

CRITICAL ASSESSMENT OF THE TECHNICAL BASIS AND IMPLEMENTATION OF THE WRPS HANFORD SITE WASTE TANK FARM INDUSTRIAL HYGIENE PROGRAM

Center for Toxicology and Environmental Health, LLC

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Executive Summary

The Center for Toxicology and Environmental Health, LLC (CTEH®) was charged by Washington River Protection Solutions (WRPS) to conduct an independent, 3rd-party evaluation of the technical basis underlying the WRPS industrial hygiene (IH) program implemented in the U.S. Department of Energy's (DOE) Hanford Site (Hanford) waste tank farms.

This evaluation was conducted within the framework of a classical IH approach to addressing airborne chemical hazards, which includes 1) identifying potential airborne hazards, 2) conducting a hazard assessment to determine which potential hazards may present an actual risk to worker safety and health, and 3) controlling hazards with the implementation of proper IH controls.

Identifying Potential Airborne Hazards

At the time of the Hanford IH program Technical Basis publication in 2006, 1,826 chemicals had been identified as possible volatile tank waste chemicals, with over 1,200 present in the headspace vapors. Since 2006, the Chemicals of Potential Concern (COPC) list has been amended to now include 59 total chemicals. In 2016, WRPS created the Health Process Plan (HPP) group of personnel from WRPS, PNNL, and DOE Office of River Protection (ORP). The group began development of a database to capture ongoing tank farm analytical data collection efforts implementation of a system whereby the publically-available toxicological literature is periodically reviewed to identify new health effects data for current and candidate COPCs, and is scheduled to develop a system for external scientific peer review of health effects and odor threshold data as it is entered into the database. CTEH® believes that this process is scientifically sound.

Conducting a Hazard Assessment to Determine Potential Health Hazards

Various types of instrumentation are utilized by the IH group to monitor for chemical vapors within the tank farms. Detection limits of direct reading instrumentation (DRI) used within the tank farms are adequate to detect these typically sampled analytes at or below the site specific occupational exposure limits and associated action levels. Many of the analytes monitored by real-time instruments are also monitored through means of analytical sampling.

A pilot program is underway using a suite of new real-time instruments to characterize both COPC presence in the tank farms as well as track migration of these compounds across the tank farm boundaries. These new technologies are collectively called the Vapor Management Detection System (VMDS). In addition to the VMDS-characterization of known and fugitive emission sources located by the IHT-Vapors group, WRPS has enlisted a mobile Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) laboratory within an automotive van which is driven throughout the tank farm areas, monitoring and cataloging chemicals in the ambient atmosphere outside of the tank farms. The air monitoring capabilities of this equipment include the capability to detect chlorinated solvents, aromatic and polyaromatic hydrocarbon compounds, pesticides and agricultural emissions, furans, nitrosamines and acetonitriles. Additionally,

the unit has the capability to monitor air on a continuous basis, in real time, with detection levels in the parts per trillion level for many common volatile organic chemicals (VOC), while allowing for analysis without preparing or pre-treating samples.

The Tank Vapor Assessment Team, commissioned by DOE in 2014, produced a report containing conclusions, recommendations, and discussion of technical issues related to tank farm vapors. CTEH® agrees with the TVAT the need to assess worker exposures to acute vapor exposures, as well as the need for increasing IH field staff competency levels with respect to collecting and interpreting IH data in the farms. The TVAT report also describes the potential impact of a bolus exposure, citing air modeling plume simulation results in which relatively little dilution occurred, suggesting that a vapor plume could maintain relatively high fractions of the source vapor concentrations at appreciable distances from the vent. CTEH® notes that the bolus theory, as presented in the TVAT report, conflicts with existing air quality data and the standard and accepted IH and field air dispersion plume models.

The current COPC AOELs were derived by utilizing previously established OELs, emergency response planning guidance values. The majority of current AOELs are based on protection of workers from adverse health effects from chronic occupational exposures CTEH® agrees with the TVAT that there is a need to develop a parallel set of COPC AOELs that are based on known critical effects from acute or momentary exposures.

Controlling Hazards with Proper IH Controls

CTEH® examined the work environment, procedures, and policies established by WRPS to ascertain their impact on the protection of workers from chemical hazards within the tank farms. Current efforts to train Industrial Hygiene Technicians (IHTs) have raised concerns among some IHTs about the lack of training regarding the interpretation of the instrumentation's readings; many were unable to convey the meaning of an elevated reading from their instrumentation.

The oversight of IHTs by the IHPs was observed to be inconsistent across the various work groups. CTEH® believes that this inconsistency has resulted in a lack of workforce confidence in the IH group as a whole. CTEH® also believes that a job hazard matrix, a tool used to ensure hazards, tasks, and controls related to specific job titles and serve as supporting documentation, is missing from the WRPS IH program and needs to be developed and rolled out to the workforce at large.

