increases, were associated with tank A-103 vapor emissions during the test period.

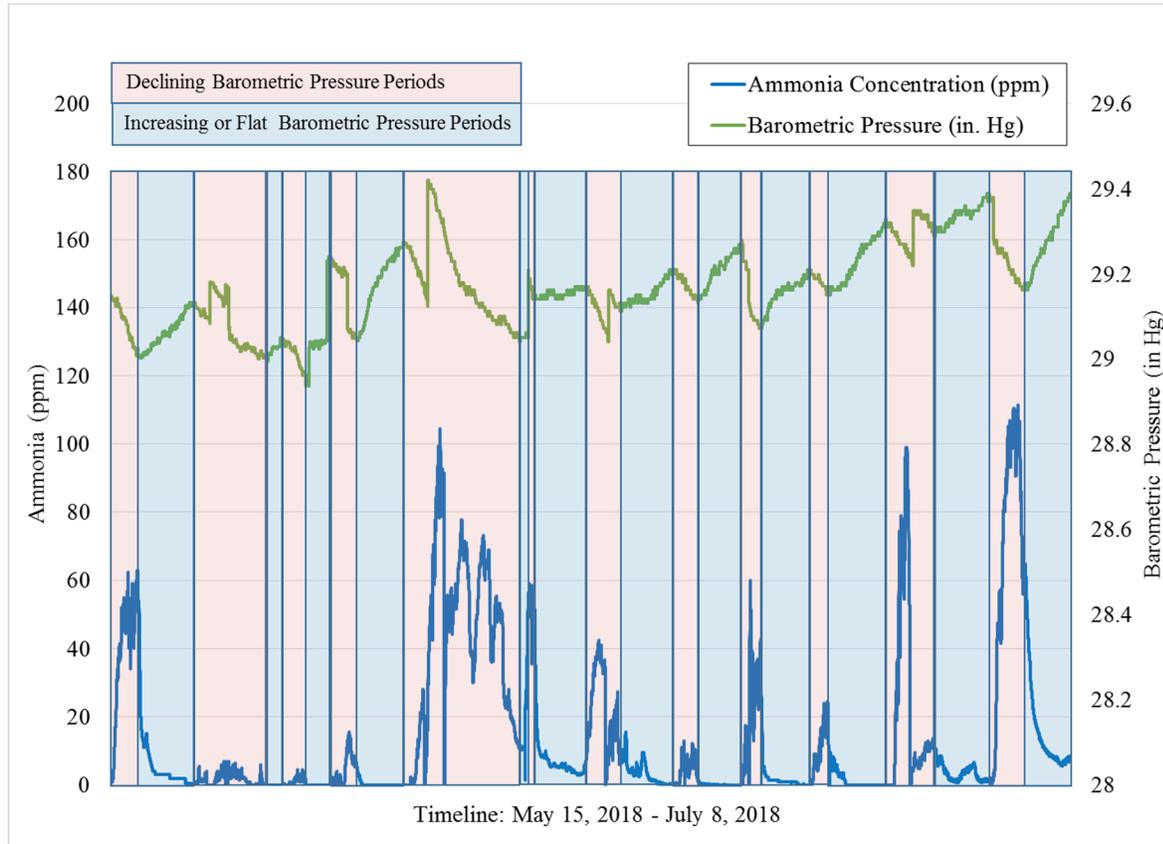


Figure 2-10. Ammonia Concentration Peaking at the Tank A-103 PBF Compared to Barometric Pressure.

The ammonia concentration trends were also compared to wind speed (venturi effect) and ambient temperature (buoyancy-induced flow). The periods of peak ammonia concentration were distributed equally among low (0 to 10 mph), medium (10 to 20 mph) and high (>30 mph) wind velocity periods, indicating that the venturi effect was not observably related for tank emissions for the tank A-103 PBF during the test period. It was also noted that the effect of ambient temperature was not as expected: tank A-103 exhaust tended to increase, rather than decrease, with increasing outside air temperature. The fact that periods of barometric pressure decrease tended to coincide with higher temperatures left it unclear whether higher temperatures had any independent relationship to tank A-103 PBF emissions during the test period.

In general, passive ventilation rates have not been measured directly because air flow rates tend to be low and variable (air flow can occur in both directions through the PBFs) and because

²³ The data shown in Figure 2-10 are not continuous over the time period indicated; there are gaps in the x-axis. Large vertical jumps in the data are due to discontinuities in the data timing; they do not indicate instantaneous changes in barometric pressure or ammonia concentration.

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some air flow occurs via inaccessible pathways (e.g., buried cascade lines that connect the tank headspaces). The best current estimates of passive ventilation rates are based on an indirect method that relates measured changes in the concentration of a headspace gas to the ventilation rate. This technique has been applied to headspace gases that are sporadically released by the waste (HNF-SD-WM-TI-797, Rev. 2; PNNL-11926, *Ventilation Rates Calculated from Hydrogen Release Data in Tanks Equipped with Standard Hydrogen Monitoring Systems [SHMS]*) and to tracer gases injected into the headspace for the purpose of estimating ventilation rates (PNNL-11683, *Measurements of Waste Tank Passive Ventilation Rates Using Tracer Gases*; PNNL-13029, *Gas Release during Saltwell Pumping: Interpretation of Operational Data*). Testing was completed on tanks with the older-style riser shown in the right panel of Figure 2-9; for lack of other information, results are assumed to be similar for the other filter configuration.

Table 2-1 lists the estimated average passive ventilation rates from tracer gas studies. Passive ventilation rates (in the second column of the table) are significantly higher than those that can be directly attributed to barometric pressure fluctuations alone, which are presented in the last column. The average ventilation rate generated by changes in barometric pressure is a function of the volume (included in the third column) and the average barometric pressure change of 0.45% per day (RPP-5926, *Steady-State Flammable Gas Release Rate Calculation and Lower Flammability Level Evaluation for Hanford Tank Waste*).

The passive ventilation rates in Table 2-1 represent averages over weeks to months; however, there can be more than a factor of 100 difference day-to-day. Additional data included in this table are the mean residence times, which range from 3.4 days to 52 days, and the headspace temperature, which is included as an indicator of passive ventilation driven by differential temperatures between the headspace and the atmosphere.

Table 2-2 shows results from the SST S-106 studies where daily tracer gas concentrations were measured and compared. The lowest daily-average passive ventilation rate was 0.1 ft³/min and the highest was 24 ft³/min. This shows that there is significant day-to-day variation possible in net passive ventilation rates, which may include both airflow into the riser as well as airflow out of the riser. Inflow, which was not quantified, would have caused dilution of the tracer used to measure these flows.

2.3 ACTIVE VENTILATION

Active ventilation is applied to all DST headspaces and to any SST headspaces that are undergoing waste retrieval operations. When active ventilation is off, the affected tanks are passively ventilated via their filtered air inlets. Without the exhauster to provide a slight negative pressure in the headspace, emissions may occur from these filtered inlets (as with PBFs) and from other points, including pits, flanges, and instrument cabinets. However, both the filtered stack and other emissions will initially be at the low headspace concentrations produced by the high air inflow rate of active ventilation. Concentrations within DSTs tied to an exhauster that has been shut down will increase until it reaches equilibrium concentrations; at that point, concentrations are expected to be similar to SST headspaces.

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Table 2-1. Average Passive Ventilation Rates, Barometric Rates, and Mean Residence Times.

Tank	Average Passive Ventilation Rate^a (ft³/min)	Headspace Volume^b (ft³)	Calculated Mean Residence Time (days)	Headspace Temperature^c (°F)	Average Barometric Rate (ft³/min)
A-101	10	49,328	3.4	97	0.15
AX-102	16	174,876	7.6	77	0.55
AX-103	25	163,480	4.5	87	0.51
BY-105	16	78,325	3.4	71	0.24
C-107	1.1	82,673	52	101	0.26
S-102	2.2	64,999	21	85 to 75	0.20
S-106	9.7	80,072	5.7	66	0.25
TX-104	3.5	128,322	26	65	0.40
U-102	2.1	60,248	20	73 to 70	0.19
U-103	1.6	47,749	14	79 to 75	0.15
U-105	5.0	53,631	7.4	77 to 79	0.17
U-106	1.3	80,467	43	73 to 70	0.25
U-111	1.9	66,497	24	72 to 68	0.21

(a) Data from PNNL-11683, *Measurements of Waste Tank Passive Ventilation Rates Using Tracer Gases*; PNNL-11925, *Waste Tank Ventilation Rates Measured with a Tracer Gas Method*; and PNNL-13029, *Gas Release during Saltwell Pumping: Interpretation of Operational Data*.

(b) Total volumes calculated by subtracting waste volume at time of test from total tank volume.

(c) Shorter duration tracer gas studies showed negligible changes in headspace temperatures while longer-term studies over weeks to months showed a range of headspace temperature from the start to the end of the tests.

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Table 2-2. Single-Shell Tank S-106 Daily Average Passive Ventilation Rates.

Date	Ventilation Rate (ft ³ /min)	Date	Ventilation Rate (ft ³ /min)
4/16/1999	10.7	5/19/1999	8.8
4/17/1999	8.4	5/20/1999	14.6
4/18/1999	7.0	5/21/1999	12.5
4/19/1999	6.4	5/22/1999	6.0
4/20/1999	8.8	5/23/1999	15.8
4/21/1999	8.2	5/24/1999	3.0
4/22/1999	9.3	5/25/1999	24.0
4/23/1999	8.2	5/26/1999	15.7
4/24/1999	6.8	5/27/1999	3.2
4/25/1999	12.7	5/28/1999	15.4
4/26/1999	11.9	5/29/1999	13.0
4/27/1999	11.9	5/30/1999	12.9
4/28/1999	11.1	5/31/1999	12.9
4/29/1999	12.2	6/1/1999	12.4
4/30/1999	5.9	6/2/1999	6.4
5/01/1999	19.2	6/3/1999	5.2
5/02/1999	3.6	6/4/1999	11.5
5/03/1999	12.0	6/5/1999	7.2
5/04/1999	14.5	6/6/1999	0.1
5/05/1999	8.5	6/7/1999	9.1
5/06/1999	10.2	6/8/1999	6.5
---	---	6/9/1999	6.7
---	---	6/10/1999	5.8
---	---	6/11/1999	0.6
---	---	6/12/1999	7.9
---	---	6/13/1999	12.1

From PNNL-13029, *Gas Release during Saltwell Pumping: Interpretation of Operational Data.*

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Active ventilation typically exhausts all tanks in a tank farm simultaneously. Each tank is equipped with a filtered inlet and a single exhaust outlet. The outlets from each tank join a common manifold that is connected to the tank farm exhauster. The actively ventilated waste tank exhauster stacks are elevated to reduce the concentration of gases and vapors in the worker breathing zone (Figure 2-11). The exhaust velocity enhances mixing and dilution in the atmosphere. Because the rates at which gases and vapors are released from the waste are usually independent of their headspace concentrations (see example below), active ventilation also ensures continuous headspace dilution.



Figure 2-11. AP Tank Farm Double-Shell Tank Exhauster.

The decrease in gas and vapor concentrations when moving from passive to active ventilation is demonstrated by data collected in the AX Tank Farm. In November and December of 2014 when the tanks were only passively ventilated, AX-101, AX-102, AX-103, and AX-104 headspace ammonia concentrations measured 94, 8, 5, and <0.7 ppm, respectively (TWINS). From Table 2-1, average passive ventilation rates in the AX Tank Farm tank headspaces was about 20 ft³/min. Active ventilation (about 900 ft³/min) was placed in the tank farm on March 15, 2017. Two exhausters (POR136 and POR127) were installed, and typically only one exhauster is operated at a time. The configuration allows for flow through of one to four tanks at a time. The next time stack samples were taken from the AX Tank Farm exhauster, all four AX Tank Farm tanks were being ventilated simultaneously and ammonia concentrations in the

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stack measured 2.4 and 3.2 ppm on October 27, and October 28, 2017, respectively, which results in an average of 2.8 ppm.

Based on the conditions described in the previous paragraph, the ammonia concentrations from the individual tanks under passive ventilation and the ammonia concentration from the stack under active ventilation are used to compare the resulting flow rates of ammonia. The calculation below shows that the total ammonia volumetric flow rate under passive ventilation was about 0.0021 ft³ NH₃/min. Under active ventilation, the total ammonia volumetric flow rate remained about the same, approximately 0.0025 ft³ NH₃/min. This indicates that about a factor of 10 increase in ventilation rate resulted in about a factor of 10 decrease in overall ammonia concentration. (The average passive ventilation concentration was (94+8+5ppm/3) = 35.6 ppm, compared with the average active ventilation concentration of 2.8 ppm.) Because of the design and operation of the active ventilation, changes in headspace concentration of one or more tanks in the system do not result in a proportional increase in the stack concentration due to dilution from the rest of the system. An example of tank AN-105 (a BDGRE tank) and the AN Tank Farm exhaustor was discussed in Section 2.1.3.

$$Q_{\text{NH}_3 \text{ Passive}} = \left(\frac{20 \text{ ft}^3 \text{ total}}{\text{min}} \right) \left(\frac{0.000094 \text{ ft}^3 \text{ NH}_3}{\text{ft}^3 \text{ total}} \right) + \left(\frac{16 \text{ ft}^3 \text{ total}}{\text{min}} \right) \left(\frac{0.000008 \text{ ft}^3 \text{ NH}_3}{\text{ft}^3 \text{ total}} \right) + \left(\frac{25 \text{ ft}^3 \text{ total}}{\text{min}} \right) \left(\frac{0.000005 \text{ ft}^3 \text{ NH}_3}{\text{ft}^3 \text{ total}} \right) \approx \frac{0.0021 \text{ ft}^3 \text{ NH}_3}{\text{min}}$$

$$Q_{\text{NH}_3 \text{ Active}} = \left(\frac{900 \text{ ft}^3 \text{ total}}{\text{min}} \right) \left(\frac{0.0000028 \text{ ft}^3 \text{ NH}_3}{\text{ft}^3 \text{ total}} \right) \approx \frac{0.0025 \text{ ft}^3 \text{ NH}_3}{\text{min}}$$

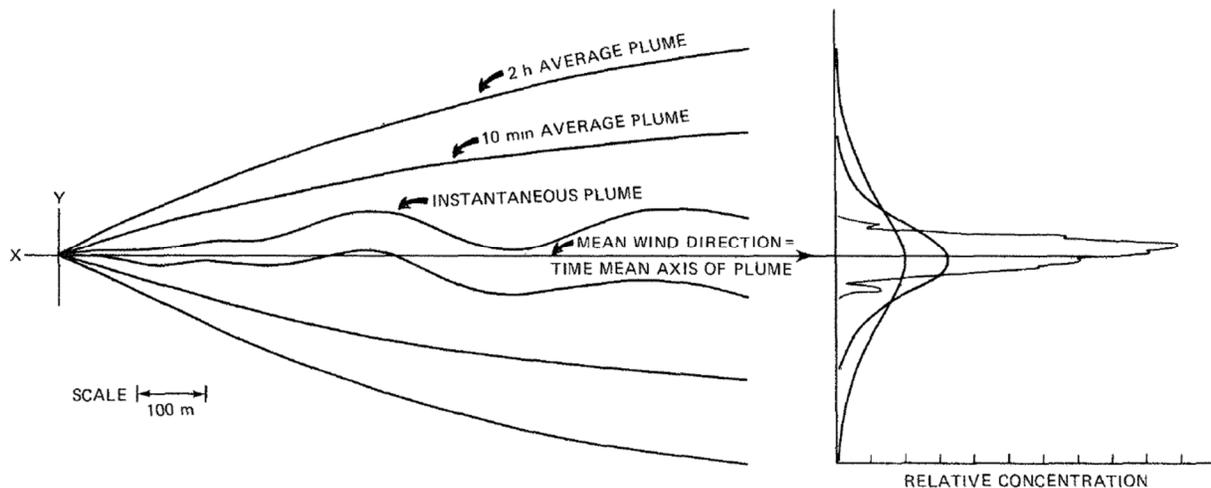
Not all DST ventilation systems operate identically. For example, in the combined AY/AZ system (702-AZ), air can be recycled with a small purge volume discharged from a forced ventilation stack. In some tank farms substantial dilution is achieved by inlet of ambient air and exhaust from forced ventilation stacks. Headspace and discharged concentrations would be proportionally higher if less dilution air is supplied.

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3.0 ATMOSPHERIC DISPERSION

The atmosphere acts upon the various emissions that exist in the Hanford tank farms to transport and diffuse material from the emission point to a receptor (i.e., person or instrument). The combination of transport and turbulence-induced diffusion is referred to as dispersion. The amount of dispersion that occurs is a function of source characteristics (e.g., ventilation rate, waste temperature, source geometry), as well as atmospheric conditions, which may vary in both time and space. Atmospheric conditions include ambient temperature, wind speed, mixing height, stability, and turbulence characteristics (e.g., terrain, structures, solar heating, wind speed/direction variability). Chemical or physical properties of tank farms emissions are generally negligible at the concentration levels of tank farms emissions.

Elevated concentrations of short duration at a given receptor position may occur as a result of transient releases. More commonly they result from continuous slowly varying releases, combined with atmospheric dispersion conditions (e.g., fumigation or meander) that shift the bulk of the plume vertically or laterally and lead to peak short-duration concentrations. These transient concentrations may also occur when a worker happens to be located within the instantaneous plume, which tends to be narrow with significant concentration gradients. Figure 3-1 illustrates an instantaneous plume and shows its width and relative concentration compared with time-averaged plumes. Concentrations within the instantaneous plume are often significantly higher than the time-averaged plume, and the concentration values are not smoothly distributed from the centerline to the edges, as is seen with the time-averaged plume. Hour-long averages of plume concentration can be a factor of 10 lower than the local instantaneous concentration (EPA 1970, *Workbook of Atmospheric Dispersion Estimates: An Introduction to Dispersion Modeling*).



From DOE/TIC-27601, *Atmospheric Science and Power Production*.

Note: The left panel represent a plan view of the plume, while the right panel represents the cross-plume concentration distribution.

Figure 3-1. Comparison of Instantaneous and Time-Averaged Plumes.

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The mechanisms that produce turbulent diffusion are the reason for the irregular concentration distribution. The turbulence that is present in the atmosphere even at near-calm wind speeds is a complicated and partly random set of air movements at scales that cover the range from tens of meters down to about a millimeter. Gas released into the atmosphere therefore is locally sheared until the fine structure of the instantaneous plume becomes a loose conglomeration of strands of higher-concentration release gas separated from each other by air (Jones 1983, "On the Structure of Instantaneous Plumes in the Atmosphere"). As a result, at a point in space inside a plume, the concentration distribution appears as an intermittent series of bursts of concentrations that are high relative to the plume average, separated by periods of concentration well below the plume average. Although near the source the individual strands inhaled or otherwise experienced by a worker might not be far diluted from the source concentration, the air between the strands would provide some dilution. Thus, the plume concentration over the course of a breath, a few seconds, is necessarily lower than the source concentration because transport and dispersion mechanisms produce some dilution. Computational fluid dynamics (CFD) modeling can provide some assistance in calculating the higher-than-average instantaneous concentration, and limited CFD results for 2-second predictions of concentration are presented later in this section.

The differences between the instantaneous peak concentration and the time-averaged concentration are greatest near the source, while the ratio between these concentrations approaches unity at large distances (EPA 1970). As discussed in PNNL-14767, *Characterization of the Near-Field Transport and Dispersion of Vapors Released from the Headspaces of Hanford Site Underground Storage Tanks*, the Ramsdell and Hinds (1971), "Concentration Fluctuations and Peak-to-Mean Concentration ratios in Plumes from a Ground-Level Continuous Point Source," carried out ^{85}Kr tracer tests at ground level on the Hanford Site, using release durations of about 15 minutes and a sampling period of 38.4 seconds. Samples were collected at 200 and 800 m from the source, under four different combinations of wind speed and stability. The peak-to-mean ratio for fluctuations – the local 38-second peak concentration divided by the local average concentration during plume passage – was <4 near the center of the plume and 10 to 12 at the lateral edge of the plume. Thus, the peak-to-mean ratios were highest in the parts of the plume where the absolute concentration was lowest. Ramsdell and Hinds (1971) does not give either the source concentration or the ratios of average concentration to source concentration at the two distances.