CTEH® health scientists have observed over the years that the majority of U.S. workers and members of the general public often do not make the distinction between a health hazard and a health risk. CTEH® believes that an understanding by tank farm workers of basic toxicological odor biology principles discussed in this report may help to put into proper perspective their experiences with detected or "*felt*" odors, data provided by available air monitoring instrumentation, and air levels that truly represent risk of injury. Many people often confuse specific physiological stress responses, designed to aid in escape, with signs of onset of a toxic, injurious reaction. Human exposure to adverse odors has been shown to cause measureable changes in breathing, heart rate, blood pressure, and digestive processes. However,

these changes can result in symptoms including lightheadedness, headache, and breathlessness (resulting in the “going down” sensation described by some tank farm workers), as well as nausea and, in the case of individuals with dilated nasal capillaries, nose bleeds. Such understanding of these concepts as they relate to tank farm vapors would likely put into context the seeming inconsistencies between odor detection and sensory irritation, DRI readings of non-detections, and air sampling data indicating very low levels of vapors in tank farm air.

CTEH® evaluated the technical basis of the WRPS Hanford tank farm IH program as well as its implementation. Overall, the technical basis is sound from both a toxicological and industrial hygiene standpoint. CTEH® believes that the current concerns related to tank vapor exposure and health impacts relate to acute, sometimes momentary exposures to airborne chemicals present at odiferous and possibly irritant levels. For this reason, a comprehensive library of odor-generating locations outside of the tank farms related to other site remediation tasks should be characterized to aid in source identification for future complaints. Further, a set of AOELs for acute effects, primarily respiratory irritant and neurological effects, need to be developed and introduced into the IH program. Because of the biological nature of odor and irritant responses in humans, particularly as they differ from toxic effects, CTEH® believes that worker training in these basic concepts would help workers to better discriminate toxic versus non-toxic exposures, and to better interpret results from real-time and analytical air monitoring and sampling results.

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1.0 Introduction

Washington River Protection Solutions (WRPS) requested that the Center for Toxicology and Environmental Health, LLC (CTEH®) conduct an independent, third-party evaluation of the technical basis underlying the WRPS industrial hygiene (IH) program implemented in the U.S. Department of Energy's (DOE) Hanford Site (Hanford) waste tank farms. Central to this evaluation are considerations made for the protection of Hanford tank farm workers from adverse health effects that may potentially occur following exposure to vapors and gases originating from wastes stored in and transferred to/from underground storage tanks. WRPS is the DOE's prime contractor for processing and permanently disposing of the radioactive and chemical wastes stored in the tanks. CTEH® was charged with the task of evaluating the technical basis of the waste tank vapors IH program. The scope of this work included evaluating the underlying technical documentation and the implementation and effectiveness of the IH program, and providing validation of the current methods/procedures in place or recommendations for improvement.

CTEH® is an environmental and human health consultancy specializing in hazardous materials emergency response health issues. Toxicologists, industrial hygienists, safety professionals, and environmental scientists at CTEH® have been assessing worker exposure issues and providing real-time incident consultation since 1997. In that time, CTEH® experts have responded to over one thousand HazMat incidents and performed hundreds of industrial hygiene assessments. CTEH® clients span the rail, maritime, and highway transportation, petroleum, petrochemical, general chemical, durable goods, and food industries, as well as federal and state agencies. Since 2001, CTEH® toxicologists and occupational health staff have responded to over 3,500 worker exposure incidents, many of which involved odors from a variety of compounds, within Class 1 railroads in North America.

1.1 Brief Description of Hanford

Hanford was originally established during World War II as part of the U.S. Army Corp of Engineer's Manhattan Project. The Site was built to produce plutonium for the developing nuclear weapons program. Utilizing nine production reactors over its lifetime, Hanford began plutonium production in 1943, and ceased production in 1988. In the plutonium production process, irradiated uranium fuel rods collected from the Hanford production reactors were chemically processed to separate and purify the residual plutonium and other fission by-products. The recovered plutonium was at first shipped to Los Alamos, NM for fabrication into weapon components, but these components were later fabricated onsite. Liquid wastes from these processes were eventually stored in underground concrete and steel single-shelled tanks (SSTs), whose construction began in 1945. Ultimately, 149 SSTs would be constructed. In 1968, construction of double-shelled tanks (DSTs) began, of which a total of 28 were eventually constructed. In 1988, the Tri-Party Agreement was entered into by the DOE, the United States Environmental Protection Agency (USEPA), and the Washington State Department of Ecology to begin final waste disposition and environmental remediation of Hanford, including the treatment and permanent disposal of tank wastes.