A literature search was conducted for this report and did not find references that described concentration fluctuations within 50 m or less of a source. Jones (1983) made measurements within 15 m of a source by using ionized air as a tracer, but it appears that his dispersion results are better explained by ionic repulsion than by atmospheric dispersion and may not be generally applicable. Other work has been done with tracer releases in water in small-scale flumes, or in air in wind tunnels, but it is not clear how to scale these results to atmospheric dispersion in the field. In addition, laboratory tests are limited to neutral stability conditions, and do not include other stabilities that are likely to be more important in the field.

Section 3.1 describes the Hanford Site climatology to aid in the discussion of peak concentrations for ground-level sources and elevated sources. The height difference between the source and receptor is an important factor in the potential maximum concentration at the receptor, as well as the conditions under which that maximum is most likely to occur, so discussions are separated between the two source heights. Section 3.2 gives an overview of dispersion models and their applications. Additional modeling results that are specific to source

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heights are described in the following sections. Section 3.3 discusses releases from near-ground sources (e.g., the filtered risers on passively-ventilated tanks), and Section 0 discusses the elevated releases from exhauster stacks.

3.1 HANFORD SITE METEOROLOGICAL CONDITIONS

Twenty-nine meteorological stations are distributed across the Hanford Site and beyond to support environmental studies, planning operations, consequence assessment, and emergency response. Table 3-1 and Table 3-2 present joint frequency distributions of the wind speed and wind direction from the Hanford Meteorological Network 200 East and 200 West Stations, respectively. Each numerical value in these tables represents the percentage of time when the given wind direction (column headings) and wind speed (row labels) combination was observed at that location based on 23 years of measurement data. These data are the most current summary of wind speed and wind directions available for these sites; no joint frequency summaries of Hanford station winds have been produced since PNNL-15160, *Hanford Site Climatological Summary 2004 with Historical Data*.

Table 3-1. Joint Frequency Distribution for the 200 East Station.

Station: (6) 200E																		
Begin: 1/1982 End: 12/2004 Total Hours: 197532																		
Direction																		
Speed	N	NNE	NE	ENE	E	ESE	SE	SSE	S	SSW	SW	WSW	W	WNW	NW	NNW	Calm	Total
CALM	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.1	1.1
1-3	1.5	1.3	1.4	1.5	1.7	1.7	1.7	1.3	1.1	1	1	1.1	1.4	1.8	1.9	1.6	0	23
4-7	1.6	1.3	1	1	1.5	2.1	3	2.4	1.5	1.1	1.5	2.4	4.3	6.1	4.4	2.1	0	37.3
8-12	0.7	0.7	0.3	0.1	0.3	0.4	0.9	1.1	0.6	0.5	1	2.2	4.5	7.6	2.7	0.7	0	24.2
13-18	0.2	0.2	0.1	0	0	0	0.1	0.2	0.2	0.3	0.8	1.3	1.4	3.5	1.4	0.1	0	10
19-24	0	0.1	0	0	0	0	0	0	0.1	0.2	0.5	0.6	0.3	1	0.7	0	0	3.5
25-31	0	0	0	0	0	0	0	0	0	0.1	0.2	0.2	0.1	0.2	0.2	0	0	0.8
32-38	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.1
39-46	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
> 46	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	3.9	3.6	2.9	2.6	3.4	4.3	5.6	5	3.5	3.2	5.1	7.8	12	20.1	11.3	4.5	1.1	100

From PNNL-15160, *Hanford Site Climatological Summary 2004 with Historical Data*.

Notes: Distributions are percentages. Wind measurements made at 30 ft. Wind speed units are mph.

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Table 3-2. Joint Frequency Distribution for the 200 West Station.

Station: (7) 200W																			
Begin: 1/1982 End: 12/2004 Total Hours: 183404																			
Direction																			
Speed	N	NNE	NE	ENE	E	ESE	SE	SSE	S	SSW	SW	WSW	W	WNW	NW	NNW	Calm	Total	
CALM	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.6	1.6	
1-3	2.2	1.8	1.6	1.4	1.6	1.8	2.1	2	1.8	1.6	1.9	2.4	3.4	4.2	3.6	2.6	0	36	
4-7	2.9	1.6	1	0.8	1	1.6	1.8	1	0.7	0.8	1.2	1.8	3.7	6.7	5.2	3.4	0	35.2	
8-12	0.8	0.5	0.2	0.1	0.1	0.3	0.4	0.2	0.2	0.6	1	1.7	2.5	3.1	3.4	1.8	0	16.8	
13-18	0.1	0.2	0.1	0	0	0	0	0	0.1	0.4	0.9	1.4	0.8	0.8	2	0.5	0	7.4	
19-24	0	0	0	0	0	0	0	0	0	0.1	0.5	0.5	0.2	0.1	0.8	0.1	0	2.4	
25-31	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	0	0.1	0	0	0.5	
32-38	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.1	
39-46	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
>46	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Total	6	4.1	2.9	2.3	2.7	3.7	4.3	3.2	2.8	3.4	5.7	8	10.7	14.9	15.2	8.3	1.6	100	

From PNNL-15160, *Hanford Site Climatological Summary 2004 with Historical Data*.

Notes: Distributions are percentages. Wind measurements made at 30 ft. Wind speed units are mph.

The 200 East Station (Station Number 6) is located south of the C Tank Farm in the 200 East Area, while the 200 West Station (Station Number 7) is located slightly west of the 200 West Area. The joint frequency distributions show that conditions are similar, but not identical between these two sites. At each location, wind speeds are between 4 and 12 mph approximately 50 to 60% of the time. At the 200 East Station, wind speeds between 1 and 3 mph occurred 23% of the time, while at the 200 West Station, these wind speeds occurred 36% of the time. Calm winds, which are less than 1 mph, occur less than 2% of the time at both locations. The atmosphere is expected to provide significant dilution for all source types for a majority of the time, since wind speeds in excess of 5 mph are most often observed. Low wind speeds, between 1 and 3 mph, may be periods when dispersion is limited.

Table 3-3 presents the joint frequency distribution of the stability class and wind speed from the Hanford Meteorological Station. Each numerical value in these tables represents the percentage of time when the given wind speed (column) and stability class (row) combination was observed at the station location. These distributions are based on measurement data from 1983 through 2006 and is the most recent analysis available. Hanford Meteorological Station Number 21 is located between the 200 East and West Areas. The stability class was computed using the U.S. Nuclear Regulatory Commission Delta-T method (NRC Regulatory Guide 1.23, *Meteorological Monitoring Programs for Nuclear Power Plants*) with temperatures from the 200- and 30-ft heights from the 400-ft tower. Stability class indicates the propensity of a parcel of air to undergo turbulent diffusion in the atmosphere because of mechanisms related to buoyancy forces. Turbulent diffusion is highest for the case of stability class A (the most unstable condition), and lowest for stability classes F and G (the most stable conditions).

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Typically, well-mixed conditions are expected under unstable conditions, which occur about 23% of the time (sum of Total column for Classes A through C). Neutral conditions, which, as the name implies, are neither highly mixed nor limited in mixing, occur approximately 26% of the time. The remaining 51% of conditions are stable, during which atmospheric mixing may be limited. Stable conditions are most likely to occur during winter months, or between sunset and an hour after sunrise during all seasons. The most dispersion-limiting conditions among the stable conditions are likely to be under low wind speeds, which is approximately 13% of the time (sum of 2 mph column for stability classes E through G). This means that about half of the low wind speed cases (which occur 26.7% of the time) are conditions during which dispersion may be limited.

Inversions can trap releases near the ground and shorten the distance over which elevated releases mix down to ground level. PNNL-6415, *Hanford Site National Environmental Policy Act (NEPA) Characterization*, notes that ground-based temperature inversions are common, in all seasons, in the interval from sunset to about an hour after sunrise, the same period when the atmosphere is stable. Inversions, once established, were least likely to persist for more than 12 hours in May and June (probability about 10%) and most likely to do so in September and October (probability about 64%). This implies that the longer inversions may persist even through parts of the day when, because of heating of the ground, unstable mixing is present in the volume trapped under the inversion.

Table 3-3. Joint Frequency Distribution for the Hanford Meteorological Station.

Stability Class	Average Wind Speed						Total
	2 mph	6 mph	10.5 mph	16 mph	22 mph	29 mph	
A	3.0	6.1	3.1	1.7	0.5	0.1	14.4
B	1.3	2.1	0.9	0.4	0.1	0.0	4.9
C	1.2	1.7	0.7	0.3	0.1	0.0	4.1
D	8.3	8.6	5.2	3.0	0.8	0.1	25.9
E	6.6	10.6	7.0	2.5	0.4	0.1	27.1
F	4.5	10.2	2.2	0.1	0.0	0.0	17.0
G	1.7	4.1	0.8	0.0	0.0	0.0	6.7
Total	26.7	43.3	19.9	8.0	1.9	0.3	100

Adapted from PNNL-6415, *Hanford Site National Environmental Policy Act (NEPA) Characterization*.

Notes: Wind speed distributions are percentages. Wind measurements made at 30 ft.

A = extremely unstable.

D = neutral.

F = moderately stable.

B = moderately unstable.

E = slightly stable.

G = very stable.

C = slightly unstable.

3.2 DISPERSION MODELING

Dispersion modeling has been performed for a variety of tank farms needs in recent years. These needs have included stack height evaluations, vapor control zone (VCZ) determinations, and risk assessments. A number of different modeling tools have also been employed for these different applications; these have been described and evaluated for applicability in PNNL-25654, *Atmospheric Dispersion Modeling Tools for Hanford Tank Farms Applications*. In most cases,

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plume models evaluate 10-minute or 1-hour time-average concentrations, rather than concentrations varying over periods of a few seconds or minutes. This means that plume-model predictions are not typically pertinent in evaluating short-duration vapor events of <10 minutes. However, a discussion of some of the modeling that has been performed for the tank farms is informative in considering the potential range of ground-level concentrations under certain modeled conditions. These models and applications are briefly described below, while results are discussed in Sections 3.3 and 0.

It is recognized that plumes may overlap, producing zones of increased concentration compared with single plumes. Ground-level sources such as the PBFs are most likely to result in combined plume effects; however, areas of combined plumes are generally not the highest concentration areas, which is the focus of this report. The results of the physical release and transport mechanisms that result in peak concentrations as described by modeling are presented here.

PNNL-14767 performed a parametric Gaussian plume-model evaluation of downwind dispersion to predict 1-hour average concentrations from selected ground-level and elevated stack sources in the tank farms, under a wide range of meteorological conditions. The TVAT report (SRNL-RP-2014-00791) describes the results of the PNNL-14767 study as supporting the potential for certain conditions to produce “concentrations approaching 80% of the headspace concentration...10 feet downwind from the release point.” This was an inappropriate conclusion by the TVAT from these modeling results. Predictions made within the first 100 m from Gaussian plume models should not be considered quantitatively because the data used to develop the diffusion coefficients used within the model were collected from 100 m to 10 km. As a result, diffusion coefficients are being extrapolated outside their applicable range when used at distances as short as 3 m. Additionally, the characteristics of the source, including geometry and turbulence effects, have significant impact on the concentrations near the source such that the errors associated with Gaussian plume estimates within the first 100 m should be considered large. This limitation is stated in Section 2.5 of PNNL-14767.

Concentration estimates based on high-fidelity, short time step CFD modeling provide more realistic estimates of concentrations at these distances. Section 3.3 compares CFD model predictions for near-ground-level sources (PBFs) to the predictions made by PNNL-14767. The inputs for stack heights and flow rates were too different between PNNL-14767 and later CFD modeling to allow a meaningful comparison for elevated sources.

AREVA 152-9235204-000, *Atmospheric Dispersion Modeling of Tank Farm Stacks at the Hanford Site Using Air Quality Code AERMOD and Computational Fluid Dynamics Code ANSYS CFX*, presents stack dispersion modeling predictions from both the AERMOD Gaussian plume model and the CFX model (a CFD model that is part of the ANSYS suite of codes). AERMOD is a sophisticated model that adapts the Gaussian plume formulation to include varying vertical profiles of wind speed and stability. CFX uses a k- ϵ turbulence model to numerically solve a form of the Navier-Stokes equations appropriate for a range of types of flows, including atmospheric flows. For both of these models, 1-hour average concentrations from the AW Tank Farm stack were modeled for several meteorological conditions selected from a 5-year data set to give highest predicted concentrations. Stack parameters were within the ranges either in use in 2015 or planned for facility upgrades. Both of the models were run with or without terrain and structural downwash in different phases of the project, depending on which of several types of information were being pursued: model comparison; effect of building downwash and increased stack height; tracing of abnormal operating procedure AOP-015,

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Response to Reported Odors or Unexpected Changes to Vapor Conditions, events; and other downstream concentration assessments. The grid used for AERMOD runs included rings of receptors within 100-m of the source, where AERMOD results would have larger errors because of Gaussian plume model limitations as described above. This polar grid extended to 500 to 1600 m, depending on the purpose of modeling. The cylindrical computational mesh for the CFX model used an element size that was on the order of 2.5 to 3 m, depending on the purpose of modeling, which is typical and appropriate for this type of model.

The Fire Dynamics Simulator (FDS), developed by the National Institute of Standards and Technology, is a large-eddy simulation CFD code that numerically solves a form of the Navier-Stokes equations appropriate for low-speed, thermally driven flow. It was developed specifically for atmospheric applications. This model was used to examine vapor dispersion from ground sources (e.g., PBFs and air inlet stations) and elevated sources (e.g., exhausters and vessel vents). Results for the A, AP, and AW Tank Farms were documented in quantitative risk analyses (QRA) Kenexis 568.002-023:0, *Quantitative Risk Analysis, 241-A*; Kenexis 568.002-024:0, *Quantitative Risk Analysis, 241-AP*; and Kenexis 568.002-020:0, *Quantitative Risk Analysis, 241-AW*. QRAs for the 242-A Evaporator and the remaining tank farms are underway or planned. In these simulations, FDS was used to simulate turbulence formed from wind and temperature gradients in the atmosphere. The model had a spatial resolution of 0.6 to 0.7 m cell size and time resolution of 2 seconds (the time step size). The tank farm air space was divided into approximately 1 to 2 million cells. The model was employed with several meteorological conditions that were selected to produce the highest concentrations on the local terrain and at buildings. Mechanisms in the model included the effects of atmospheric phenomena such as low boundary layers (low inversions) and higher instability very near the ground.

3.3 GROUND-LEVEL SOURCES

Ground-level sources in and around the tank farms may result in the highest relative concentrations in the worker breathing zones because the vertical distance between the source and receptor is small, so the plume centerline is likely to be near worker breathing heights under a variety of conditions. These ground-level, or near-ground-level, sources of headspace vapor releases include the modern style of PBFs on short risers as shown in the left panel of Figure 2-9, the older taller filtered risers of the type shown in the right panel of Figure 2-9 as well as fugitive sources such as pits, instrument cabinets, and blank flanges. Although the focus of this report is on tank vapors, other fugitive ground-level emissions around the tank farms, such as diesel generators or sewer systems are expected to generally behave as described within this section.

Near-ground-level sources produce low-momentum flows that therefore are expected to have lower levels of initial turbulence within the source outlet itself, compared with actively ventilated elevated stacks. Mechanical turbulence may be generated within the outlet by the radial high-efficiency particulate air (HEPA) filter and the metal “hat” over the filter, but these are expected to contribute a relatively small amount of mixing to the exhaust plume, compared to local wind-generated turbulence near the outlet. Based on the discussion of passive ventilation in Section 2.2, the emissions from passive-ventilation emissions sources at ground level are likely to be intermittent and variable.

For ground-level sources, maximum instantaneous concentrations generally occur under stable, poorly mixed conditions (EPA 1970). Under these conditions, wind speeds tend to be low and

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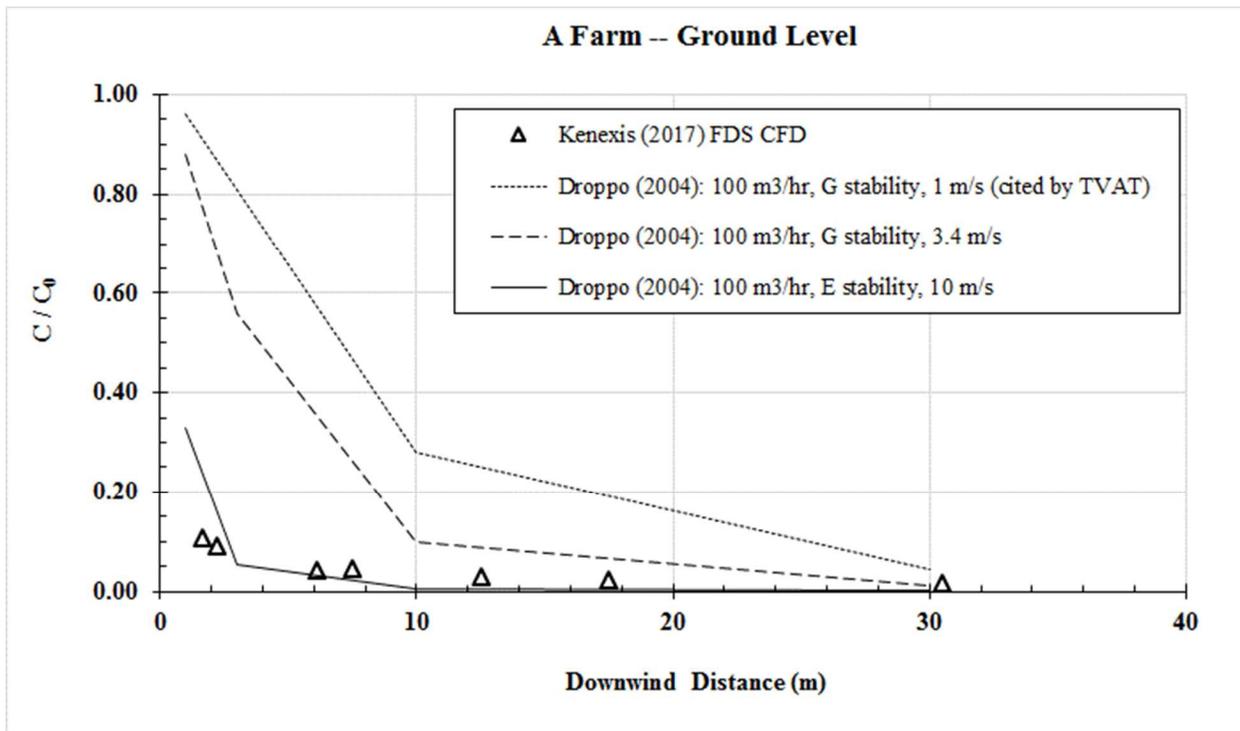
wind direction often meanders; that is, the bulk motion of the air swings back and forth over time periods of tens of minutes. This means that locations of the higher-than-background in-plume concentrations can occur over a relatively large arc around the release point, and last for longer periods of time. Plume folding can also occur, whereby the plume moves back and forth over the same location, causing elevated concentration locations. Because the plume height is low for these ground-level sources, even low inversions (30 m height or less) do not affect the concentrations in the breathing zone.