1.2 Brief History of Tank Waste Handling

As a result of four decades of plutonium production, millions of gallons of wastes were produced and stored in the Hanford tank farms. Within the tanks, wastes may exist as porous solids containing interstitial liquid and trapped gases (sludge), drained porous solids (salt cake), bulk liquid (supernatant), and gases/vapors in the tank headspace (Meacham et al., 2006; Huckaby et al., 2004). Waste tank components from which vapors can escape from tanks include leaks from the subterranean tank wall structures and cascade piping from tank to tank, or from protrusions from the tanks to the ground surface, including risers (pipes) designed for introduction of sampling equipment, cameras, maintenance equipment, and waste manipulation tools. Risers from SSTs to rebreather filters allow for passive maintenance of tank gas pressure and release of vapors to the tank farm air, while DSTs are ventilated by mechanical introduction of ambient air and exhaust from the tanks via centralized exhaust stacks that release tank vapors to the ambient air at heights well above the worker breathing zone.

Loss of tank integrity in some SSTs necessitated transfer of wastes to new DSTs. Further, normal operations to empty older tanks and reduce liquid wastes via the 242-A evaporator unit campaigns have included transfer of liquid supernatant and sludge between tanks. Waste transfer operations include physical disruption of sludge and salt cake fractions to facilitate waste transfer. Potential routes of release of waste gases/vapors from the tank headspaces into the breathing zone of tank farm workers include passive and active venting of tank headspace via surface risers and stacks, leakage from transfer and overflow lines, and tank equipment maintenance operations.

The Hanford tank farms pose unique IH challenges because a) the underground storage tanks contain a complex mixture of solid/liquid/gas forms of wastes, some being highly radioactive, with chemistries that have been posited to change over time due to thermal and radiolytic reactions occurring in the tanks since their construction, and b) the unpredictable release times and rates of gases and vapors from the tanks via exhaust stacks and ventilation risers. Estimates of the number of different chemicals in the aggregate headspace of all 177 tanks vary, but over 1,200 have been positively identified (Stock, 2004; Meacham et al., 2006). In addition to the wide variety of headspace chemicals within the storage tanks, the relative chemical composition varies from farm to farm and tank to tank. The older SSTs passively vent to the surface via risers, whereas the newer DSTs are mechanically ventilated through exhaust stacks. A number of factors have been suggested that may impact the volume and frequency of gas/vapor releases from the SSTs, including thermal variations within the tanks, waste layer disturbing operations, atmospheric barometric changes, and seasonal surface temperature fluctuations.

1.3 History of Tank Vapor Issues at the Hanford Tank Farms

The history of tank vapor worker exposure began with a DOE investigation conducted in 1992. IH air monitoring data collection began that same year (Meacham et al., 2006). Since then, the issue of tank farm worker exposures has gone hand-in-hand with worker odor detection. Numerous technical reports, investigative efforts, and legal actions have addressed the vapor presence and characterization issues.

In 2003, the Government Accountability Project (GAP), a U.S. whistleblower advocacy organization, alleged worker vapor exposures and illnesses purportedly from deficiencies in worker protection, and alleged that improper medical record keeping was practiced to undermine worker compensation claims. These charges resulted in a focused effort by CH2M Hill the same year to improve the technical basis on which the IH program was based, and moved the DOE Office of Independent Oversight and Performance Assurance (OA) to launch an investigation in 2004 into current and past worker safety practices. With regard to vapor exposures, the OA concluded that, while no known exposures above exposure limits were measured, tank farm vapors characterization deficiencies in the industrial hygiene program prevented adequate assessment that worker exposures are below regulatory limits.

In 2006, CH2M Hill published the IH Technical Basis document being presently evaluated. In 2008, the Hanford Concerns Council commissioned a review of the IH Technical Basis. That committee stated that the proposed methodology for Occupational Exposure Limit (OEL) development was in accordance with IH best practices, but recommended a more statistically stringent process for identifying Chemicals of Potential Concern (COPCs) in the tanks. In 2014, DOE commissioned the Savannah River National Laboratory, via the Tank Vapor Assessment Team (TVAT), to assess the WRPS IH Technical Basis and its implementation. This assessment is discussed in Section 2.4 of the present report. That same year, WRPS issued an implementation plan to address the TVAT concerns and recommendations.

In 2015, the State of Washington Attorney General filed suit against DOE and WRPS, alleging adverse health effects to workers exposed to tank vapors, and demanding that DOE enter into a legally binding agreement to protect worker health from tank vapor exposures. According to Hanford Challenge, an advocacy group for Hanford workers, over 100 workers have been exposed to tank vapors since January of 2015, and that over 70 workers complained of vapor exposures in April and May of 2016. The tank farm vapor issues have received extensive television media coverage in the State of Washington. In July of 2016, work within the Hanford tank farms was halted by the Hanford Atomic Metals Trades Council, an umbrella organization of 15 trade unions at Hanford, citing the need for required supplied air breathing protection for workers. In August of 2016, a U.S. Federal judge issues an injunction against DOE and WRPS requiring provision of supplied-air respirator for all tank farm workers.