The A Tank Farm QRA report includes an assessment, performed with the FDS code (a CFD model), of the potential exposure zones for the chemicals of interest (Section 3.3 of Kenexis 568.002-023:0). The modeling used a set of six meteorological conditions that were expected to generate the highest concentrations. Three of the six conditions were for low wind speed (2 mph) at A, D, and F stability. Each condition was modeled in each of eight directions to capture the effect of terrain and buildings. This modeling generated contour plots of 2-second concentrations that showed the potential exposure zones – the greatest distances in each direction at which the source concentration for the bounding analysis produced certain values of downwind concentration for COPCs. The bounding analysis emissions scenario was based on maximum headspace concentrations and annual-maximum hourly release rates that varied with wind speed.

By measuring the distance on the plots from the source to each concentration, using only the direction for which the contour was furthest from the source, it was possible to approximate the maximum distances at which certain ratios of local to source concentration (C/C_0) could be reached at the minimum-dispersion conditions (although the QRA does not state which conditions produced these concentrations). The results can be seen in the CFD data symbols in Figure 3-2. The model-predicted concentrations for these worst-case meteorological conditions decreased from source by about a factor of 10 within 2 grid cells – less than 1.2 m.

Figure 3-2 also provides a comparison between the CFD predictions for the A Tank Farm near-ground-level sources and those made by PNNL-14767 for the near-surface box filter vents. TVAT report SRNL-RP-2014-00791 describes the results of the PNNL-14767 study as supporting the potential for certain conditions to produce plume-average “concentrations approaching 80% of the headspace concentration...10 feet downwind from the release point.” The inputs for this cited worst-case result were 100 m³/hr release rate, G stability, and 1 m/sec wind speed (about 2 mph). The effect produced by this combination of inputs is unlikely for two reasons. First, the plume model overestimates plume-average concentrations because the dispersion coefficients do not account for the extra dispersion from meander that is likely to be present at high stability and low wind speed. Second, the 100 m³/hr release rate is double the highest release rate so far measured for passively ventilated tanks (PNNL-14831). It is also more than 10× the annual maximum hourly venting rate (9.0 m³/hr) estimated in the A Tank Farm QRA for low wind speeds such as 2 mph and is 4× the rate (26 m³/hr) estimated for high wind speeds. It is not plausible that such a high release rate could occur except at higher wind-speed conditions, because the venturi effect would be needed to drive the ventilation.

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Ground-level sources modeled using Fire Dynamics Simulator (Kenexis 568.002-023:0, *Quantitative Risk Analysis*, 241-A).

Selected plume modeling results using PNNL-14767, *Characterization of the Near-Field Transport and Dispersion of Vapors Released from the Headspace of Hanford Site Underground Storage Tanks*.

Figure 3-2. Minimum Dispersion C/C_0 as a Function of Distance.

Figure 3-2 shows PNNL-14767 predictions for the same 100 m³/hr release rate and two other sets of stable, higher-wind conditions that have low but non-zero probability in the observed joint frequency distribution (Table 3-3). At the shortest distances, the plume model predictions, based on extrapolated dispersion coefficients, are consistently higher than the CFD model predictions of minimum-dispersion concentrations at resolution of 2 seconds and 0.6 m. The CFD model, with its greater resolution and more realistic handling of turbulent diffusion, calculated 2-second-resolution concentrations that were substantially lower than the plume-model prediction that plume-average C/C_0 could be as high as 80% at 3 m distance. By contrast, the 2-second C/C_0 from the FDS model was about 10% at a shorter distance, 1.7 m.

The effect of the combination of two overlapping near-ground-level plumes can be roughly evaluated by using the C/C_0 values in Figure 3-2. Consider the special case where the wind carries a plume from one ground-level source directly over another source, causing centerlines to fall on the same line, and make the reasonable assumption that the centerlines are at approximately the same elevation above grade, producing the closest possible overlap. For illustrative purposes, assume both of the sources have the same emission rate. If the two sources are 1.7 m apart, then the upwind source contributes about 10% to the joint concentration at the downwind source: the upwind source C/C_0 is about 10% at 1.7 m, added to C/C_0 of 100% at the downwind source. At a distance of 6 m downwind from the downwind source, the C/C_0 contribution from the upwind source (at 7.7 m downwind distance) is about 4% and the contribution from the downwind source (at 6 m) is also about 4%. The new C/C_0 for this combined plume case is about 8%, a significant increase produced by combination but more than

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a factor of 10 dilution compared to either of the source concentrations. Thus, even with two closely spaced near-ground-level sources, and the assumption that the 2-second concentration maxima from the two sources occur at the same place and time, the downwind combined concentration is substantially lower than the source concentration.

3.4 ELEVATED SOURCES

Elevated sources of tank vapors are primarily actively ventilated stacks. These sources are expected to result in relatively low concentrations in the worker breathing zones because there is a significant vertical distance between the source and the receptor (tens of feet), and even transport with minimal diffusion will reduce the concentration at a ground-level receptor. Additionally, the source itself is turbulent and tends to result in enhanced plume mixing with the environment. These stacks have high exit velocities (relative to velocities through PBFs) and, because of exhausters heaters, have temperatures that are frequently elevated above ambient. Both the velocity and the temperature at the stack tip act to increase the effective stack height, depending on meteorological conditions, with the highest prediction for effective stack height being higher by 20 ft or more.

For elevated sources, maximum instantaneous concentrations generally occur during unstable conditions when portions of the plume that have undergone little dispersion are brought down to the ground. These concentrations occur close to the point of emission (on the order of 1 to 3 stack heights away). For longer averaging times (i.e., on the order of a half-hour), peak concentrations can occur with fumigation conditions. Presence of a strong stable layer (inversion) above the release point can also limit dispersion (i.e., plume trapping), but concentrations are often less than those associated with fumigation. Under stable conditions, the maximum concentration from elevated sources are less than those that occur under unstable conditions and occur at greater distances from the source (EPA 1970).

The combination of multiple elevated-stack plumes is even less likely to produce substantial increases in the elevated-concentration areas at ground level than was the case for plumes resulting from near-ground-level sources. This statement is based on two facts: the elevated stacks at the Hanford Site are distant from each other (compared to distances between near-ground-level sources), and the effective plume heights are likely to differ from each other, reducing overlap of plume centerlines. Plume edge overlap from elevated sources is not likely to produce peak ground-level concentrations.

HW-7-4806, *Characteristics of Mixing and the Dilution of Waste Stack Gases in the Atmosphere*, describes oil-fog experiments performed at a 16-inch diameter, 200-ft tall stack located on the Hanford Site. The oil droplets in the fog were 1 μm in diameter, small enough to serve as tracers and follow the local airflow without settling. Photographs of different plume types observed during these experiments are presented in Figure 3-3 through Figure 3-5. Fanning, shown in the upper panel of Figure 3-3, occurred under stable atmospheric conditions and the wind speed was less than 16 mph. The plume remains at the height of the stack, and the plume rarely reaches the ground. Fanning conditions were observed to change to looping conditions when the atmospheric stability changed from stable to unstable. This could occur over just a few minutes when mixing results in unstable conditions at the height of the emission. Looping, which is shown in the lower panel of Figure 3-3, occurred when the wind speed was relatively uniform from the surface to 200 ft, but was less than 20 mph. The authors computed

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plume descent rates of about 4 ft/sec in the summer and 3 ft/sec in the winter (although there was a large range of observed descent rates). As discussed above, looping occurred under unstable conditions.

Coning, shown in the upper panel of Figure 3-4, occurred when the atmosphere was near neutral and wind speeds were 20 mph or greater. Coning plumes did not touch the ground until distances greater than about $10\times$ the stack height. This figure also shows an example of a lofting plume in the lower panel, which occurs when an inversion below the plume limits dispersion to the surface.

Fumigation is shown in Figure 3-5, and generally occurs when shallow early morning mixed layers intercept an elevated plume as a result of surface heating as the sun rises. The plume is quickly transported to the surface, which may result in a rapid increase in ground-level concentrations. These events tend to be brief (lasting a half hour) as the mixed layer depth continues to increase with further surface heating (EPA 1970).

Stack downwash is another phenomenon that may bring the plume down to the worker breathing zone. Typically, stack tip downwash is observed on the downwind side of the stack as the lower pressure draws the plume downward, reducing the effective stack height. This reduction is often on the order of one to two stack diameters (DOE/TIC-27601, *Atmospheric Science and Power Production*). Other mechanisms for downwash are physical structures that serve to reduce the pressure, or in some cases create eddies that pull the plume down toward the ground surface. However, stack downwash to the extent that the plume is brought all the way down to the surface is relatively rare. Previous work, reported in DOE/TIC-27601, showed that when the stack exit velocity is $1.5\times$ the wind speed at the stack height, essentially no downwash behind a stack is observed. However, when these two velocities are similar, downwash may occur, with the plume height reduced by approximately one stack diameter. AREVA 152-9235204-000 used the AERMOD model to compute concentrations around selected tank farm stacks with and without downwash and found that the highest concentrations could occur either with downwash or without downwash included in the simulation, depending on the stack.

An example of downwash from the nuclear power industry is also described in DOE/TIC-27601. Ground fog, or downwash of plumes with visible moisture, in which the plume intersects the ground surface, often occurs behind mechanical draft cooling towers at nuclear power plants when winds are 3 to 5 m/sec, but buoyancy lifts the plume off the ground at around 200 m (10 stack heights) from the tower. Mechanical draft cooling towers are often arranged in rows of 10 to 20 fans along a 200-m structure. Natural draft cooling towers, on the other hand, are often arranged in groups of two to four, spaced 200 to 500 m apart. Natural draft cooling towers rarely produce ground fog. Since tank farm stacks are typically stand-alone structures with an open platform surrounding the stacks, it is unlikely that these stacks will produce plumes with downwash that intersects the ground surface. Additionally, to produce downwash within a few stack heights downwind of the stack, for stack exit velocities of 6 to 20 m/sec, winds would need to be on the order of 20 to 80 mph, which would result in significant dilution.

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Top: Plume fanning. Bottom: Plume looping.

Source: HW-7-4806, *Characteristics of Mixing and the Dilution of Waste Stack Gases in the Atmosphere*.

Figure 3-3. Hanford Site Oil Fog Experiments for Visualizing Plume Fanning and Looping from Experiments Performed on a 200-ft Tall Stack in the 1940s.

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Top: Plume coning. Bottom: Plume lofting.

Source: HW-7-4806, *Characteristics of Mixing and the Dilution of Waste Stack Gases in the Atmosphere*.

Figure 3-4. Hanford Site Oil Fog Experiments for Visualizing Plume Coning and Lofting from Experiments Performed on a 200-ft Tall Stack in the 1940s.

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Source: HW-7-4806, *Characteristics of Mixing and the Dilution of Waste Stack Gases in the Atmosphere*.

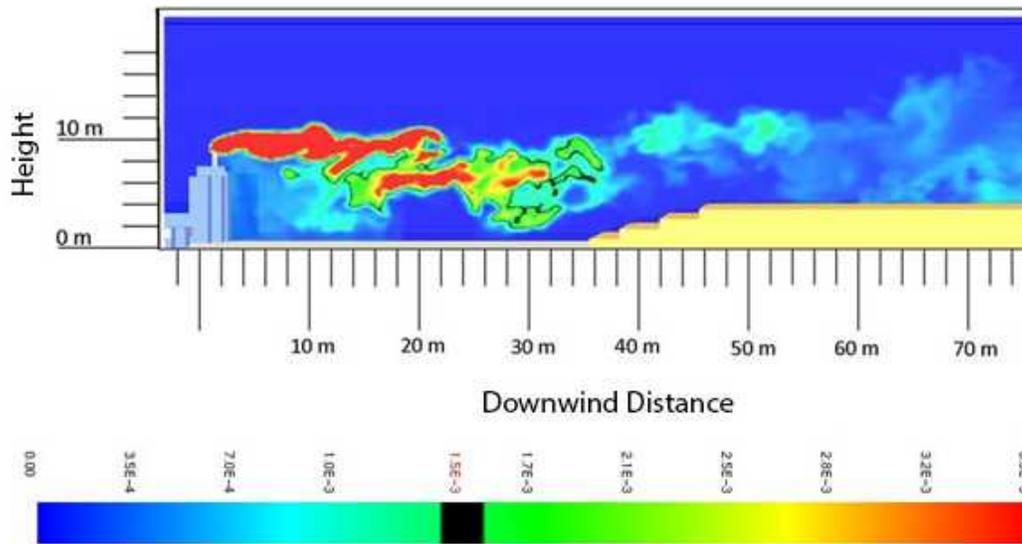
Figure 3-5. Hanford Site Oil Fog Experiments for Visualizing Plume Fumigation from Experiments Performed on a 200-ft Tall Stack in the 1940s.

The AREVA 152-9235204-000 simulations for the AW Tank Farm stack predicted that the maximum concentration occurs under light wind speeds and relatively low inversion heights. Capping inversions can cause elevated exhaust sources to reach the ground closer to the source than would occur for conditions without inversions. These weather conditions are rare (happening only 2.2% of the time). The maximum ground-level concentration predicted by both the AERMOD and CFX models was nearly 2,000× lower than the source concentration and was located in excess of 60 m from the 28 ft tall stack, whose stack velocity was 8.7 m/sec (1720 ft/min). Terrain and structural downwash effects were not included in the particular model applications that calculated these concentrations, though they were used in other phases of modeling.

For comparison, the AW Tank Farm QRA report (Kenexis 568.002-020:0) used the FDS CFD code to model the AW Tank Farm exhaust stack, using a stack height of 28 ft, a linear velocity of 1,200 ft/min, a flow rate of 650 ft³/min, and a stack temperature of 10 °C above ambient. The effects of terrain and structures were included in modeling. The time resolution was 2 seconds and the grid-cell size 0.6 m. The modeling used a set of six combinations of wind speed and stability that were expected to generate the highest concentrations. Three of the six combinations were for low wind speed (2 mph) at A, D, and F stability. The effects of inversions were also considered. Each condition was modeled in each of eight directions to capture the effect of terrain and buildings. The effective stack height was between approximately 11 and 24 m, depending on ambient temperature and wind speed.

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Figure 3-6 shows the modeled mercury concentration profile at one representative 2-second point in time. These results are based on waste-disturbing conditions in the tank, which produce the highest modeled headspace concentrations of the emissions scenarios that were modeled. The meteorological conditions were moderately stable nighttime conditions, moderate wind speed, with a surface inversion. A plume whose source concentration was 0.41 ppm mercury, approached the ground near the stack over a range out to about 17 m downwind; the figure suggests that in spite of the initial plume rise, building wake brought a portion of the plume down to the breathing zone. The ground-level concentration here was 7E-04 ppm or less, a dilution of a factor of about 600. Further downwind, where the terrain rose and intercepted the plume, concentrations of as high as about 9E-04 ppm were predicted. This point was at about 70 m downwind, and the factor of dilution was about 450. Over most of the downwind distance, out to 75 m where the modeling domain ended, predicted concentrations were a factor of 450 to 2,000 less than the source. The QRA results also showed similar concentration dilution behavior out to 125 m distance for NDMA releases during waste-disturbing conditions, under unstable low-wind conditions with a capping inversion at 23 m.



During sunny day, very unstable surface conditions, low wind speed and unlimited mixing depth, modeled with Fire Dynamics Simulator for the AW Tank Farm quantitative risk analysis. Gradient is in units of ppm.

Figure 3-6. CFD Dispersion Model Predictions of 2-Second-Resolution Mercury Concentration from AW Tank Farm Exhauster.

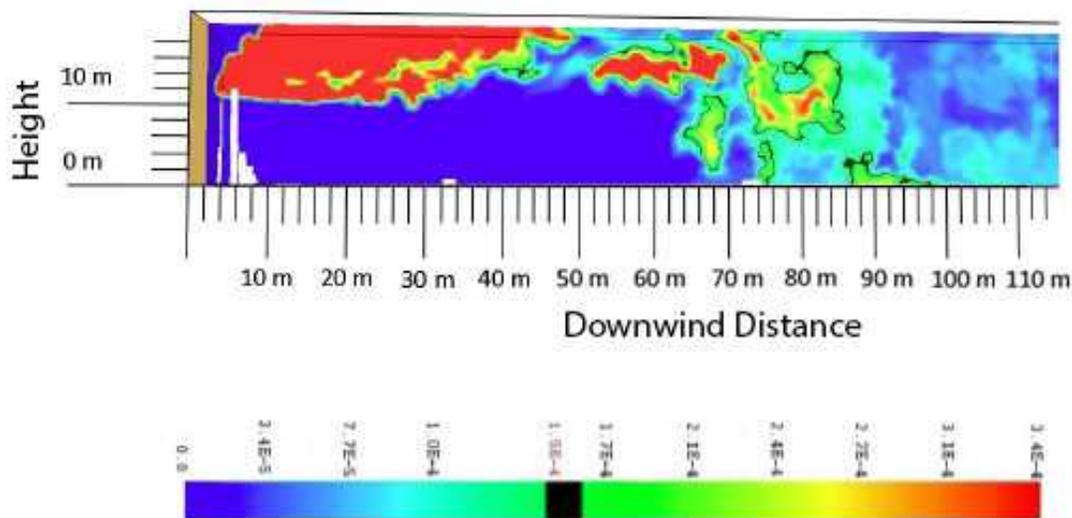
Figure 3-7 shows the results of FDS modeling of the AP Tank Farm Exhauster, as performed for the AP Tank Farm QRA (Kenexis 568.002-024:0). The model inputs included a stack height of 40 ft, a minimum linear velocity of 2,500 ft/min, a flow rate of 1,500 ft³/min, and a stack temperature of 95 °F (35 °C). The effects of terrain and structures were included in modeling. The time resolution was 2 seconds and the grid-cell size 0.7 m. The modeling used a set of six combinations of wind speed and stability that were expected to generate the highest concentrations. Three of the six combinations were for low wind speed (2 mph) at A, D, and F stability. The effects of inversions were also considered. Each condition was modeled in each of

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eight directions to capture the effect of terrain and buildings. The effective stack height was between approximately 14 and 21 m, depending on ambient temperature and wind speed.

Figure 3-7 shows the predicted nitrosamine concentration profile at one representative point in time. The headspace nitrosamine concentration was 0.12 ppm, as estimated for waste-disturbing conditions. The plume exhibited an initial plume rise and did not drop down to the worker breathing zone until about 60 to 70 m downwind. The ground-level concentrations downwind of that distance, out to the end of the modeling region at 115 m, were between about $8\text{E-}05$ and $2.4\text{E-}04$ ppm. These concentrations were no higher than 0.2% of the source, a factor of 500 or more dilution.

The CFD modeling results indicate that plume transport from an elevated release to the ground-level worker breathing zone travels many tens of feet, over which the concentration decreases by a factor of 100 or more.



During sunny day, very unstable surface conditions, low wind speed and strong capping inversion aloft modeled with Fire Dynamics Simulator for the AP Tank Farm quantitative risk analysis. Gradient is in units of ppm.

Figure 3-7. CFD Dispersion Model Predictions of 2-Second Resolution NDMA Concentration from AP Tank Farm Exhauster.

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4.0 RECEPTOR CHARACTERISTICS

4.1 POTENTIAL RECEPTOR AREAS

Hanford Site workers and contractors conducting work in the vicinity of the 18 SST and DST farms in the 200 East and 200 West Areas represent the primary potential receptors of vapor emissions from tank farm sources. Potential tank vapor sources include the 177 underground storage tanks within the 18 tank farms, the catch tanks, and the 242-A Evaporator. Receptors include workers operating within the fence line of each tank farm, as well as workers adjacent to the tank farms but outside the fence line boundaries. The breathing zone, or receptor area, is represented principally by the open, ambient areas within and outside the tank farm boundaries. In addition, limited, enclosed, or semi-enclosed areas within and outside the tank farm boundaries are also potential receptor areas. These include temporary tented areas (e.g., workspace or change areas), trailers, permanent structures such as the 242-A Evaporator or 702-AZ exhauster buildings, and adjacent smaller enclosures (e.g., pits, instrument or electrical cabinets).

Work activities associated with typical tank farm operations are evaluated and assigned a risk classification (RC) as part of a tank sourced chemical vapor management strategy designed to control potential exposures (TFC-ESHQ-S_IH-C-48, *Managing Tank Chemical Vapors*). RC 1 through RC 4 work activities are based on the exposure pathway (e.g., open, restricted or controlled, or isolated) and represent increasing exposure potential and risk from RC 1 (lowest risk of exposure) to RC 4 (highest risk of exposure). Low-risk RC 1 activities are categorized as general tank farm entry where potential vapor exposure is controlled by limiting access or entry into areas such as VCZs or systems that contain tank headspace vapors, and no intrusion into headspace containment systems is allowed. RC 2 activities are categorized as access into a system where engineering controls prevent worker exposure to tank headspace vapors. Intrusion into a system that contains tank vapors is allowed only when either an exhauster maintains a negative pressure on the headspace vapor side of a threshold, and/or another engineering control can be applied to prevent worker exposure. Higher-risk RC 3 and RC 4 activities include access or entry into systems where the risk of exposure to vapors is higher, including entry into VCZs; access into areas such as control cabinets, pits, or risers, or operations involving waste-disturbing activities; and when exhausters are not operating. In all of these work activities, both engineering and administrative controls including isolation and appropriate respiratory protection, are used to prevent potential exposure.

When a Hanford worker reports an unexpected and unidentified odor in or around the tank farms, WRPS follows a prescribed set of procedures, AOP-015, for responding to reported chemical odors or unexpected changes to vapor conditions in the tank farms.²⁴ AOP-015 is implemented if chemical odors have caused employee symptoms, or if stronger-than-normal odor is detected by multiple personnel outside of areas where potential or actual vapor concerns are expected. The TVAT assessed reports of worker exposure available at the time of their assessment and concluded that “symptoms and signs reported only during times workers are physically on the tank farm” and that there was a “perfect correlation between adverse acute inhalation effect and

²⁴ AOP-015 is summarized on the vapors website at <https://hanfordvapors.com/when-odors-are-reported/aop-015-procedure/>.

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presence on farm” for tank farm workers reporting odors and medical symptoms potentially related to the smell. Table 4-1 provides a summary of the event investigation reports (EIR) and injury reports of all AOP-015 events reported prior to and following issuance of the TVAT report in 2014. Fifty six (56) AOP-015 event investigations have been conducted and documented between 2014-2018.²⁵ In addition, 58 vapor events were documented in injury or event reports between 2008 and 2014 that were the subject of the TVAT assessment, and are included in Table 4-1. Prior to the TVAT report, the majority of reported events (82% of all events between 2008 and 2014) occurred while workers were in a tank farm, and symptoms were reported for slightly more than half (54%) of all events during this time.²⁶ However, events documented between 2014 and 2018 following the TVAT analysis are almost equally split between inside and outside a tank farm. A total of 35 events (52%) occurred outside of a tank farm boundary. In addition, the number of AOP-015 events where symptoms were reported was roughly equally distributed between inside and outside of a tank farm – 22 and 21 events, respectively. Furthermore, the number of AOP-015 events is significantly smaller than the number of tank farm entries. For example, an estimated 84,500 entries were made into the tank farms in 2018. Figure 4-1 and Figure 4-2 provide aerial maps of the 200 East and 200 West Area tank farms with locations indicated of all AOP-015 events documented in EIRs since 2013. While many events occurred near tank farms, the events and investigation evidence suggest fugitive emissions from non-tank farm sources are also contributing factors. Therefore, the incidents of detected odors and symptoms are not perfectly correlated with presence on the tank farm, and symptoms and signs have been reported almost equally in and outside the tank farms. As a result, additional efforts are underway to more fully assess the source and nature of fugitive emissions.

²⁵ AOP-015 EIRs are available at <https://hanfordvapors.com/whats-in-the-tanks/vapors-events/aop-015-event-investigation-reports/>. As of 6/30/19, nine events had been documented in 2019.

²⁶ Symptoms included any report of a physical feature such as irritation, discomfort or outward physical sign. Typical symptoms included sore throat, burning, nose bleed, headache, or nausea. Reports of odor smell or taste without a physical symptom were categorized as no symptoms.

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Table 4-1. Summary of AOP-015 Events Documented in Investigation Reports and Injury Reports.

Year	No. of AOP-015 Events ^a or Vapor-Related Injury Reports ^b	Inside Tank Farm ^{c,d}			Outside Tank Farm		
		Total	Symptoms	No Symptoms	Total	Symptoms	No Symptoms
2008	1	1	1	-	-	-	-
2009	12	10	4	6	2	-	2
2010	13	12	6	6	1	-	1
2011	7	7	5	2	-	-	-
2012	4	3	1	2 ^f	1	1	-
2013	10	10	5	5	-	-	-
2014	25	16	11	5	9	5	4
2015	9	4	4	--	5	4	1
2016	18	8	5 ^c	3 ^c	10	7	3
2017	6	2 ^d	1	1 ^c	4	1	3
2018	9	2 ^e	1	1 ^c	7	4	3
Total	114	75	44	31	39	22	17

(a) Data obtained from AOP-015 event investigation reports documented through 12/31/18 at <https://hanfordvapors.com/whats-in-the-tanks/vapors-events/aop-015-event-investigation-reports/>

(b) Injury report data obtained from Appendix A of PNNL-23884, *The Sufficiency of Existing Hanford Data for Making Statistical Inferences about Tank Vapors*.

(c) Includes five events in 2016-2018 at the 702-AZ exhauster building, which is not within the AY or AZ Tank Farms fence lines but represents a source of tank vapors.

(d) As of August 2016, supplied air has been required inside tank farms, which probably resulted in a decrease in AOP-015 events in 2017-2018.

(e) During 2018, approximately 84,500 tank farm entries were made. Other years are expected to have similar numbers of tank farm entries but may vary according to differences in work scope for the year. The number of workers outside the tank farms cannot be readily approximated.

(f) Includes two events logged both inside and outside AY Tank Farm.

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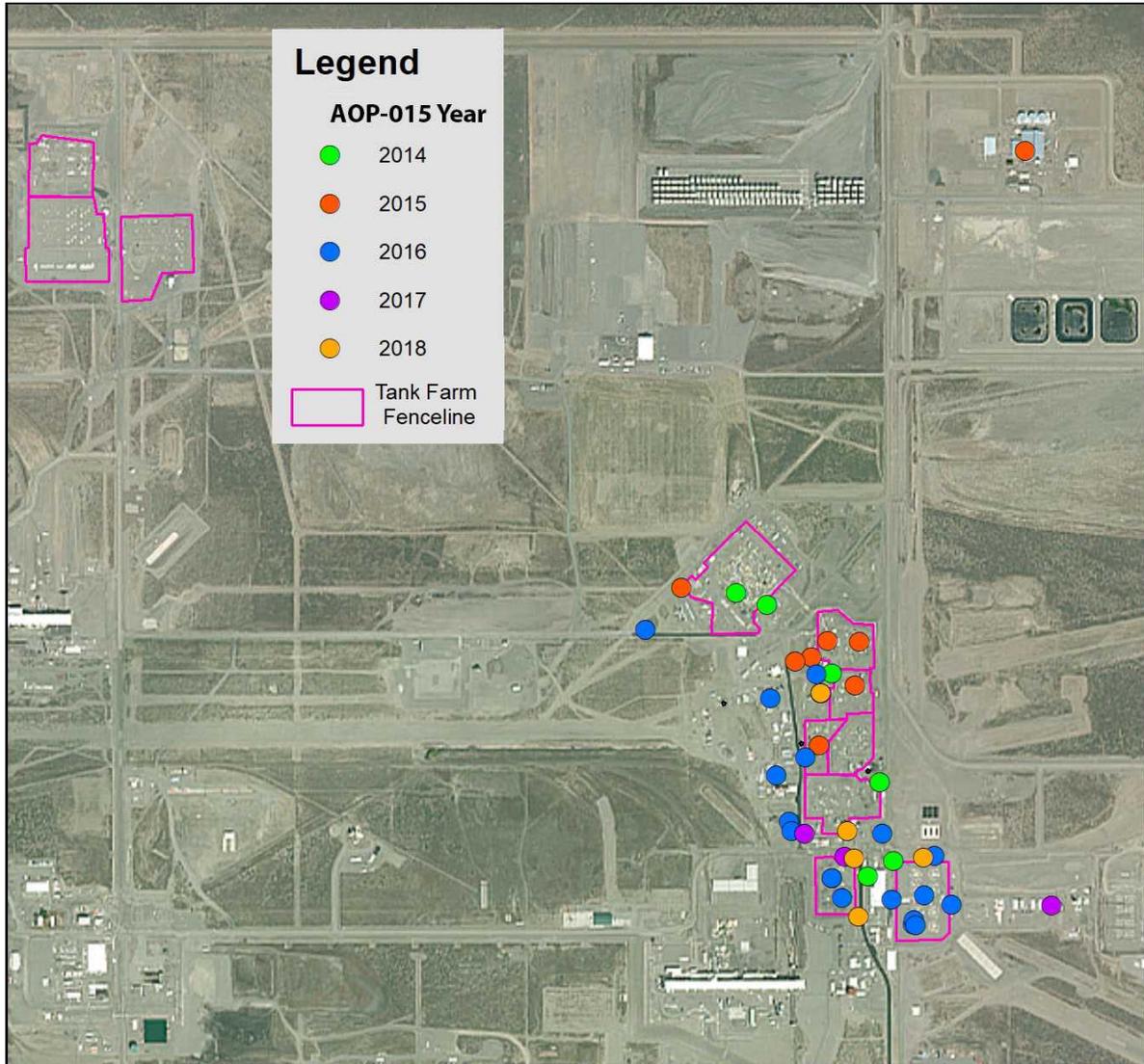


Figure 4-1. Location of 200 East Area AOP-015 Events from 2014-2018.

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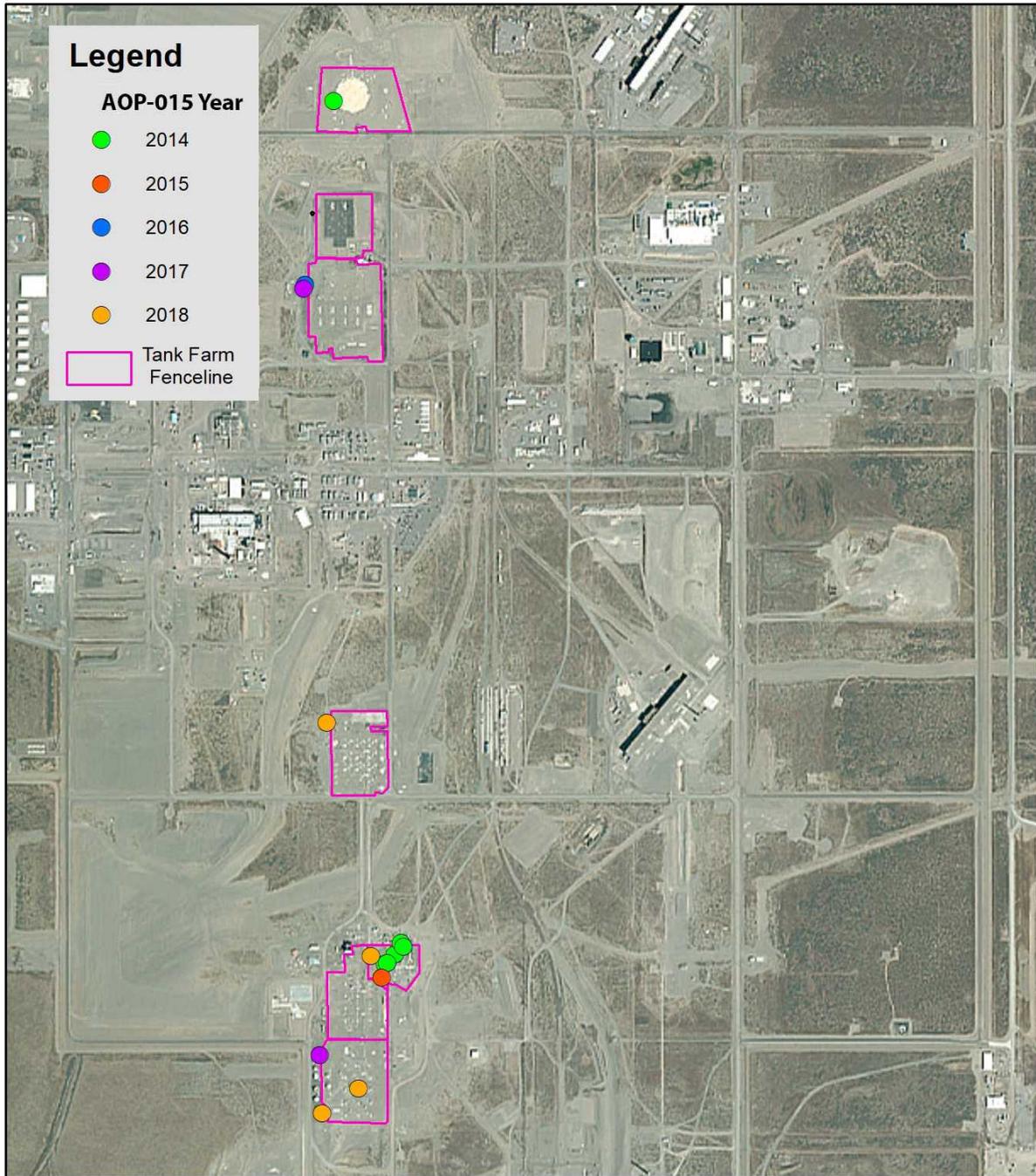


Figure 4-2. Location of 200 West Area AOP-015 Events from 2014-2018.

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4.2 MEASUREMENT DATA SUPPORTING EXPOSURE ASSESSMENT/HAZARD ANALYSIS

Extensive sampling and monitoring of sources (headspace or exhaust), ambient air within potential receptor areas in the tank farm work zone, and on personnel while working in the tank farm is performed as part of the chemical vapor management program. Sampling and monitoring requirements are defined for each tank farm and based on RCs and pre-determined sampling and monitoring requirements formalized in industrial hygiene sampling plans. The number and frequency of sampling and monitoring is greater for higher risk (e.g., RC 3 and RC 4) activities.

WRPS defines sampling as the collection of chemical concentration information utilizing standardized (typically Occupational Safety and Health Administration and/or National Institute for Occupational Safety and Health based) sampling methods on or in media, and subsequent analysis by accredited laboratories. Air sampling is typically performed by collecting vapors over longer duration periods (e.g., 2 to 8 hours) on solid media, but can also include shorter duration sampling (e.g., minutes to hours) on sorbent tubes or using gas sample containers such as SUMMA canisters. Monitoring is defined as the collection of chemical concentration information utilizing direct-reading instruments (DRI), operated in accordance with established procedures and manufacturer guidance, and calibrated using manufacturer guidance to National Institute of Standards and Technology traceable standards. Sampling allows for quantitative characterization of specific chemical species, including the 61 chemicals of potential concern (COPC) and non-COPC vapor constituents. Monitoring allows for more limited, but real-time quantitative characterization of a subset of chemical species, typically at higher levels of quantitation (i.e., detection limits) compared with sampling. The most common monitoring methods involve portable photoionization detectors for quantitation of total volatile organic compounds (VOC),²⁷ and electrochemical detectors for ammonia.

Sampling and monitoring of potential receptor exposures is performed in work areas (area sampling) by Industrial Hygiene (IH) technicians as well as through devices worn by workers during the work shift (personal sampling), and can include both longer duration, time-weighted measurements (minutes to hours) using sampling devices as well as near-instantaneous measurements (seconds to minutes) using monitoring instruments.

Beginning in September 2016, vapor monitoring and detection system (VMDS) equipment was deployed for testing in the A corridor of the Hanford tank farms as part of pilot-scale testing activities.²⁸ Some equipment will not operate on a permanent basis in the tank farms as a result of equipment limitations. However, several types of spectroscopic equipment, which produce near-instantaneous concentration measurements of a number of different chemical species, will continue to be operated within the tank farms to aid in characterizing both source and area concentrations. This equipment includes the stack monitor containing a Fourier transformed infrared (FTIR) spectrometer and an ultraviolet differential optical absorption spectrometer (UV-DOAS), and tank farm ambient air using open path (OP) FTIR spectrometers and an OP UV-DOAS. These real-time monitoring instruments enable more continuous monitoring of

²⁷ Note that photoionization detectors respond not only to VOCs but to ammonia and some other volatile inorganic compounds; however, the instrument responds less strongly to ammonia than to most organics.

²⁸ The absolute concentrations measured by the VMDS may not be accurate due to lack of calibration, but the timing and relative concentration trends are representative.

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sources and work areas for a broader set of chemical constituents, and at lower levels of detection than hand-held instruments routinely used for source and area monitoring.

4.2.1 Historical Area Sampling and Monitoring

The IH technical basis (RPP-22491) summarized available source, area and personal data from vapor monitoring and sampling from 1992 through 2006. A summary of these data is tabulated in Table 4-2. The overall conclusion was that:

Worker breathing zone data (area samples and monitors and personal sampling) indicate that gas and vapor concentration are a factor of 10 or more lower than concentrations found in tank headspaces, consistent with dispersion modeling results. Most COPCs are below sampling and analytical detection limits, and those that have been detected are well below occupational exposure levels (OEL) concentrations.

However, the majority of reported vapor area and personal measurements resulted from time-weighted average (TWA) sampling activities over minutes to hours, as opposed to peak measurements (seconds to minutes) representing a potential short-term elevated concentration event. Approximately 2000 source and area locations were also monitored with instruments providing near-instantaneous (seconds to minutes) measurements for VOCs and ammonia. In all reported sampling and monitoring, maximum area or personal measurements ranged from $>20\times$ to $7,000\times$ lower than maximum source concentrations. The majority of area and personal sampling measurement results were non-detections (i.e., below analytical detection or reporting limits). For ammonia, mercury, and most organic COPCs measured, 90 to 100% of the area and personal sampling results were non-detects. Nitrous oxide and formaldehyde were the only COPCs with higher percentage of detections, but with maximum concentrations below levels of concern.

4.2.2 Recent Area Sampling and Monitoring

Area and personal sampling and monitoring data have continued to be regularly collected, with tens of thousands of individual area samples and more than 80,000 DRI monitoring measurements recorded since 2008. DRI monitoring is performed by IH technicians principally supporting rounds and routines and work activity-specific surveys to support inside- and outside-tank-farm maintenance, monitoring, and construction tasks. Table 4-3 provides a summary of a portion of this data from the Site-Wide Industrial Hygiene Database (SWIHD), including sampling data presented in the data analysis and visualization system as of October 1, 2018. (<https://www.tankvaporexplorer.com>).

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Table 4-2. Source, Area, and Personal Sampling and Monitoring from 1992-2006 Summarized in RPP-22491.