1.4 Work Conducted by CTEH[®]

CTEH[®] was charged with the task of evaluating the technical basis of the waste tank vapors IH program. This evaluation was conducted within the framework of a classical IH approach to assessing, addressing, and managing potentially harmful airborne exposures in occupational settings. This is a multi-step process outlined in detail below, and consisting of the following major components: 1) Identifying potential airborne hazards, 2) Conducting a hazard assessment to determine which potential hazards may present an actual risk to worker safety and health, and 3) Controlling hazards with the implementation of proper IH controls. The current tank vapors IH program was evaluated using this methodology as a frame of reference.

The work described above was conducted using a multi-faceted approach involving both onsite and offsite data collection and analysis. During Phase I of the project, CTEH® personnel conducted an initial project-scoping site visit June 8 through June 9, 2016. During this visit, CTEH® personnel met with key members of the WRPS and DOE administration and WRPS technical staff to better understand the concerns regarding tank vapor-related worker health, the history of the tank vapors program, and the underlying foundation of the tank farms IH program. CTEH® personnel also conducted a site inspection of both the SST and DST tank farms and observed work practices at these locations. Phase II of the project represents the work detailed in this report. Phase II began in early July, 2016, and continued until September 30, 2016. Phase II included a CTEH® presence onsite at the WRPS facilities beginning on July 10, 2016 and continued through September 9, 2016. Onsite personnel for CTEH® included Certified Industrial Hygienists (CIHs), toxicologists and data managers. While onsite, CTEH® personnel conducted document review and analysis; data retrieval, compilation, and analysis; interfaced with WRPS and DOE staff; conducted site inspections; and conducted interviews with many groups of tank farm workers. After completion of the field portion of Phase II, further data analysis and report drafting was conducted off-site, and continued through September 29, 2016.

2.0 Tank Vapor-Related Documents Reviewed for CTEH® Evaluation

WRPS provided IH documentation in addition to the IH Technical Basis for the review of the IH Vapors Program implementation assessment. As additional documents were identified, WRPS provided them to CTEH®. The documents and regulations used in the review are listed below.

2.1 Central Document for Hanford Tank Vapor IH Program: IH Technical Basis (2006)

The IH Technical Basis (Meacham et al., 2006) document was developed by CH2MHill Hanford Group, Inc. with the stated purpose of *“identifying all chemicals within a waste vapor source...that are potentially hazardous and might be released in to worker breathing zones. It provides the Industrial Hygiene program with the basis to make decisions and set controls that ensure worker protection.”* The document provides a detailed characterization of occupational exposures and exposure sources that are unique to the Hanford tank farms, and describes likely chemical hazards associated with waste tank vapor releases.

The IH Technical Basis document described tank and gas vapor sources with respect to the historical role of the waste tanks to store chemicals used or generated during the many decades of plutonium production at Hanford. The waste streams feeding into the tanks included cladding wastes from uranium fuel rod cladding removal, metal wastes from isolating plutonium and other fissile species, reactor cleanout decontamination wastes, and miscellaneous wastes from on-site laboratories and equipment maintenance operations. Chemical and radioactive wastes stored in the tanks feed ongoing radiolytic chemical reactions to form a variety of small molecular organic species, metal containing compounds including organometals, halogenates, nitrogen-containing compounds, and sulfur and silicon compounds.

The document described the physical characteristics of the tank wastes, which may include porous solids holding trapped gases and interstitial liquids, drained solids, bulk liquids, and headspace gases and vapors. The processes whereby gases and vapors migrate from the solid and liquid phases of the tank wastes in the gas phase are described, as is the thermodynamic mechanisms in place that drive convection within the tanks and (to a lesser extent) the tank risers to maintain a fairly constant headspace chemical concentration. The IH Technical Basis document (Meacham et al., 2006) states that *“There is no basis for expecting large, rapid changes in the headspace concentrations in any of the passively-ventilated SSTs in the absence of significant waste-disturbing activities”*, citing multiple technical reports (WHC-SD-WM-ER-344; WHC-SD-WM-SARR-001; FAI/95-63; PNNL-11640; PNNL-11683).

The IH Technical Basis document (Meacham et al., 2006) described the techniques used to determine, both by measurement and description of chemical dynamics, the headspace composition of the tank wastes. The basic principles and techniques of chemical sampling were described, including collection of vapor samples from the tank headspaces, sources (rebreather filters, stacks, and other risers), and tank farm air into evacuated canisters and sorbent traps designed to bind chemicals of interest as streams of sample air are passed over and through solid sorbent media. The samples were then sent to an analytical laboratory where they were subjected to various spectroscopic methods to identify the organics, inorganics, and metals in the samples.