Timeframe	Measurement Type	Location	Measured Vapors	Total Number of Measurements or Locations	Number of Non-Detects (<DL/<RL)	Area Measure. % of Non-Detects (<DL/<RL)	Maximum Source Concentrations (ppmv [hr if TWA])	Maximum Area Concentrations (ppmv [hr if TWA])	Sample Times
3/1992-1993	Source and Area Monitoring	Various Tank Farms	VOCs	2000	NR	NR	100	<2	inst.
			Ammonia				500	<25	
1/1993-6/1996	Personal Sampling	Various Tank Farms	Ammonia	350	NR	NR	NA	2.6 [8]	20 min - 5 hrs
			Nitrous Oxide					3.9 [8]	
			1-Butanol					0.4 [8]	
1997-2003	Area and Personal Sampling	Various Tank Farms	Ammonia	Periodic ops. with emissions potential	NR	NR	NA	<25 [8]	Various
			Nitrous Oxide					<50 [8]	
			VOCs					<2 [8]	
11/1998-4/1999	Area, Personal, & Source Sampling	C-106 Sluicing	Ammonia	128 area; 22 personal; 180 source	NR	NR	34	<1 [8]	Various
			Nitrous Oxide				760	<2 [8]	
			VOCs				368	<1 [8]	
2004	Source (PBF)	Single-Shell Tank Farm PBFs	Nitrous Oxide	307	307	n/a	<1 [12-24]	Various	
	Area (1-5 ft from PBF)			30	0		1-10 [12-24]		
4/2004-7/2004	Personal Sampling		Ammonia	195	181	93%	NA	0.03 [8]	11-203 min (med.=57)
			Nitrous Oxide	245	123	50%		2.1 [8]	11-203 min (med.=69)
5/2005-9/2005	Source and Area Sampling	A-Complex Tank Farms	Ammonia	900	NR	NR	104	0.215	NR
			Formaldehyde				0.03	<DL	
			Ethylamine				0.83	<DL	
			Mercury				0.016 mg/m3	<DL	
			Nitrous Oxide				120	0.017	
			NDMA				0.042	<DL	
			NMEA				0.0007	<DL	
			N-Nitrosomorpholine				0.0004	<DL	
			Acetonitrile				<DL	0.544	
Other COPCs ⁽¹⁾	<DL	<0.05							
5/2005-4/2006	Personal Sampling	A-Complex, SY, and C Tank Farms	Ammonia	327	326	99.7%	NA	0.02 [8]	NR
			Formaldehyde	7	0	0%		0.005 [8]	
			Mercury	348	315	91%		0.018 mg/m3 [8]	
			Nitrous Oxide	271	147	54%		2 [8]	
			Nitrosamines	6	6	100%		<DL	
			VOCs (by TDU)	6	6	100%		<DL	
			SVOCs (by TDU)	8	8	100%		<DL	

⁽¹⁾ Four other COPCs were measured above detection limits in area samples, but below 0.05 ppm (<3% of OEL), including 1-butanol, 2-hexanone, acetaldehyde, and butanal

NA - not available

NR - not reported

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Table 4-3. Source, Area, Sampling and Monitoring Data from 2008-2018.

Timeframe	Measurement Type	Location	Measured Vapors	Total Number of Measurements or Locations	Number of Area Detects (>DL/>RL)	Number of Area Non-Detects (<DL/<RL)	Area Measure. % of Non-Detects (<DL/<RL)	Maximum Source Concentrations (ppmv [hr if TWA])	Maximum Area Concentrations (ppmv [hr if TWA])	Sample Times
10/2008-2/2018	Source and Area Sampling	AZ Farm	Ammonia	98	1	79	99.6%	211	0.21	7.3-8 hrs
			Ammonia	308	1	273	99.6%	84	0.088	4-7.4 hrs
		AN Farm	Mercury	291	2	266	99.3%	0.46 mg/m ³	0.0017 mg/m ³	4-8 hrs
			NDMA	296	1	273	99.6%	0.26	0.000067	5-8 hrs
			Ammonia	211	2	120	98.4%	103	0.087	5-7.2 hrs
		AP Farm	Mercury	167	2	109	98.2%	0.12 mg/m ³	0.0057 mg/m ³	1.3-4 hrs
			NDMA	196	2	128	98.5%	0.019	0.0000046	4-8 hrs
			Ammonia	703	5	637	99.2%	631	0.22	10 min - 6.3 hrs
		C Farm	Mercury	655	5	616	99.2%	0.23 mg/m ³	0.017 mg/m ³	15 min - 1 hr
			NDMA	654	3	625	99.5%	1.1	0.000068	1-6.3 hrs
Ammonia	34208 ⁽¹⁾		1403	32805	95.9%	650	10.2 ⁽²⁾	inst.		
VOCs	34727 ⁽¹⁾	6020	28707	82.7%	963	27.1 ⁽²⁾				

inst. - near-instantaneous (seconds to minutes) measurements

⁽¹⁾ Represents total number of direct reading instrument measurements designated "Area"

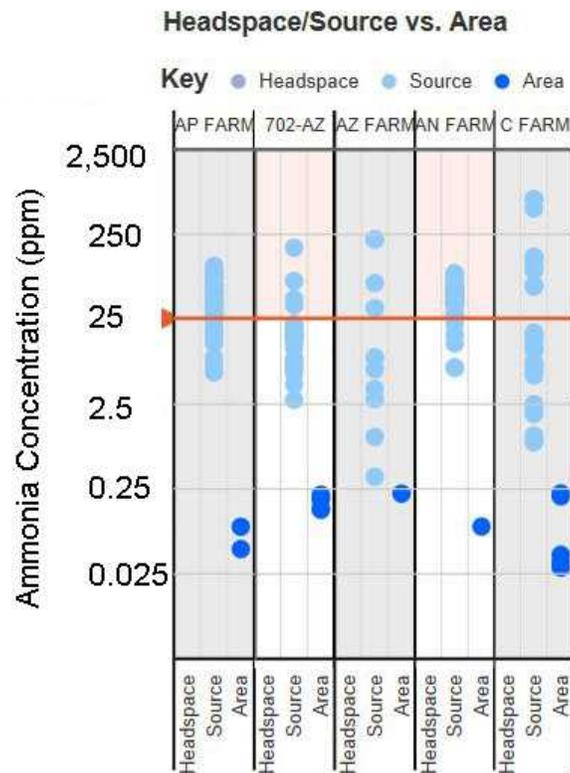
⁽²⁾ Area surveys were filtered to screen out those surveys that were actually from a source rather than area, were suspect due to discrepancies between the database information and actual survey report, or associated with enclosed spaces or maintenance activities involving non-tank waste chemicals (e.g., painting, grouting). Survey reports for any elevated readings were evaluated to confirm that the measurement location and circumstances were categorized correctly.

Ammonia is one of the most prevalent COPCs with elevated concentrations routinely detected in tank sources. Source and area sampling results from tank farms where at least one area sample measured a detectable concentration of ammonia are included in Table 4-3. The AZ, AN, AP, and C Tank Farms all reported elevated source concentrations of ammonia along with detectable concentrations in an area sample. With over 1,300 ammonia source and area samples taken in these four tank farms since 2008, greater than 98% of the area samples were non-detects.²⁹ Sample analysis data has been reviewed by IH to ensure that the results are from valid samples (e.g., adequate sample volume and corresponding analytical detection limit), including those samples with non-detects (i.e., less than reporting or detection limits). Maximum detectable area concentrations (TWA – typically 1 to 2 hours) of ammonia ranged from 0.084 to 0.22 ppm, approximately one-thousandth or less maximum source concentrations measured in each tank farm. These area results compared directly to source concentrations are also shown graphically in Figure 4-3, together with a red line indicating the ammonia TWA occupational exposure limit. Mercury and N-Nitrosodimethylamine (NDMA) were also detected in area samples in these same tank farms. Maximum mercury area concentrations ranged from 0.002 to 0.02 mg/m³, approximately a factor of 10 to 100 lower than corresponding maximum source concentrations. NDMA maximum area concentrations ranged from approximately 0.005 to 0.07 ppb, or a factor of 1,000 to 10,000 lower than maximum source concentrations. Consistent with ammonia sampling, more than 98% of mercury and NDMA area samples were non-detects.³⁰ Source and area sampling results from 2008 to present continue to support conclusions from the IH technical basis that area concentrations are a factor of 10 or more lower than source concentrations, and well below occupational exposure limit concentrations.

²⁹ The detection limit for ammonia averaged less than 0.5 ppm. The maximum detection limit for samples without data quality issues was 2.2 ppm.

³⁰ Detection limits for mercury and NDMA averaged less than 0.0008 mg/m³ and 0.01 ppb, respectively. The maximum detection limits for samples without data quality issues were 0.007 mg/m³ and 0.1 ppb, respectively.

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Graphic adapted from data analysis and visualization system (<https://www.tankvaporsexplorer.com>). The red line is the time-weighted average occupational exposure limit for ammonia.

Figure 4-3. Ammonia Source and Area Sampling Results for Tank Farms with At Least One Detectable Area Result.

Whereas area sampling results provide ample evidence that TWA concentrations are well below levels of concern, they do not explicitly demonstrate that elevated concentrations of COPCs are not occurring over very short-time frames. However, DRI readings for ammonia and VOCs represent near-instantaneous measurements compared to the TWA sampling results, and do provide evidence of very few detections of short-term elevated area concentrations, and at least a factor of 10 to 100 differences between source and short-term area measurements (see Table 4-3). Of more than 68,000 individual area monitoring measurements since 2010, 96 and 83% of all ammonia and VOC measurements, respectively, resulted in concentrations recorded in the database as zero or as below detection limits. The vast majority of measurements indicating zero or non-detect would be expected for a distribution representing rare events (e.g., elevated concentrations) within a large population of data. Table 4-4 and Table 4-5 provide further details on the recent ammonia and VOC area DRI monitoring results by tank farm, respectively. More than 160,000 individual DRI monitoring measurements from source, area, vapor control and reduction zones, and buffer zones were available for evaluation. Pre-2011 data was screened out because it contained DRI bump test results from checks of instrument functionality that could not be readily separated from true area readings. The evaluation also focused on survey results that were identified as area monitoring only to assess data from breathing zones that were not associated with a direct source measurement.

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Table 4-4. Summary of Ammonia Direct-Reading Instrument Area Data for Tank Farm Surveys Likely to Represent True Area Samples.

Facility	Count of all Post-2010 NH ₃ Area Data	Percentage of All Post-2010 NH ₃ Area Data Likely Bolus-Relevant and Above Detection Limit	Max (ppm) for Post-2010 NH ₃ Area Data Likely to be Bolus-Relevant
702-AZ building	778	N/A	N/A
A Tank Farm	930	0.8	2.0 ^a
AN Tank Farm	3009	0.1	2.0
AP Tank Farm	4419	0.7	3.0
AW Tank Farm	2204	0.3	1.0
AX Tank Farm	4177	0.5	1.4
AY Tank Farm	5250	0.2	3.0 ^b
AZ Tank Farm	2390	0.3	4.0 ^c
B Tank Farm	68	0.0	0.0
BX Tank Farm	48	0.0	0.0
BY Tank Farm	241	0.0	0.0
C Tank Farm	8642	3.6	10.2
S Tank Farm	151	0.0	0.0
SX Tank Farm	193	0.0	0.0
SY Tank Farm	1326	0.0	0.0
T Tank Farm	245	0.0	0.0
TX Tank Farm	72	0.0	0.0
TY Tank Farm	26	0.0	0.0
U Tank Farm	39	0.0	0.0
Total	34208	1.2	10.2

(a) Survey 14-05879, from ground scans along a steam line. Two higher concentrations in the DRI database were categorized by the automatic logic as being relevant, based on information in the database, but the survey showed they were not relevant. For survey 18-01255, the report identifies measurements of 31.6 and 6.9 ppm; the first of these was stated to be from a breather filter and the second, though not explicitly described as from a breather filter, probably also was.

(b) Survey 15-01138 measured on rounds while in the AY Tank Farm. One higher concentration of 20.9 ppm had been measured in the tank farm (survey 15-01464), but the survey shows no readings above 0 ppm; the database is apparently in error.

(c) Survey 15-01138 measured on rounds while in the AZ Tank Farm. One higher concentration of 20.9 ppm had been measured in the tank farm (survey 15-01464), but the survey shows no readings above 0 ppm; the database is apparently in error. The survey for the measurement that appears in this table says "after entering farm NH₃ readings climbed to 4 ppm, but only held that reading for less than 5 seconds. Readings then dropped and hovered between 1 and 2 ppm for NH₃."

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Table 4-5. Summary of VOCs Direct-Reading Instrument Area Data for Tank Farm Surveys Likely to Represent True Area Samples.

Facility	Count of All Post-2010 VOC Area Data	Percentage of All Post-2010 VOC Area data Likely Bolus-Relevant and Above Detection Limit	Max (ppm) for Post-2010 VOC Area Data Likely to be Bolus-Relevant
702-AZ building	784	N/A	N/A
A Tank Farm	887	2.0	1.3
AN Tank Farm	3078	1.9	0.4
AP Tank Farm	4491	2.8	4.8
AW Tank Farm	2207	3.4	0.6
AX Tank Farm	4206	1.9	2.5
AY Tank Farm	5295	2.0	2.6
AZ Tank Farm	2380	3.0	8.49 ^(a)
B Tank Farm	68	0.0	0
BX Tank Farm	47	6.4	0.087
BY Tank Farm	241	0.0	0
C Tank Farm	8985	5.5	27.1 ^(b)
S Tank Farm	151	0.0	0
SX Tank Farm	195	0.5	0 ^(c)
SY Tank Farm	1331	3.8	0.2
T Tank Farm	246	0.4	0.02
TX Tank Farm	70	0.0	0
TY Tank Farm	26	11.5	0.08
U Tank Farm	39	0.0	0
Total	34,727	3.1	27.1

(a) Survey 14-05825, from ground scans. Two higher concentrations were found, but the survey showed those data were suspect or were not relevant. In survey 14-05825, the report gave a maximum measurement of 1731 ppm; there seems to have been a unit's error substituting ppm for ppb (i.e., 1.731 ppm as the true concentration). There are numerous measurements in the range of 1,000 to 10,000 ppb VOC in this survey but nothing else in the range of 1E6 ppb. Another high concentration was 18.7 ppm (from survey 11-01383), but this seems to have been measured under a canopy and so is not relevant.

(b) Survey 15-00352, from boundary area RAEs. Two higher concentrations were found, but the survey showed those data were invalid. In survey 15-01966, the survey says the high measurement of 1351 ppm was invalid, and the instrument was taken out of service. The next highest relevant measurement in C Tank Farm was 942.8 ppm (from survey 14-08389); the survey says this measurement was invalid.

(c) The only SX Tank Farm measurement that was categorized as relevant and that was non-zero was from survey 13-00947. According to the survey, the sample was taken at a vadose hole outside SX Tank Farm. It was therefore irrelevant. All other SX Tank Farm area data that were categorized as likely to be relevant were 0 ppm.

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However, it was apparent that the area results included many surveys that were taken from enclosures (e.g., pits, cabinets, sealed bags) or other sources that would not be representative of a bolus-relevant event in a breathing zone. Therefore, additional screening of the available data was performed to exclude those surveys where data fields provided information indicating they were actually from sources or activities involving direct waste or other chemical measurements where elevated concentrations would be expected. The resulting data set after screening—referred to as bolus-relevant data—represented approximately 23% of the total post-2010 area monitoring results, or about 16,000 survey results. Only 1.2% of the bolus-relevant ammonia survey results were above detection limits, and the maximum concentration recorded was 10.2 ppm in C Tank Farm. Similar results were observed for VOC measurements, where only 3.1% of the bolus-relevant survey results were above detection limits, and the maximum concentration recorded was 27.1 ppm, also in C Tank Farm.

The DRI results indicate that elevated concentrations in the relevant area surveys are rarely detected and represent only 1 to 3% of the total area surveys since 2011.³¹ In addition, the highest concentrations measured are a factor of 10 to 100 lower than source concentrations. The duration of observed elevated concentrations measured during DRI surveys could not be consistently assessed from the survey data available. While DRI instruments may be operated near-continuously during in-tank-farm use, the data are not logged continuously. Therefore, duration data are limited to notes captured in the survey documentation and not in the results database. Because DRI monitoring is principally performed in support of rounds and routines and work-activity-specific tasks, the large number of measurements may not be representative of the concentration and frequency of rare or infrequent events in the tank farms and for all meteorological conditions. The data do support the conclusion that elevated area concentrations are infrequent and low relative to source concentrations; however, this study did not attempt to perform statistical analysis on this to quantify the confidence of the data and conclusion.

4.2.3 Evidence of Shorter Duration Elevated Concentrations in Area Monitoring

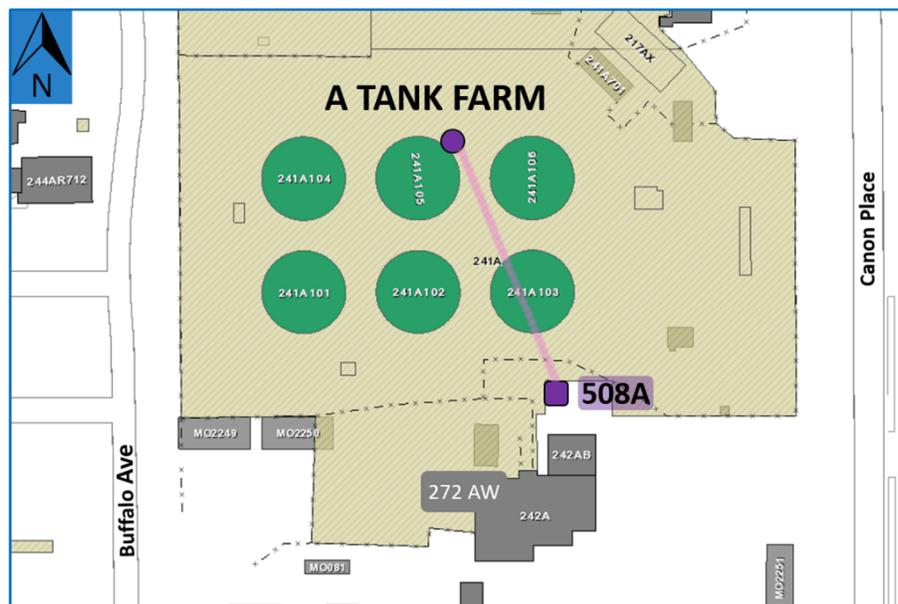
Area monitoring data with the potential to directly detect, measure, and record the duration of short-term, elevated vapor concentrations is currently limited to deployment of the VMDS area monitoring equipment in A and AP Tank Farms during fiscal years 2016-2017 pilot-scale demonstration activities. However, monitoring activities recently performed on the tank A-103 PBF, which represents a primary source of emissions from specific tanks and tank farms that are not actively ventilated, provide additional insight into the potential for elevated area concentrations. The area immediately adjacent to the PBF outlet represents that transition zone between an emission source and the receptor area or breathing zone. Therefore, continuous PBF monitoring provides an opportunity to assess the frequency, duration, and relative magnitude of elevated concentration emissions before they are significantly diluted and dissipate a short distance from the PBF. The PBF monitoring activities included the deployment of the mobile van with proton-transfer-reaction mass spectrometer (PTRMS) and other monitoring methods on the tank A-103 PBF in 2016 and 2017.

³¹ Thousands of DRI measurements have been recorded that generally support a key conclusion from risk analyses modeling that elevated concentration events in the breathing zone are infrequent. However, monitoring results to date may not adequately address all tank farm locations or meteorological conditions that have been considered through modeling.

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4.2.3.1 VMDS Area Monitoring

The VMDS Pilot-Scale Test Phase 2 activities were designed to produce data to enable evaluation of the viability of each technology for use as part of the VMDS, and this evaluation is documented in RPP-RPT-60386, *Test Vapor Monitoring and Detection System Pilot-Scale Test Phase II Report (FY2017)*. The testing involved both source and area monitoring within AP and A Tank Farms. Of particular interest to this analysis is continuous area monitoring that may provide evidence of short duration, elevated concentrations. For the vast majority of time VMDS monitoring equipment was operational, there were very few elevated readings from area monitoring. However, during the time frame from late March through mid-April 2017, the OP UV-DOAS instrument 508A deployed in A Tank Farm (see Figure 4-4) and OP-FTIR instruments deployed in AP Tank Farm (506A and 506B) detected numerous, low-level increases in ammonia concentrations for short periods of time (i.e., minutes). The ammonia readings during this time were low (<1.0 ppm) and not a health concern. The increased concentrations of ammonia have not been tied to any type of event, but they do appear to occur more often late in the evening and early in the morning when the atmosphere is more stable.