The document reported that the headspace vapors were composed of over 1,200 organic compounds including alkanes, cycloalkanes, alkenes and alkadienes, alcohols, phenols, esters, ketones, heterocyclic compounds, halocarbons, esters, aldehydes, and nitriles. Metals, ammonia, and nitrous oxide were also identified. Variability of headspace composition over time was discussed, with variability of less than an order of magnitude being reported. The waste disturbing activities involved with waste retrieval were described as possibly significant sources of tank headspace composition variability. These activities include water sluicing (segmenting solid waste using water jets), dissolution, and mixer pump operations,

The characterization of worker breathing zone gases and vapors was accomplished by describing the physical factors involved in vapor release from the SSTs and DSTs as well as summarizing a number of studies from 1992 and later that contain data regarding tank vapor release and chemicals that have been measured over time. The process of active ventilation of the DSTs and SSTs that are undergoing waste retrieval was described. It was noted that, when active ventilation systems are shut down, passive ventilation may occur through filtered air inlets. Active ventilation to exhauster stacks results in vapor releases above the worker breathing zone. Active ventilation also serves to dilute headspace vapor concentrations and maintain a negative pressure on the tank system to minimize or eliminate fugitive emissions from tank piping and equipment connections. Passive ventilation of the SSTs was described as being driven by three primary forces: changes in barometric pressure, buoyancy forces within the tanks, and wind within the tank farms.

The IH Technical Basis document (Meacham et al., 2006) reported that direct measurement of vapor release rates from passively ventilated tanks was not practical due to the effect that instrument

component resistance would have on the low flow volumes coming from the tanks. The report did, however, describe data from several tracer gas studies that indicated typical ventilation rates in the 3-6 m³/hr range, with some measurements as high as 42 m³/hr. Atmospheric modeling data developed by the Pacific Northwest National Laboratory (PNNL) were discussed, with results from the most likely tank ventilation flow rates predicting significant breathing zone concentration dilution by at least a factor of 10 within a few feet from tank vents and stacks.

The document summarized IH source, area, and personal data collected from 1992 to 2006. These data represented surveys taken at approximately 2,000 locations in and around the tank farms. Levels of compounds for which OELs had previously been established were well below OELs (on a time-weighted average basis) in the personal samples. The document concluded that stack exhausting was effective at reducing ground-level exposures to vapors during waste disturbing operations. It also noted that work performed in 2004 suggested that ammonia levels may not always be higher than other COPCs to the extent that acceptable ammonia exposures are indicative of acceptable exposures to all other COPCs. However, the document did not provide analysis of headspace, source, area, or personal sampling data to see if a consistent relationship in the ammonia-to-COPC ratio existed.

A toxicological screening process was performed in which previously established OELs from both U.S. and international regulatory and scientific bodies were sought for all of the initial list (Stock, 2004) of over 1,800 possible volatile chemicals in the tank waste. Surrogate values, based on similarity in chemical structure and class to chemicals with OELs, were assigned to compounds that had no established OELs. Based on criteria established by DOE (DOE G 440.1-3), all compounds that had been measured at or above 10% of their respective screening values were added to the COPC list. At the time of the IH Technical Basis document publication in 2006, there were 52 COPCs. For these chemicals, Hanford-specific Acceptable OELs (AOELs) were derived, either using established OELs, or by derivation of values from chemically-similar surrogate chemicals for which there were established OELs. AOELs derived from surrogate chemical OELs incorporated additional uncertainty factors of 3 to 10 based on uncertain differences from surrogates in biological response to exposure. Thus, many of the COPC AOELs are 3 to 10-fold lower than surrogate OELs based on a policy decision to err on the side of caution, rather than on scientific data.

The IH Technical Basis document (Meacham et al., 2006) provides a rationale for the application of generally accepted industrial hygiene and worker protection practices to the unique circumstances of possible vapor exposures in Hanford's waste tank farms. From this basis document has come the development of numerous site-specific guidance documents for implementing the tank farm IH program as it relates to tank vapor exposures (see Section 5.0).

2.2 Documents Reviewed for Tank Farm-Related IH Program Implementation

Documents were reviewed with a narrow scope of applicability to the IH Vapors program implementation. Several forms discussed in the initial documents were requested by CTEH® and were provided by WRPS staff. The list below forms the core documents for completing this review.