From Fig. 5.10 of RPP-RPT-60386, *Test Vapor Monitoring and Detection System Pilot-Scale Test Phase II Report (FY2017)*.

Figure 4-4. Approximate Location of OP UV-DOAS 508A Pilot-Scale Test.

The low-level concentration peaks at instrument 508A where ammonia concentration exceeded 0.05 ppm had typical durations of 10 minutes or less, but approximately a third of the peaks during the test period ranged from 14 to 32 minutes. The maximum concentration reported over the instrument's entire 500 ft path length was 0.19 ppm. Because the OP UV-DOAS detects ammonia over the entire 500 ft path length (pink line in Figure 4-4) and cannot distinguish the exact location or concentration at a given point along the path, the concentration of 0.19 ppm, measured as an average over 500 ft, might have represented a higher concentration that was present only in a narrower plume with a local source. It was not possible to determine whether the source was local or distant (e.g., off-tank-farm sources). However, based on the fact that multiple instruments measured the plumes at the same time, it is likely that the plumes were

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large, and the sources were relatively distant. In addition to duration and maximum concentration, wind speed and direction measurements were compared for the same time frame of the concentration data. Elevated concentrations appeared to consistently coincide with lower wind speeds (less than 5 to 7 mph), while wind direction varied.

508A measurements from the VMDS pilot-scale test are presented in Section A3.0 of Appendix A.

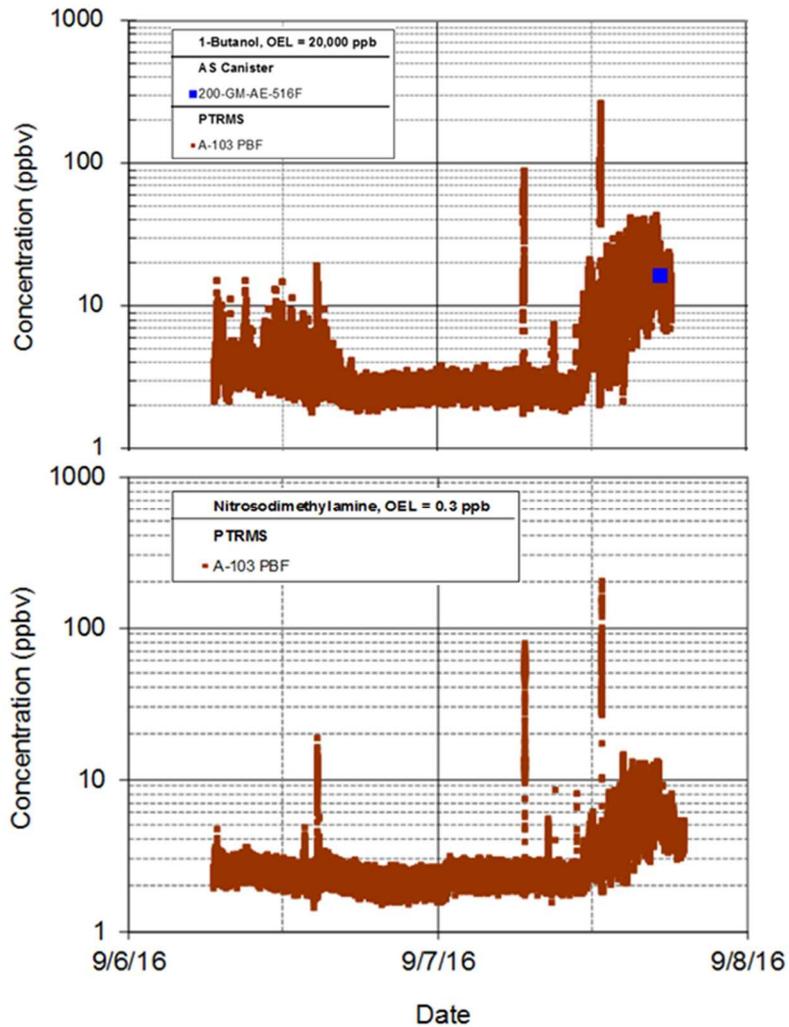
4.2.3.2 PTRMS Monitoring at Tank A-103 Passive Breather Filter

During two separate field measurement campaigns in 2016 and 2017, the mobile laboratory was set up outside A Tank Farm to continuously measure vapors at the tank A-103 PBF. A sample tube was inserted up and under the weather guard (see Figure 2-9, left panel for example PBF), between the enclosed radial HEPA filter and outer weather guard, and vapors were drawn from the PBF to the mobile van stationed outside the tank farm. Because the PTRMS quantifies chemical compounds by mass number, there can be known analytical interferences for some of the COPCs that could not be distinguished at the time these measurements were taken. Therefore, the concentrations recorded for the detected COPCs are not quantitatively confirmed and care must be taken in drawing conclusions about the concentration. However, the detection and duration of elevated concentrations or excursions of tank vapor chemicals is evident from the data.

Continuous monitoring from September 6 to 8, 2016, with the PTRMS detected a number of short-duration increases in concentrations of several relevant chemicals, including the COPCs methanol, 1-butanol, NDMA, furan, and the non-COPC acetone. The PTRMS measures at sub-second intervals and records 2-second average readings, creating a near continuous output of concentration readings. Excursions from a running baseline concentration were evaluated for each COPC, and several parameters quantified for each excursion including duration, time to maximum, and both maximum and median concentration observed during the excursion. Representative plots of data for 1-butanol and NDMA are shown in Figure 4-5 with several short-duration concurrent concentration peaks of both COPCs being apparent. These excursions ranged from approximately 20 seconds to 4.6 minutes in duration and reported maximum concentrations from approximately 19 to 260 ppb.³² Similar data were obtained for other chemicals detected. A table that summarizes the concentrations and durations of short-term concentration increases from the 2016 tests can be found in Section A1.0 of Appendix A.

³² The actual magnitude of these concentrations is uncertain due to known interferences of other compounds with the same mass number as the COPCs. Later studies described in subsequent paragraphs were better able to quantify COPC concentrations.

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From RPP-RPT-60386, *Test Vapor Monitoring and Detection System Pilot-Scale Test Phase II Report (FY2017)*.

Figure 4-5. 1-Butanol and NDMA Measured During Tank A-103 PBF Monitoring with the PTRMS in 2016.

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In May 2017, the mobile laboratory was deployed a second time at the tank A-103 PBF with an upgraded system that reduced but did not eliminate interference from other non-COPC species. The reduction in interferences was most notable for NDMA, where the prior year's study had noted interference from ambient smoke, ethyl formate, as well as methyl acetate, all of which had elevated the apparent concentrations reported for NDMA in the 2016 testing.

Figure 4-6 shows plots of concentration over time for several COPCs and non-COPCs detected during the May 23 to 25, 2017 re-deployment. The plots also show the reporting limit if known, as well as the COPC-specific criterion above which concentration peaks were selected as being discrete events rather than continuing noise. There were several gaps when the instruments were not operating; these blank areas in the plots do not represent measurements of zero concentration.

As with the earlier 2016 mobile laboratory deployment, several of the chemicals measured were observed with concurrent excursions. These excursions ranged from approximately 10 seconds to 1.5 minutes in duration and reported maximum concentrations from approximately 2 to 392 ppb. The maximum durations of the excursions were significantly lower in the 2017 study, but the data were generally consistent showing periods of hours when the time-average concentration was elevated. In these periods the fine temporal detail showed numbers of discrete peaks of very short duration (minutes), some of the peaks being well above the time-average concentration. Section 6.0A1.0 of Appendix A presents a table listing the concentrations and durations from the May 2017 mobile laboratory deployment.

These near-source measurements over several days depict irregular but relatively frequent, up to several times per day, increases in concentrations in immediate proximity to the PBF source emission point for very short (seconds to minutes) periods of time. For three of the chemicals – NDMA, acetone, and methanol – maximum headspace concentrations are available from recent (April 2016) tank A-103 sampling. The maximum concentrations observed with the PTRMS for these three chemicals are generally comparable to peak headspace concentrations.³³

Note that it is impossible that concentrations in the tank headspace itself could change as significantly as shown in the monitoring plots over a period of less than a minute, or even a period of hours. The waste-gas release rates and ventilation rates for passively-ventilated tank headspaces are so low, compared to headspace volumes, that the headspace concentration requires days to weeks to respond to changes, as shown in Table 2-1. Changes in meteorological conditions over hours, or parts of hours, can cause the three-tank cascade that includes tank A-103 to emit headspace gases through the A Tank Farm vents other than the tank A-103 PBF, potentially accounting for elevated concentrations lasting for hours at the tank A-103 PBF and then dropping to baseline. The effect of meteorological conditions is further discussed in Section A2.0 of Appendix A. The 1-minute or shorter peaks and noise in the data are probably accounted for by local turbulence under the cap (weather shield) of the PBF. As discussed in Section 3.0, when a release encounters atmospheric turbulence it is pulled apart by the turbulent vortices.

³³ The maximum NDMA, acetone, and methanol concentrations detected in recent April 2016 tank A-103 headspace samples were 9.6 ppb, 53 ppb, and 754 ppb, respectively.

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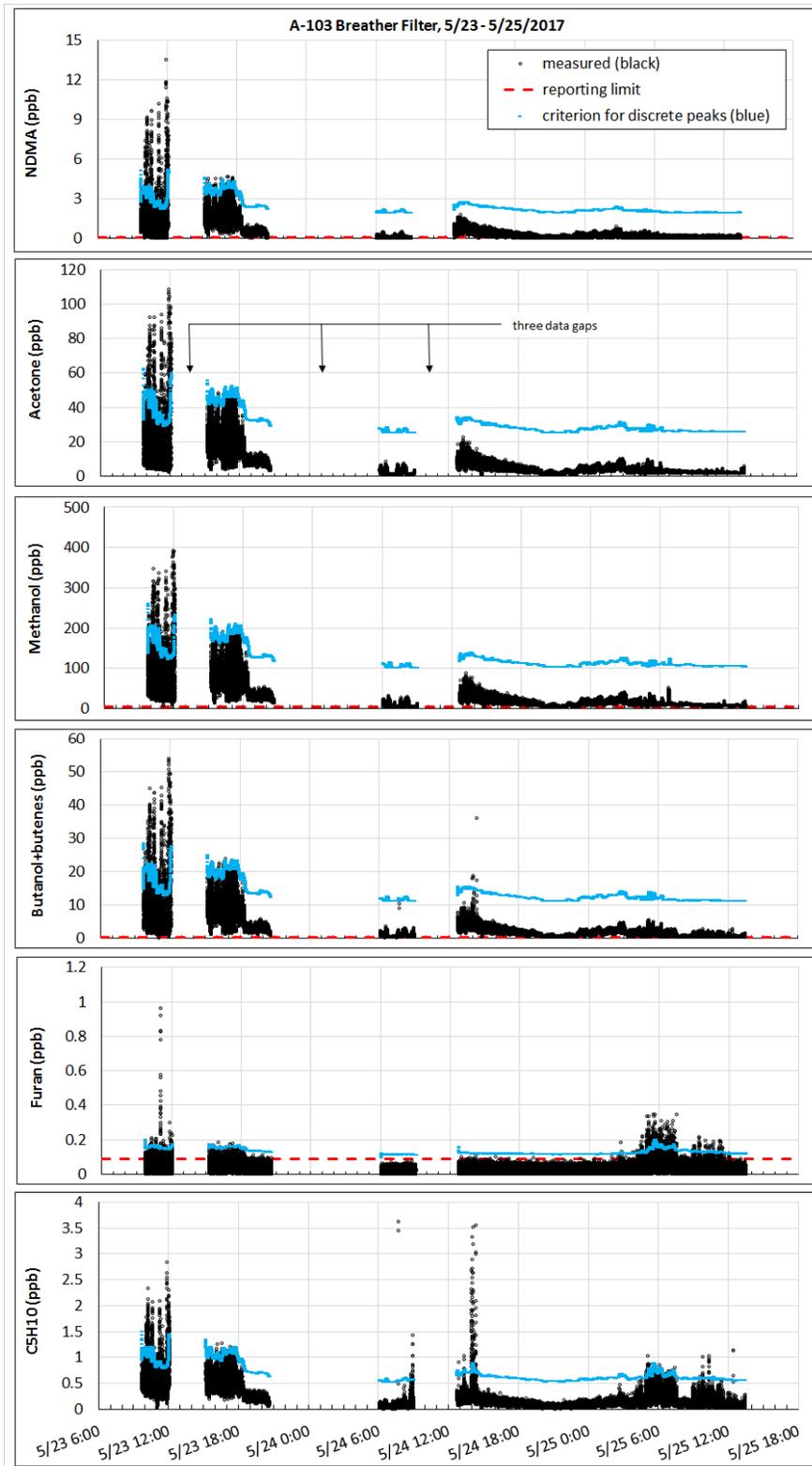


Figure 4-6. Selected Chemicals Measured During Tank A-103 PBF Monitoring with the PTRMS in 2017.

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In summary, the 2016 and 2017 PTRMS measurements of vapor concentrations under the hood of the tank A-103 PBF at the face of the filter indicated relatively short (seconds to minutes) peaks of several COPCs that can be near headspace concentrations at this transition point between source and area. Longer duration periods of elevated time-averaged concentration are also evident.

In addition to the specific measurement campaigns identified above, the mobile laboratory has been deployed in a separate “background” study to evaluate the typical concentrations in and around the Hanford Site as well as in the Tri-Cities across the four seasons. These studies demonstrated that hourly averaged concentrations of ammonia, nitrosamine, and furan were typically below 10% of the OEL values. However, during periods with heavy wildfire smoke, furan concentrations could be as high as several times the OEL value for brief periods. The mobile laboratory is now deployed regularly (most weekdays) to provide continued area monitoring, identify fugitive emissions, and characterize concentrations following AOP-015 events. These measurements have a temporal resolution of 2 seconds and aim to address questions around short-duration concentration fluctuations and to attribute sources to the chemical mixtures that are measured.

4.3 IMPACTS OF SHORT-DURATION VAPOR CONCENTRATIONS ON REPORTED EXPOSURES

To assess the potential impacts of both observed (Section 4.2) and predicted (Section 3.3) reductions in tank source vapor concentrations by 10× to 100× within short distances of a source, a comparison of maximum ammonia headspace source concentrations, projected reductions, odor thresholds and chronic and acute exposure limits was performed. Maximum headspace ammonia concentrations for passively ventilated tanks were obtained from SWIHD data available from the tank vapors data analysis and visualization explorer (DAV).³⁴ Figure 4-7 presents these maximum headspace concentrations along with concentrations representing 10× and 100× projected reductions, which were the levels of concentration reduction that occurred within a short distance of the source as observed from monitoring data and predicted from CFD modeling. Odor thresholds for ammonia have been reported to vary significantly from person to person but are generally reported with a lower threshold of 1.5 ppm and upper threshold of 50 ppm (Leonardos et al., 1969, “Odor Threshold Determinations of 53 Odorant Chemicals.”). This ammonia odor threshold is presented as a range, colored in a yellow gradient, in Figure 4-7. Some individuals may be more sensitive to ammonia, as evidenced in Salem and Katz 2010, *Inhalation Toxicology*, which indicates 0.04 ppm is the very lowest ammonia odor threshold reported. The TWA (8-hr) occupational exposure limit for ammonia is 25 ppm, and the short-term exposure limit (15-min) is 35 ppm, which are represented by separate green and red lines on Figure 4-7, respectively.

³⁴ Data from the DAV found at <https://www.tankvaporexplorer.com/swihds/explorer> was accessed June 11, 2019. All passively ventilated tank farms with headspace ammonia data were included in this analysis. C Tank Farm was not included because the tank waste has been retrieved and headspace data is not presented in the DAV. U and B Tank Farms are not presented because there is no headspace ammonia data presented in the DAV.

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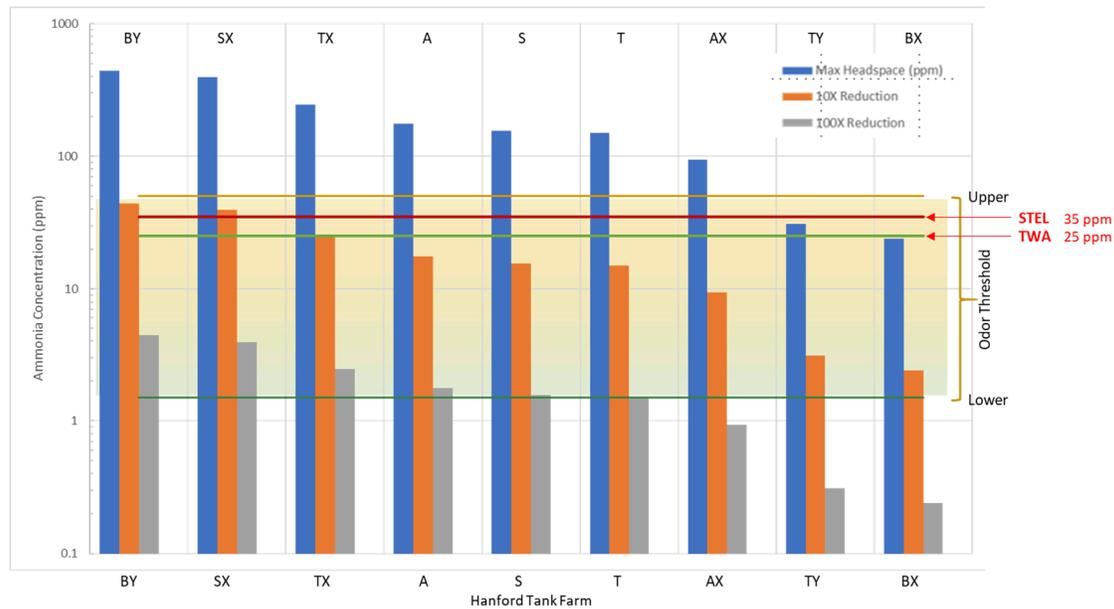


Figure 4-7. Comparison of Maximum Headspace Ammonia Concentrations and Projected Concentration Reductions to Odor Thresholds and Exposure Limits.

The analysis indicates that for most passively ventilated tank farms, a 10× reduction in ammonia concentration from maximum measured headspace levels results in ambient air concentrations a short distance from the source (e.g., PBF) below both the 15-minute STEL and 8-hour TWA exposure limits. Only under maximum headspace concentrations observed in BY and SX Tank Farms could a 10× reduction result in an ambient concentration above the TWA and STEL³⁵. A 100× reduction in the maximum headspace concentration would produce ambient ammonia concentrations approximately 10× lower than the 8-hour TWA, and very close to the lower odor threshold limit. Figure 4-7 also shows that even with 10× and 100× projected reductions, ammonia concentrations could readily exceed the odor thresholds for many individuals. While ammonia odor may be detected and irritation may occur, concentrations are primarily at levels that are safe for those exposed, based current scientific knowledge. Eleven other COPCs with documented short-term exposure limits from regulatory bodies were also considered for similar comparison.³⁶ In all cases, a 10× reduction in maximum measured headspace concentration was well below acute and chronic exposure limits and odor thresholds. However, similar to ammonia, there may be other COPC or non-COPC chemicals present in tank vapors with low odor thresholds that may be detected well below harmful concentration levels. For BY, SX, and U Tank Farms where the highest headspace maximums have been observed, QRAs and specific hazard assessments take these higher source terms into consideration when assessing appropriate operational controls to limit exposure potential.

³⁵U tank farm is not included in Figure 4-7 because ammonia sampling was not conducted during the time frame of the data represented in the DAV – 10/2008 to 5/2019. Data from tank U-105 presented in Figure 2-1 and Figure 2-4 indicate that ammonia headspace concentrations have been measured at levels higher than either BY or SX Tank Farms maximums, and therefore could result in even higher ambient concentrations at both 10× and 100× reductions.