- RPP-22491 Rev 1 IH Technical Basis
- TFC-PLN-34, Rev E-6 Industrial Hygiene Exposure Assessment Strategy
- TFC-EHSQ-S_IH-C-48, Rev B-2 Managing Tank Chemical Vapors
- TF-ESHQ-IH-STD-03 Rev D-5 Exposure Monitoring, Reporting, and Record Management
- TF-AOP-015 Response to Reported Odors or Unexpected Changes to Vapor Conditions
- TFC-BSM-TQ-STD-01, REV D-10 Technical Staff and Technician Qualification Requirements
- Form A-6004-732 REV 3 Industrial Hygiene Sample Plan
- Form A-6005-744, TF-AOP-015 Industrial Hygiene Investigation Report
- Form A-6004-101 REV 21 WRPS Job Hazard Analysis Checklist

2.3 Documents Reviewed for Tank Farm-Related Vapor Characterization and Toxicological Evaluation

Documents were reviewed related to the chemical characterization of tank space wastes, their behavior and transport in and out of the tanks, and their concentration measurement at various points in the tank farms. Technical reports for toxicological screening and OEL development and implementation were also reviewed, as well as directives, statements of work, presentations, and draft reports related to recently-initiated (FY2016) initiatives dealing with the tank vapor issues. A list of reviewed documents dealing with these issues follows.

- FAI/95-63 Turbulent Free-Convection Mixing in a Tank Headspace
- Implementation Plan for Hanford Tank Farm Vapors Assessment Report recommendations (WRPS)
- VMDS Technologies Presentations (Subramanian, 2016)
- PNNL-11391 Gas Retention and Release Behavior in Hanford Single-Shell Waste Tanks
- PNNL-11640 Homogeneity of Passively Ventilated Waste Tanks
- PNNL-11925 Waste Tank Ventilation Rates Measured with a Tracer Gas Method
- PNNL-13366 A Survey of Vapors in the Headspace of Single-Shell Waste Tanks
- PNNL-14767 Characterization of the Near-Field Transport and Dispersion of Vapors Released from the Headspace of Hanford Site Underground Storage Tanks
- PNNL-14949 Toxicological Assessment of Hanford Tank Headspace Chemicals - Determination of Chemicals of Potential Concern
- PNNL-15640 Screening Values for Non-Carcinogenic Hanford Waste Tank Vapor Chemicals that Lack Established Occupational Exposures Limits

- PNNL-15736 Proposed OEL for Non-Carcinogenic Hanford Waste Tank Vapor Chemicals
- RPP-21854 Occurrence and Chemistry of Organic Compounds in Hanford Site Waste Tanks
- RPP-23074 Tank Vapors Chemicals of Potential Concern
- WHC-MR-0521 The Plutonium Production Story at the Hanford Site: Processes and Facilities History

2.4 Hanford Tank Vapor Assessment Team (TVAT) Report

In 2014, WRPS asked the Savannah River National Laboratory to assemble and lead a team of experts to assess the WRPS industrial hygiene program as it relates to tank vapors. The resulting group, the TVAT, was comprised of 11 academic, federal government, private consulting, labor union, and national laboratory scientists and technical experts. The TVAT was specifically charged “...to determine the adequacy of the established WRPS program and prevalent site practices to protect workers from adverse health effects of exposure to chemical vapors on the Hanford tank farms.” The TVAT reviewed IH program-related reports and documents, met with stakeholder leadership and representatives, interviewed site workers individually and in focus groups, and observed work performed in the tank farms. On October 30, 2104, the TVAT issued the Hanford Tank Vapor Assessment Report (SRNL, 2014), which described the team’s assessment within the framework of the risk assessment/management paradigm as currently implemented in the U.S. occupational and environmental health regulatory community. The areas of assessment were categorized as site characterization, exposure assessment, dose-response assessment, risk characterization, and risk management.

The TVAT report included four key conclusions, 10 overarching recommendations, and discussion of 47 technical issues with associated recommendations. The four key conclusions were that the TVAT’s use of Hill’s causation criteria established a causal link between worker adverse health reports and chemical vapor releases from the waste tanks, the reported effects were representative of transitory exposures to relatively high chemical concentrations, the full-shift exposure measurement practices employed at Hanford cannot adequately assess/address the episodic nature of tank vapor release incidents, and a safe work environment cannot be maintained in the presence of ongoing vapor releases from the tanks. The 10 overarching recommendations developed to address the deficiencies identified by the team’s key conclusions are paraphrased as follows:

1. WRPS and DOE should demonstrate a commitment improve the existing IH program and resolve vapor exposure concerns,
2. Operational and cultural parity should be assured among the chemical vapor, flammability, and radiological protection programs,
3. Programmatic sampling and characterization of headspace vapors should be implemented and ongoing,
4. The IH exposure assessment strategy should be implemented to identify and remedy acute as well as chronic vapor exposures,

5. The medical evaluation program should be changed to recognize the relative strength and weaknesses of instrument and other exposure data,
6. Real-time personal monitoring equipment should be deployed and used to notify workers of bolus exposure events,
7. Advances in monitoring and engineering controls should be accelerated to identify and control bolus vapor release incidents,
8. The competency and capability of IH program workers to address tank vapor issues should be improved,
9. Vapor exposure issues and actions taken should be effectively communicated to stakeholders, and
10. Collaborative initiatives should be developed extramurally to research implementation of new technologies and methods to control tank vapor releases and mitigate exposure effects.