³⁶ Twelve COPCs have acute exposure guidelines based on current regulatory guidelines. These COPCs include ammonia, mercury, 1,3-butadiene, benzene, methanol, 2-hexanone, 3-buten-2-one, formaldehyde, acetaldehyde, 2-propenal, ethylamine, and methyl isocyanate.

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5.0 CONCLUSIONS

This document serves as a summary of the most salient points in the current knowledge of the sources of tank vapors, the effects of atmospheric dispersion, and concentrations in the worker breathing zones based on existing data and analyses within the context of short-duration elevated concentrations. Sources of tank vapors are both passively ventilated tank penetrations that are primarily PBFs, typically located near the ground surface, and actively ventilated stacks, which are typically tens of feet above the ground. Headspace concentrations are generally consistent over time, although solubility of gas and vapor within the waste may contribute to variability over long time periods. Headspace concentration variability under quiescent conditions has been observed to be approximately 10%. For waste-disturbing events, headspace concentrations have been observed to peak relatively quickly, and rapidly return to previous levels (within 24 hours) after the waste-disturbing events are terminated. BDGREs, which are a spontaneous type of waste-disturbing activity, have also been observed to result in rapid increases in headspace concentrations. However, the five BDGRE tanks are all actively ventilated, so the concentration observed from the stack is significantly lower (about 20% of the BDGRE peak concentration).

After tank vapors leave the stack, PBF riser, or miscellaneous ground-level release point, the atmosphere acts upon the emission to transport and diffuse the material. Conditions may be unstable (23% of the time), neutral (26%), or stable (51%), in decreasing order of the amount of diffusion produced by atmospheric turbulence. When emissions are near the ground surface (e.g., in the case of PBFs), stable atmospheric conditions tend to result in the highest concentrations in the worker breathing zone due to minimal mixing compared with other atmospheric conditions. At the Hanford Site, stable conditions occur approximately 51% of the time, most often during the winter months or between sunset and an hour after sunrise during all seasons. Recent QRA modeling used a set of six meteorological conditions that were expected to result in the highest ambient air concentrations and predicted that breathing-zone concentrations are $10\times$ lower than the source concentration within 2 m from the source and continue to decrease as the distance increases.

For emissions from elevated stacks, unstable conditions are expected to result in the highest breathing zone concentrations as a result of mixing conditions that bring the plume down toward the ground surface. At the Hanford Site, unstable conditions occur approximately 23% of the time, most often during summer and daytime periods. Modeling has shown that, under conditions expected to produce the highest ground-level concentrations, plume transport from an elevated release to the ground-level worker breathing zone travels many tens of feet, over which a factor of 10 or more of concentration reduction occurs.

Significant sampling and monitoring have been performed in the tank farms to characterize work zones, evaluate concentration trends, and assess personal exposure. Although the majority of sampling represents TWAs that are minutes to hours in duration rather than short-duration peak concentrations, 2,000 source and area locations were also monitored with near-real-time instruments. As an example, area measurements for ammonia available from SWIHDS ranged from 0.084 to 0.222 ppm, which were approximately factors of 10 to 100 lower than the concentration maxima of the sources, and 98% of the ammonia area measurements were below instrument detection limits. Real-time monitoring deployed as part of the VMDS has detected some short-duration increases in concentrations with open-path instrumentation. For example,

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during March and April 2017, several open-path instruments deployed within the A Tank Farm and around the AP Tank Farm simultaneously detected ammonia at low concentrations on several days for relatively short periods, ranging from 1 to 32 minutes. The concentration maxima, assuming the plume occupied the full path length of the instrument in the A Tank Farm, ranged from 0.05 to 0.19 ppm.

While most of the historical data that is available for area concentration measurements are TWA values, a mobile laboratory equipped with a PTRMS, CO₂ sensor, and ammonia sensor has been deployed for several measurement campaigns since 2016 and is now regularly deployed to evaluate fugitive emissions sources. This new capability collects concentration data for a variety of chemical compounds at 2-second temporal resolution and is an effort to identify short-duration vapor emissions and potential worker exposures.

The TVAT concluded that the presence of elevated source concentrations (e.g., headspace) concurrent with AOP-015 events within the tank farm “provide clear testimony that exposures are to acute intense concentration.” It also stated:

...while at this point in time there is little direct evidence of this linked temporal occurrence, it is believed that fugitive tank emissions always precede worker inhalation exposures. Lending credence to this temporal relationship is the co-occurrence of exposure events with low air speed on farms.

Table 5-1 summarizes the four observations offered by the TVAT in support of the hypothesis along with relevant information presented within this report. EIR data summarized in Table 4-1 provide evidence that reported events (odor, symptoms, or both) encompass almost equally events in and outside the tank farms, with and without symptoms, and frequently occur distant or upwind from tank sources. While the TVAT does not clearly define “acute intense concentration,” it does imply relatively high vapor concentrations and resulting symptoms of irritation or other effects. In contrast to this conclusion, advanced modeling of tank-farm specific emissions described in Section 3.0, combined with substantial DRI data described in Section 4.0 provide evidence that tank farm emissions reaching the breathing zone are factors of 10 to 100 below tank headspace or source concentrations, and decrease rapidly via normal atmospheric dispersion processes within a short distance of the passive vents (a few meters, typically within the VCZ).³⁷

Measurement data and modeling indicate that low wind speeds on tank farms tend to correlate with higher concentrations measured directly at the PBF face. However, as described in Section 2.0, there is an interplay between barometric pressure, wind speed, and temperature (buoyant forces) that impacts vapor emission rates from a PBF as well as dispersion and downwind concentrations.

³⁷ Thousands of DRI measurements have been recorded that generally support a key conclusion from risk analyses modeling that elevated concentration events in the breathing zone are infrequent. However, monitoring results to date may not adequately address all tank farm locations or meteorological conditions that have been considered through modeling.

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Table 5-1. Summary of TVAT Basis for Bolus Hypothesis and Current Understanding to Address Each Basis. (2 sheets)

TVAT Basis	TVAT Report Excerpt	Current Understanding
Model results predicting elevated concentrations in breathing zone	<p>“The hypothesis was substantiated by computer modeling, which indicated that under certain weather conditions, concentrations approaching 80% of the head space concentration could exist 10 feet downwind from the release point and potentially in workers’ breathing zones.” (App. C, pg. 87)</p>	<p>The results of the PNNL-14767 study were not correctly used to support this basis:</p> <ul style="list-style-type: none"> • Data used to develop the diffusion coefficients used within the Gaussian plume model were collected from 100 m to 10 km, so results within the first 100 m should not be considered quantitatively. (Section 3.2) • Characteristics of the source, including geometry and turbulence effects, have significant impact on the concentrations near the source such that the errors associated with Gaussian plume estimates within the first 100 m should be considered large. (Section 3.2) • The combination of inputs for this cited worst-case result is an unlikely scenario. (Section 3.3) <p>Current CFD modeling predicts:</p> <ul style="list-style-type: none"> • 10× concentration reduction at 1 m from ground level sources. (Section 3.3) • 100× or more concentration reduction within 20 m from elevated sources. (Section 0)
Proximity and correlation of elevated irritant source concentrations with reported personnel exposures	<p>Elevated DRI source readings of ammonia and VOCs reported concurrent with AOP-015 reported symptoms of workers:</p> <p>“symptoms and signs reported only during times workers are physically on the tank farm.” (App. C, pg. 84)</p> <p>“...there is essentially a perfect correlation between the workers having an adverse acute inhalation health effect and being physically present on a tank farm.” (App. C, pgs. 84-85)</p> <p>“provide clear testimony that exposures are to acute intense concentration.” (Sect. 6, pg. 43)</p>	<p>Reported exposures (odor, symptoms, or both) encompass events inside and outside the tank farms almost equally. (Section 4.1)</p> <p>Area measurements corroborate modeling data in that worker breathing zone concentrations are 10 to 100 times lower than source concentrations. Vapor concentrations may still result in detectable odors and possible irritation depending on a worker’s specific odor threshold and sensitivity to the chemical species. (Section 4.3)</p>
Fugitive tank emissions precede worker exposure	<p>“Thus, while at this point in time there is little direct evidence of this linked temporal occurrence, it is believed that fugitive tank emissions always precede worker inhalation exposures. Lending credence to this temporal relationship is the co-occurrence of exposure events with low air speed on farms.” (App. C, pg. 84)</p>	<p>Reported exposures (odor, symptoms, or both) encompass events inside and outside the tank farms almost equally. (Section 4.1)</p> <p>DRI results indicate that elevated concentrations in the relevant area surveys are rarely detected and represent only 1-3% of the total area surveys since 2011. (Section 4.2.2)</p>

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Table 5-1. Summary of TVAT Basis for Bolus Hypothesis and Current Understanding to Address Each Basis. (2 sheets)

TVAT Basis	TVAT Report Excerpt	Current Understanding
Correlation between exposures and tank farm presence	<p>“symptoms and signs reported only during times workers are physically on the tank farm.” (App. C, pg. 84)</p> <p>“...there is essentially a perfect correlation between the workers having an adverse acute inhalation health effect and being physically present on a tank farm.” (App. C, pgs. 84-85)</p>	The highest area concentrations measured are a factor of 10 to 100 lower than source concentrations. (Section 4.2.2)

AOP-015, *Response to Reported Odors or Unexpected Changes to Vapor Conditions.*

PNNL-14767, *Characterization of the Near-Field Transport and Dispersion of Vapors Released from the Headspaces of Hanford Site Underground Storage Tanks.*

CFD = computational fluid dynamics.

DRI = direct-reading instrument.

PBF = passive breather filter.

VOC = volatile organic compound.

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The QRA modeling efforts described in Section 3.0 addressed the range of realistic meteorological conditions and a sophisticated near-field model based on historic Hanford Site weather and reported bounding results from the conditions producing the highest potential for vapor concentrations above background. In contrast, PNNL-14767 described a bounding analysis using hypothetical meteorological and emission rate conditions, as well as a dispersion model with significant near-field limitations to project potential concentrations for conditions (e.g., high emission rate, low wind speed, stability class G) that are not likely relevant to actual tank farm conditions. Therefore, while there is evidence that tank farm vapors emitted from a PBF may produce near-headspace concentrations at the PBF face, especially at low wind conditions when the tank is venting, there is no evidence that those emissions will result in “acute intense concentrations” distant from the VCZ of the PBF.

Area monitoring results indicate infrequent detection of measurable concentrations of tank vapors, and when detected, concentrations that are at least 10× to 100× lower than headspace concentrations. Recent DRI measurement of selected chemical species at the tank A-103 PBF face indicate that near-headspace concentrations are present for short periods of time (seconds to minutes), and at elevated concentrations for up to several hours. However, the concentrations decrease by a factor of three or more within inches of the PBF face. Together, area and PBF monitoring supports a key conclusion from risk analyses modeling that elevated concentration events in the breathing zone are infrequent. While at greater than 10 times below headspace concentrations near the PBF, these vapor concentrations may still result in detectable odors depending on a worker’s specific odor threshold for the chemical species.

In short, both the empirical sampling and air monitoring data as well as sophisticated CFD air modeling results do not provide information that supports the TVAT hypothesis that workers have experienced concentrations approaching 80% of the headspace concentration up to 10 ft from tank sources. The data indicate that the volume generated by releases within the tanks is not the driving force for flow rates out of the tank. The exhaust flow rates themselves are driven by either environmental conditions (in the case of passive-ventilation emissions) or exhauster ventilation rates (in the case of actively ventilated stacks). Variability in meteorological conditions is the primary driver for the short-duration nature of vapor concentrations above background. Modeling indicates that concentrations are quickly reduced from the source, and that the greatest upper end predicted concentrations at worker breathing zones are a factor of 10 or more lower than source concentrations. Area measurements corroborate the fact that worker breathing zone concentrations are 10× to 100× lower than source concentrations, and events with elevated concentration are rare. These vapor concentrations may still result in detectable odors and possible irritation depending on a worker’s specific odor threshold and sensitivity to the chemical species. Short-duration vapor events may be mitigated by evaluating atmospheric conditions in conjunction with tank farm activities on a daily basis. Monitoring changing conditions related to tank vapors concentrations at the source and within worker breathing zone is also an important step to protect workers from short-duration elevated concentration events.

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APPENDIX A

HIGHER TEMPORAL RESOLUTION FIELD MONITORING DATA

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APPENDIX A HIGHER TEMPORAL RESOLUTION FIELD MONITORING DATA

The field data analysis discussed in this appendix were obtained in four separate measurement campaigns. The 2016 and 2017 campaigns described in Section A1.0 collected data for a variety of chemicals from the tank A-103 passive breather filter (PBF) using the proton-transfer-reaction mass spectrometer (PTRMS) instrument in the mobile van. Several days of data were collected in each campaign with measurements that were recorded every 2 seconds. The 2018 campaign also used a sampling location at the tank A-103 PBF but employed a set of direct-reading instruments (DRI) to monitor ammonia at 1-minute intervals over a period of 2 months. This 2018 campaign is described in Section A2.0. The fourth campaign collected data from the pilot scale tests of open-path instruments used in the vapor monitoring and detection system area monitoring in A and AP Tank Farms during fiscal years 2016-2017.

A1.0 2016 AND 2017 PTRMS MONITORING AT TANK A-103 PASSIVE BREATHING FILTER

As described in main text Section 4.2.3.2, tank A-103 PBF data was obtained by the mobile laboratory during two separate deployments that occurred in 2016 and 2017. Concentration peaks and durations from the 2016 deployment are presented in Table A-1. A similar table for the concentration peaks and durations from the 2017 deployment are presented in **Error!** **Reference source not found..**

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Table A-1. Duration and Maximum Concentration of Selected COPCs and Non-COPCs Concurrently Measured During Short-Term Concentration Increases at the Tank A-103 PBF with the PTRMS Mobile Laboratory in September 2016.

Chemical	Representative Peak Time	Peak Duration (min)	Time to Maximum (min)	Maximum During Peak (ppb)	Median During Peak (ppb)
NDMA	9/6/2016 14:39	0.90	0.83	18.8	12.3
1-Butanol	9/6/2016 14:39	0.37	0.23	18.9	16.7
Furan	9/6/2016 14:39	0.93	0.70	22.4	16.3
Methanol	9/6/2016 14:39	0.97	0.90	302.9	152.4
Acetone ^a	9/6/2016 14:43	1.27	0.67	37.4	11.8
Acetone ^a	9/6/2016 14:43	0.77	0.23	26.2	13.5
Methanol	9/6/2016 14:43	4.23	1.80	208.3	80.9
Acetone	9/6/2016 15:11	0.53	0.50	20.4	10.3
Methanol	9/6/2016 15:11	0.60	0.53	80.7	47.6
NDMA	9/7/2016 6:41	0.87	0.70	57.3	49.7
1-Butanol	9/7/2016 6:41	0.73	0.60	64.3	53.1
Acetone	9/7/2016 6:41	0.73	0.60	34.7	28.6
Furan	9/7/2016 6:41	0.87	0.60	72.8	57.6
Methanol	9/7/2016 6:41	0.90	0.73	344.4	245.4
NDMA	9/7/2016 6:47	4.50	3.47	78.7	26.5
1-Butanol	9/7/2016 6:47	3.07	2.40	88.3	57.6
Acetone	9/7/2016 6:47	4.07	2.77	45.6	20.9
Furan	9/7/2016 6:47	4.50	3.30	92.0	29.1
Methanol	9/7/2016 6:47	4.60	4.50	372.1	132.8
NDMA	9/7/2016 12:44	4.57	0.23	206.7	63.2
1-Butanol	9/7/2016 12:44	4.50	1.70	261.6	82.1
Acetone	9/7/2016 12:44	4.43	1.60	116.3	40.5
Furan	9/7/2016 12:44	4.63	2.80	116.6	78.4

a - The representative peak times are taken at the "end" of the peak. Thus, the acetone peak with the 1.27-minute duration indicated at the representative peak time of 9/6/2016 14:43 started during 9/6/2016 14:41, whereas the 0.77-minute peak occurred entirely during 9/6/2016 14:43.

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Table A-2. Duration and Maximum Concentration of Selected COPCs Concurrently Measured During Short-Term Concentration Increases at the Tank A-103 PBF with the PTRMS Mobile Laboratory in May 2017

Chemical	Representative Peak Time	Peak Duration (min)	Time to Maximum (min)	Maximum During Peak (ppb)	Median During Peak (ppb)
NDMA	5/23/17 10:16	1.50	0.667	9.12	6.53
1-Butanol+		0.63	0.50	44.9	36.6
Acetone		0.60	0.50	92.2	78.0
Methanol		0.60	0.50	347	292
C ₅ H ₁₀		1.33	0.50	2.33	1.70
1-Butanol+	5/23/17 10:17	0.63	0.43	39.2	33.3
Acetone		0.53	0.47	84.5	73.5
Methanol		0.53	0.47	309	279
NDMA	5/23/17 10:33	0.2	0.067	7.23	6.62
1-Butanol+		0.167	0.033	37.7	32.9
Acetone		0.167	0.033	84.8	75.2
Methanol		0.167	0.033	312	286
C ₅ H ₁₀		0.167	0.033	1.67	1.51
1-Butanol+	5/23/17 10:40	0.63	0.57	43.6	35.8
Acetone		0.63	0.57	92.2	76.4
Methanol		0.63	0.57	336	285
C ₅ H ₁₀		0.63	0.60	2.07	1.60
NDMA	5/23/17 11:18	1.33	1.17	10.2	5.90
1-Butanol+		1.30	1.20	45.2	30.6
Acetone		1.30	1.20	93.9	64.2
Methanol		1.30	1.20	341	244
C ₅ H ₁₀		1.33	1.17	2.08	1.46
NDMA	5/23/17 11:55	0.70	0.60	13.5	9.69
1-Butanol+		0.70	0.63	53.8	44.1
Acetone		0.73	0.67	109	88.6
Methanol		0.70	0.63	392	328
C ₅ H ₁₀		0.77	0.57	2.83	1.97
NDMA	5/23/17 12:00	0.90	0.77	10.6	6.15
1-Butanol+		0.93	0.87	46.8	31.7
Acetone		0.93	0.87	95.7	64.2
Methanol		0.93	0.83	353	243
C ₅ H ₁₀		0.90	0.73	2.18	1.54
NDMA	5/23/17 12:01	0.33	0.17	10.3	7.07
1-Butanol+		0.27	0.033	49.5	41.9
Acetone		0.20	0.033	104	87.2
Methanol		0.20	0.033	390	317
C ₅ H ₁₀		0.27	0.033	2.04	1.08
NDMA	5/23/17 12:03	1.07	0.50	10.4	6.97
1-Butanol+		0.67	0.47	49.1	32.6
Acetone		0.53	0.47	98.3	68.4
Methanol		0.53	0.43	357	255
C ₅ H ₁₀		0.67	0.43	2.29	1.65
1-Butanol+	5/23/17 12:04	0.23	0.10	41.3	31.2
Acetone		0.23	0.10	88.9	62.6
Methanol		0.20	0.10	334	257
C ₅ H ₁₀		0.23	0.10	1.74	1.47

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A2.0 2018 CONTINUOUS AMMONIA MONITORING BY DIRECT-READING INSTRUMENTS AT TANK A-103 PASSIVE BREATHER FILTER

Testing performed in 2018 collected tank A-103 PBF vapor data using a sample line similar to the PTRMS studies in 2016 and 2017. These tests were performed to evaluate personal monitoring instruments for ammonia (RPP-RPT-61096, *Wearable Ammonia Detector Field Trial*), and measured 1-minute-resolution concentration data from three types of DRI: the ToxiRAE Pro, Ventis Pro 5, and Micro IV (GfG) instruments. These instruments were located within a 48-qt cooler that served as a vapor sampling box to allow the instruments to sample a common air space. A pump was used to draw air from near the filter face on the stack riser and deliver the sample continuously into the sampling box. The data from these three instruments were averaged and compared to meteorological data for the test period to identify the effects of the three mechanisms of passive ventilation. The parameters explored were barometric pressure (flow driven by ambient pressure change), temperature (buoyancy-driven ventilation), and wind speed (venturi effect).