The TVAT report concludes that adverse health effects including “severe respiratory irritation” have occurred in tank farm workers due to short, sometimes momentary, exposure to very high concentrations of tank vapor that are suddenly and unexpectedly released from tanks to the affected workers’ breathing zone. The report includes an application of the Hill causation criteria to support the conclusion of worker injury, and offered the bolus exposure theory to explain the occurrence of upper respiratory irritation effects in the absence of data for high-concentration airborne vapor constituent levels required for severe irritation injuries. The report describes gaps in the ability of the currently implemented IH program to effectively 1) detect high concentration bolus exposures or other short-term increases in tank farm air vapor concentrations, 2) protect workers from such exposures via engineering controls, 3) communicate acute exposure health risk concepts to the tank farm workforce, and 4) develop competency levels in IH field staff to accurately interpret data generated by real-time air monitoring instruments in a manner that engenders tank farm worker confidence in the IH program as a whole.

Throughout the present report, CTEH® discusses various TVAT positions as they relate to specific areas of CTEH®’s own assessment of the technical basis and its implementation. CTEH® notes areas in which they are in agreement with the TVAT’s conclusions and recommendations, and provides discussion on points of disagreement. Appendix A contains a matrix of TVAT technical issues and recommendations related in scope to CTEH®’s present assessment, as well CTEH®’s assessment of those issues and recommendations.

3.0 Standard IH Approach to Addressing and Controlling Occupational Hazards

The American Industrial Hygiene Association (AIHA) defines industrial hygiene in the following manner: *“Industrial Hygiene is a science and art devoted to the anticipation, recognition, evaluation, prevention, and control of those environmental factors or stresses arising in or from the workplace which may cause sickness, impaired health and well-being, or significant discomfort among workers or among citizens of*

the community." (AIHA, 2016) The core of a comprehensive IH program is a robust exposure assessment plan (EAP) such as that described in the AIHA publication "*A Strategy for Assessing and Managing Occupational Exposures*" (Bullock and Ignacio, 2006). This publication describes the standard approach utilized by industrial hygienists in all industries for protecting worker health with respect to evaluating exposures to hazardous agents and conditions in the workplace.

Other components in a comprehensive IH program are appendages to the exposure assessment plan and must be driven by the data generated by the EAP in a continuous improvement loop. This process keeps the IH program relevant to contemporary exposures occurring in the workplace as new exposures are identified, procedures and processes are updated, or other workplace factors change.

3.1 Identifying Potential Hazards

Hazard identification is the first step in worker protection. The size or magnitude of an individual airborne chemical exposure hazard is a function of the inherent toxic potency of the compound and dose received by the affected worker. Potential occupational hazards are identified by a qualitative exposure assessment that risk-ranks exposure potential in a matrix that lists all known hazardous agents, documents potential health effects for each agent, identifies work activities where exposures can occur, identifies workers who perform said work activities, estimates potential exposure time, estimates potential exposure concentration or volume, and estimates the frequency of potential exposure activities.

Once the matrix has been created, the qualitative assessment is completed by prioritizing the potential hazards using a Health Risk Ranking (HRR) and creating Similar Exposure Groups (SEG) by grouping workers and work tasks with similar exposures. These SEGs then become the basis for creating a sampling strategy where the potential exposures with the highest HRR that affect the most workers receive the most attention until the actual exposures are determined. Some potential exposures will be deemed associated with sufficiently low risk that they do not require sampling unless conditions change. A sampling strategy is then created by determining the number of samples desired for each SEG. Six to ten samples per agent, per SEG is the suggested range by AIHA for an initial assessment.

3.2 Assessing Actual Hazards

Once the potential chemical hazards associated with various work tasks have been identified, the extent of exposure must be verified to determine whether or not a potential hazard exists. For airborne hazards, assessment is typically conducted through air sampling. Execution of the sampling strategy involves collecting air samples from the breathing zone of employees actually engaged in the work activities where identified potential exposures have a significant HRR. Resulting exposure concentrations are then compared to OELs to determine where over-exposures may be occurring and exposure controls should be implemented. It is notable that OELs do not represent bright line exposure concentrations above which adverse health effects are certain to appear, but rather are designed to be protective of worker health over a working lifetime (Bullock and Ignacio, 2006).

3.3 Controlling Hazards: Utilizing the Hierarchy of Controls

Once a potential hazard has been identified and quantified, industrial hygienists use a standard hierarchy of measures to control the exposures. The hierarchy of controls (10 CFR 851) is discussed below.