Based on the first mechanism of passive ventilation, barometric pressure change, the passively ventilated tank would be expected to exhaust when barometric pressure is falling, in order to equilibrate headspace pressure with barometric pressure. Figure A-1 shows ammonia concentration³⁸ measured at the tank A-103 PBF and the corresponding barometric pressure data during the test period. Because of sampling configuration changes, the relative heights of the ammonia concentration peaks cannot be interpreted as being caused by meteorological conditions alone. However, the occurrence of peaks can be relied on to indicate when gas is being emitted from the headspace. The light red shaded areas are periods when the barometric pressure was falling, and the blue shaded areas are periods when the barometric pressure was increasing or flat.³⁹ In essentially every case, the ammonia concentration peaked within the red shaded area and was declining or zero in the blue shaded area. This suggests that barometric pressure reductions were strongly related to tank A-103 vapor emissions during the test period.

Based on the second mechanism (buoyancy), one would expect the passively ventilated tanks to exhaust when outside air is denser (i.e., lower temperature) than the headspace air. Figure A-2 shows the ammonia concentration measured at the tank A-103 PBF and the corresponding outside air temperature data during the test period. The light red shaded areas are periods when the outside air temperature was above 75 °F, and the blue shaded areas are periods when the outside air temperature was below 75 °F. The data indicate a relationship that is the opposite of that expected from the postulated buoyancy effect (i.e., tank A-103 exhaust tended to increase with increasing outside air temperature). This evidence makes it unclear whether buoyancy was significantly related to tank A-103 PBF emissions during the test period. One possible explanation is that headspace temperatures and, therefore, buoyancy effects differed for the three interconnected tanks in this cascade – A-101, A-102, and A-103 – making it difficult to say which tank PBF is an inlet or outlet. The available data are not sufficient to either prove or disprove this conjecture.

³⁸ The smoothing effect of subsampling from the cooler causes a lag in the data response compared to externally measured weather data. Also note some periods of quasi-exponential concentration decline, which may correspond to periods when tank A-103 was exhausting through some vent other than the PBF.

³⁹ The data shown in Figure A-1 are not continuous over the time period indicated; in other words, there are gaps in the x-axis. Large vertical jumps in the data are due to discontinuities in the data timing; they do not indicate instantaneous changes in barometric pressure or ammonia concentration.

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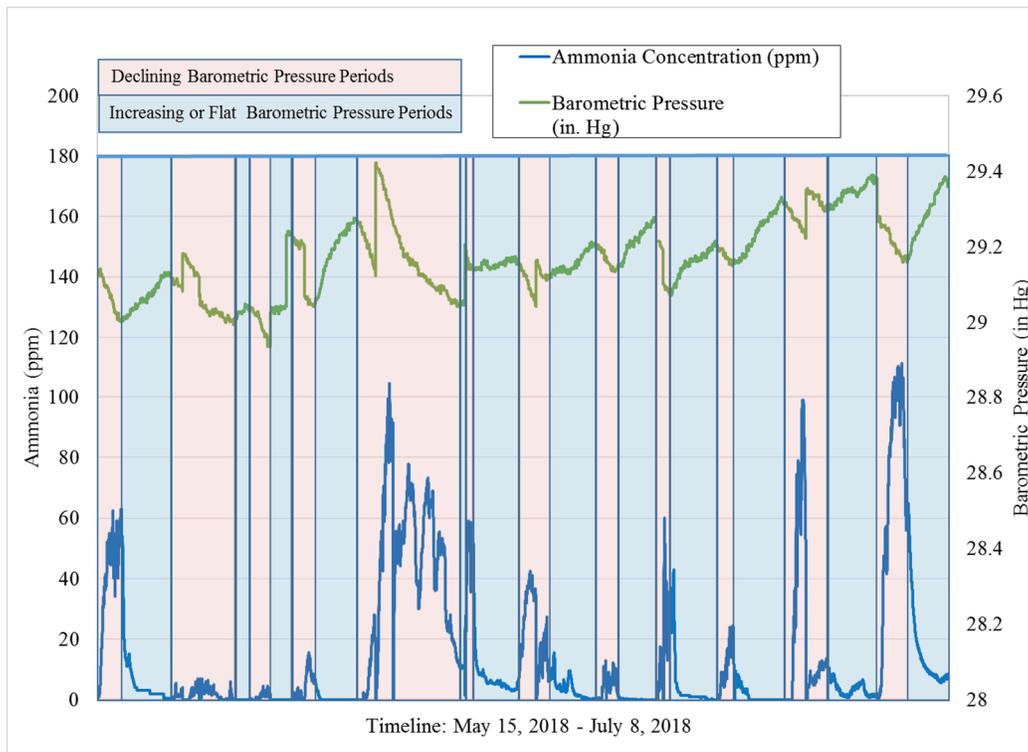


Figure A-1. Ammonia Concentration (ppm, Left Axis) Peaking at the Tank A-103 PBF Compared to Barometric Pressure (inches Hg, Right Axis)

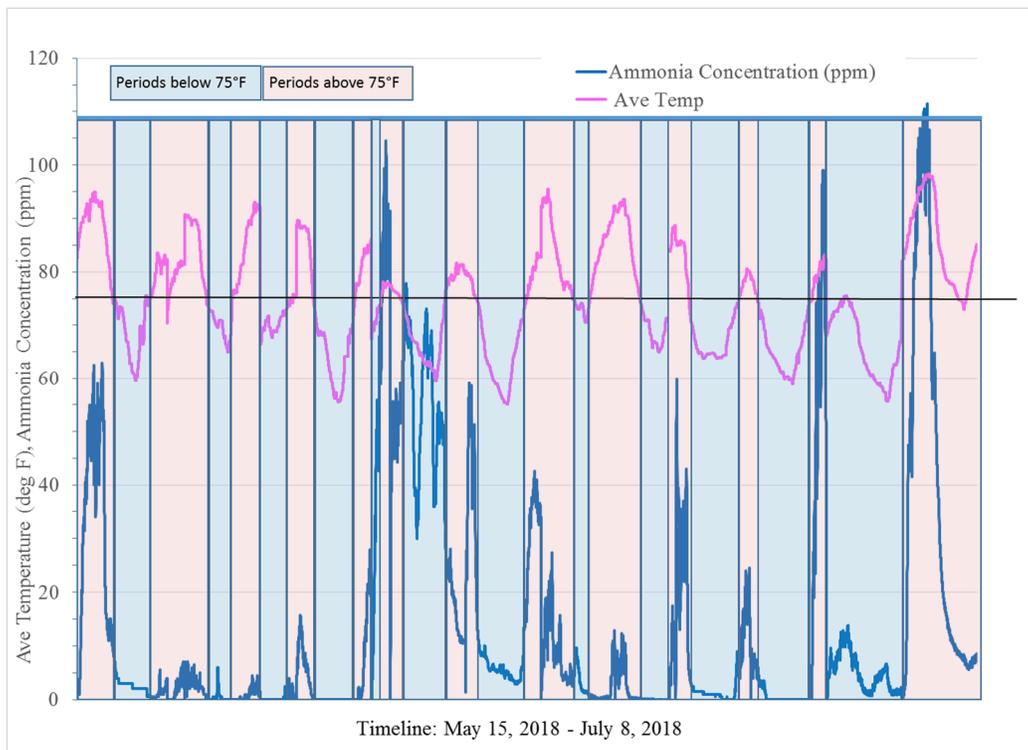


Figure A-2. Ammonia Concentration (ppm) Peaking at the Tank A-103 PBF Compared to Outside Air Temperature (°F)

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Figure A-3 shows the relationship between outside air temperature and barometric pressure during a portion of the test period. A relationship is evident between the diurnal temperature cycle and the barometric pressure fluctuations (barometric pressure decreases as temperature increases with a slight lag). Barometric pressure can also change independent of temperature due to weather fronts, but the relation to temperature was often evident during the test period (as shown in Figure A-3). The co-variant relationship of ambient air temperature and barometric pressure raises the question of whether exhausting from the tank A-103 PBF was more related to barometric pressure or to ambient temperature.

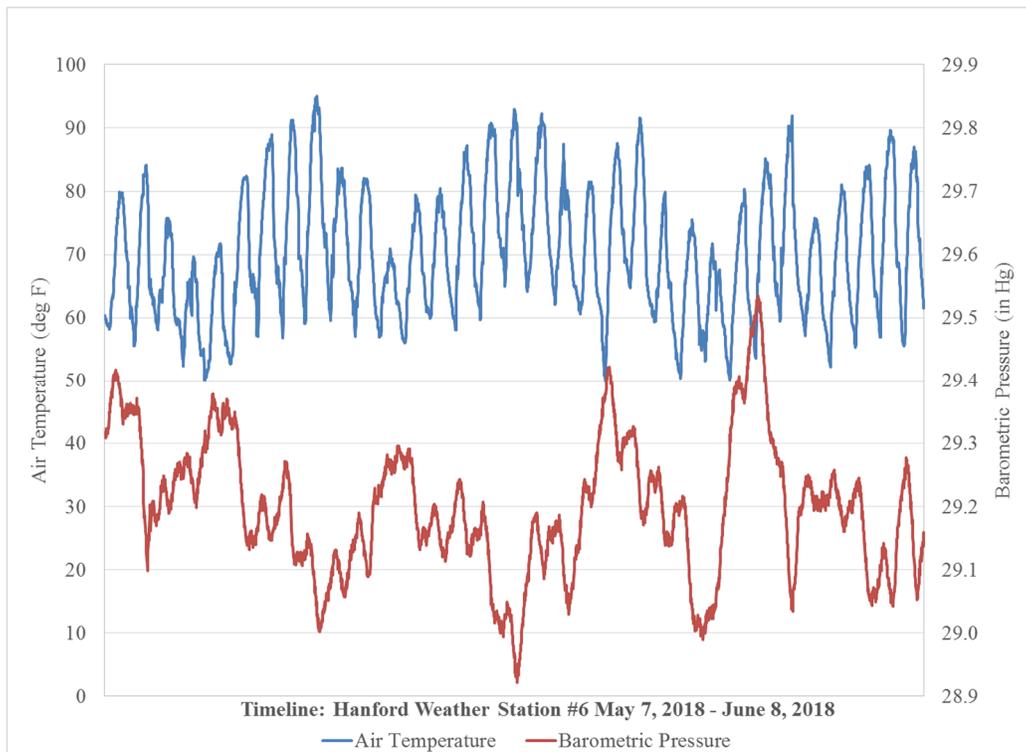


Figure A-3. Outside Air Temperature (degrees F, Left Axis) Compared to Barometric Pressure (inches Hg, Right Axis)

Based on the third mechanism (venturi effect), one would expect the passively ventilated tanks to exhaust when air velocity (wind) increases around the PBF. Figure A-4 shows the ammonia concentration measured at the tank A-103 PBF and corresponding wind speed data during the test period. The periods of peak ammonia concentration in Figure A-4 (green bars) are distributed equally among low (0 to 10 mph), medium (10 to 20 mph) and high (>30 mph) wind velocity periods, indicating that the venturi effect was not observably related to tank emissions for the tank A-103 PBF during the test period.

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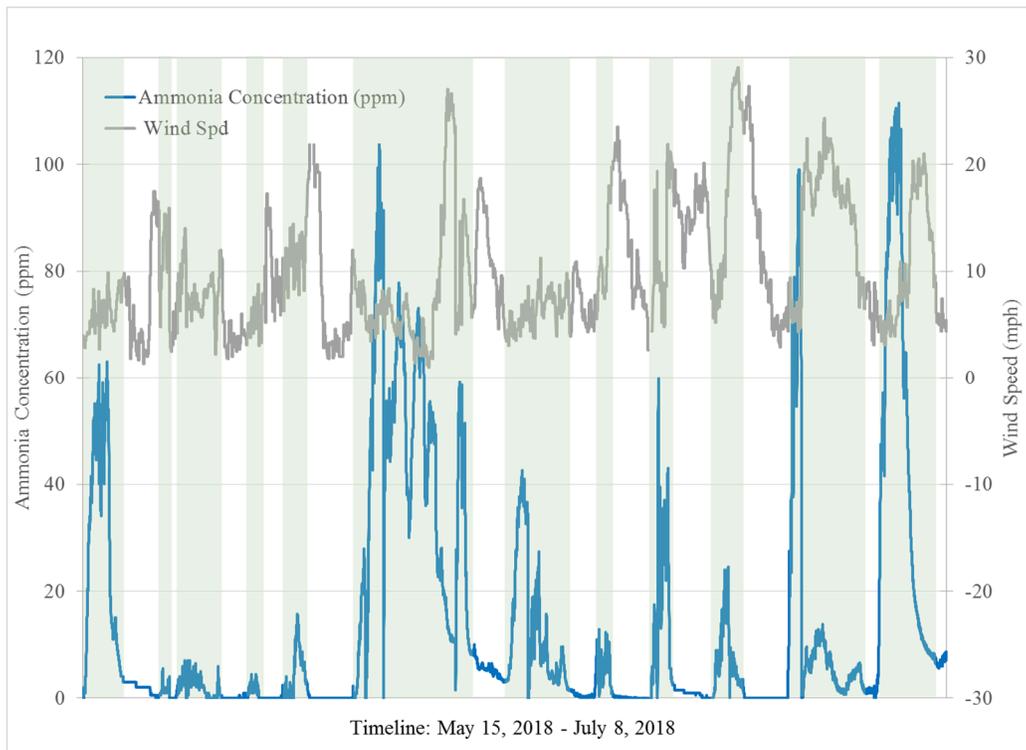


Figure A-4. Ammonia Concentration (ppm, Left Axis) Peaking at the Tank A-103 PBF Compared to Wind Speed (mph, Right Axis) Where Green Bars Identify Periods of Peak Ammonia Concentrations

A3.0 VMDS AREA MONITORING

The VMDS pilot-scale test Phase 2 activities were aimed at evaluating of the viability of each technology for use as part of the VMDS (RPP-RPT-60386). As described in Section 4.2.3.1, the open path (OP) ultraviolet differential optical absorption spectrometer (UV-DOAS) instrument 508A deployed in A Tank Farm and OP Fourier transfer infrared spectrometer (FTIR) instruments deployed in AP Tank Farm (506A and 506B) detected numerous, low-level increases in ammonia concentrations for short periods of time (i.e., minutes) during March and April 2017. Figure A-5 shows the concentrations measured by instrument 508A with markers colored according to the time of day. Concentration peaks appeared to occur more often late in the evening and early in the morning when the atmosphere was more stable. The low-level increases in ammonia concentration depicted in Figure A-5 were further analyzed to assess the magnitude and duration of the highest increases. Those increases that exceeded 0.05 ppm were reviewed and are summarized in Table A-3 with maximum concentration and duration.

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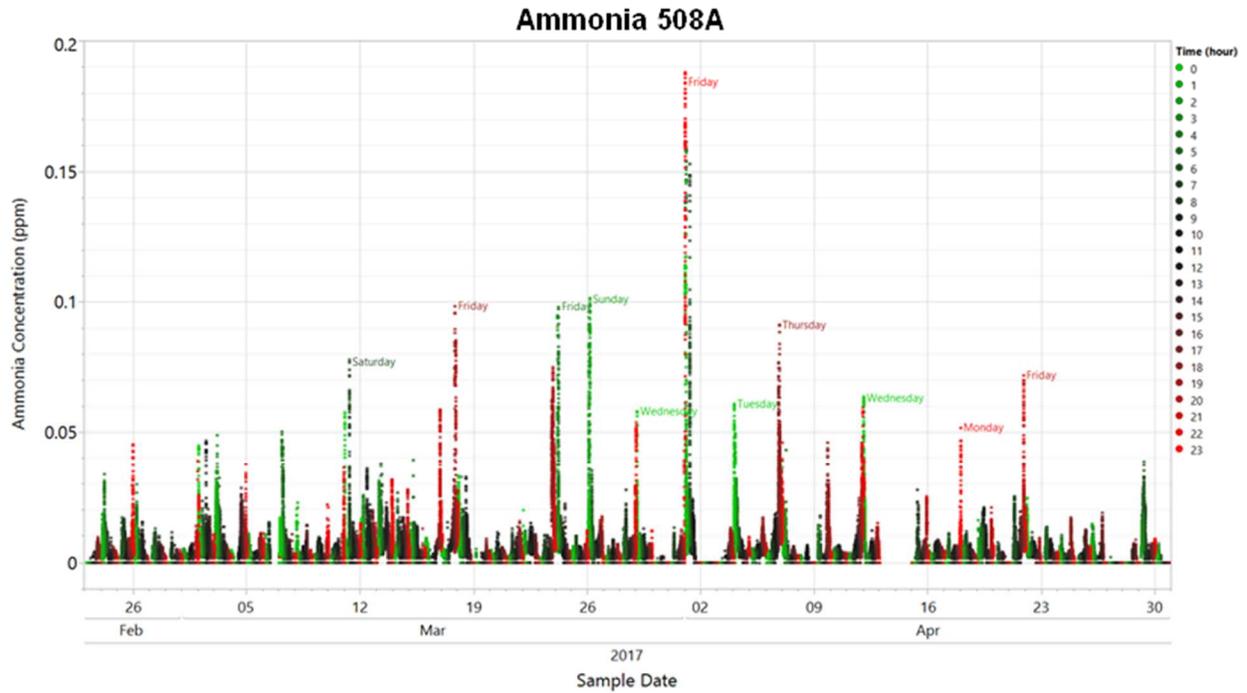


Figure A-5. Ammonia by Date for March-April 2017 Timeframe Detected in A Tank Farm from the OP UV-DOAS 508A

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Table A-3. Duration and Maximum Concentration of Elevated Ammonia Readings in A Tank Farm from OP UV-DOAS Measurements from March-April 2017

Date - Hour first Detected	Duration at elevated concentration (min.)	Maximum Ammonia Concentration (average ppm over 152m path)
3/7/17 4:00	1	0.050
3/11/17 0:00	2	0.058
3/11/17 7:00	9	0.078
3/16/17 21:00	7	0.059
3/17/17 19:00	3	0.098
3/17/17 20:00	21	0.096
3/23/17 19:00	10	0.062
3/23/17 20:00	21	0.075
3/24/17 3:00	8	0.095
3/24/17 4:00	14	0.098
3/26/17 2:00	32	0.102
3/28/17 23:00	4	0.054
3/29/17 0:00	2	0.058
3/31/17 23:00	29	0.188
4/1/17 0:00	10	0.138
4/1/17 1:00	18	0.162
4/1/17 2:00	4	0.107
4/1/17 6:00	14	0.101
4/1/17 7:00	17	0.153
4/4/17 0:00	6	0.061
4/6/17 18:00	9	0.077
4/6/17 19:00	10	0.091
4/6/17 20:00	2	0.054
4/11/17 23:00	2	0.060
4/12/17 0:00	7	0.064
4/17/17 23:00	1	0.052
4/21/17 21:00	9	0.072

A4.0 REFERENCES

RPP-RPT-60386, 2017, *Test Vapor Monitoring and Detection System Pilot-Scale Test Phase II Report (FY2017)*, Rev. 0, Washington River Protection Solutions, LLC, Richland, Washington.

RPP-RPT-61096, 2018, *Wearable Ammonia Detector Field Trial*, Rev. 0, Washington River Protection Solutions, LLC, Richland, Washington.