A. Elimination/substitution of the Hazard

Elimination/substitution of the hazardous agent is the first step in the hierarchy of controls. Where feasible, elimination/substitution of the hazard is the most effective control; however, this level of control is often not possible. This is the ultimate goal of the tank farm program, however, at the present time, until the final closure of the waste storage tanks, the vapor hazard will remain.

B. Engineering Controls

The basic concept behind engineering controls is that, to the extent feasible, the work environment and the job itself should be designed to eliminate hazards or reduce exposure to hazards. Examples of engineering controls include, enclosure systems, barrier systems, interlocking systems, ventilation systems (local exhaust, fixed and movable exhaust systems, active & passive systems, etc.). Engineering controls are preferable to administrative controls and personal protective equipment (PPE), as they do not involve the human element to be successful.

C. Administrative Controls

Whereas safe work practices can be considered forms of administrative controls, OSHA uses the term administrative controls to mean other measures aimed at reducing employee exposure to hazards. These measures include additional relief workers, exercise breaks and rotation of workers. Unlike elimination or substitution and engineering controls, administrative controls rely on personnel to follow proper processes and procedures, and as such, are not as effective as the former. Administrative controls should be implemented only after elimination/substitution and engineering controls have not been able to adequately control workplace hazards and before the implementation of personal protective equipment (PPE). More information can be found in the Department of Energy Standard DOE-STD-1186-2004 (DOE, 2004).

D. PPE

Personal protective equipment (PPE) is used where workplace exposures cannot reasonably otherwise be controlled and is considered the *last line* of defense in controlling exposures. PPE selection is based on the actual hazard determined by the comprehensive IH program. Examples of hazards include particulate or chemical splash to the eyes, objects striking head, hands, and feet, harmful gas, vapor, fume or particulate exposure to the respiratory system. Each of these hazards can be mitigated by using the appropriate PPE.

PPE must also not over protect, or protect above and beyond a measured exposure as other hazards can be created for the worker by the use of the PPE itself. (29 CFR 1910.12 App C) For example, self-contained breathing apparatus (SCBA) are typically used in the case of emergency response activities, maintenance activities which require a line opening or vessel entry into an unknown condition, or a potentially hazardous atmosphere that is immediately dangerous to life and health (IDLH), oxygen deficient atmospheres, and other confined space entry activities.

Employers are responsible for determining that the use of PPE does not itself create a hazard. SCBA usage introduces a number of potential hazards, including ergonomics, falls, sprains and strains, and increased pressure on the cardiovascular system.

4.0 Identification of Potential Airborne Chemical Hazards Associated with the Hanford Tank Farms

A prerequisite to protecting worker health in an occupational setting is the identification of hazards that may cause injury. Beginning in the early 1990's, the Hanford tank waste headspace vapor composition has been the subject of numerous analyses. The cumulative result of these analyses to date has resulted in the selection of 59 COPCs to be monitored in the tank farms for the protection of worker health. This process has involved correctly identifying all of the chemicals present in tank vapors, estimating airborne exposure levels of the identified compounds that do not pose a likely risk of adverse health effects, and identifying which of the compounds were more likely than others to appear in tank vapors at concentrations approaching or exceeding acceptable exposure levels.

4.1 COPC Determination: WRPS/PNNL Methods Prior to 2016

Since the early 1990's, tank vapor sampling and analyses have been conducted to initially develop and further update the COPC list. The technologies employed for sample collection and analysis were robust, resulting in a data set of thousands of source (tank headspace, rebreather filter, and exhaust stack) vapor measurements. Toxicological screening values, comprised of existing U.S. and international occupational exposure levels and newly-derived Alternative Occupational Exposure Limits (AOELs), were determined for identified tank vapor chemicals (Poet et al., 2006; Poet and Timchalk, 2006). Chemicals measured in the source samples at concentrations $\geq 10\%$ (Administrative Control Levels [ACLs] [DOE G 440.1-3]) of their respective screening levels were selected to be COPCs.

Initially, tank waste headspace vapor was measured in over 1,200 samples collected in the 1990's. At the time of the Hanford IH program technical basis (Meacham et al., 2006) publication in 2006, 1,826 chemicals had been identified as possible volatile tank waste chemicals, with over 1,200 identified in the headspace vapors, either from direct measurement in the headspace, tentatively identified via mass spectroscopy libraries, or potentially present because of known chemicals added to tank wastes over the operating lifetime of the tanks. Of these, 52 were determined to be COPCs, 1,538 were characterized as Chemicals Needing Further Evaluation (CNFE), and 236 were determined to be of low-probability for

workers breathing zone exposure and were not further considered. Initially, tank waste headspace vapor was measured in over 1,200 samples collected in the 1990's.

Data from studies of tank headspace vapor chemistry and thermodynamics indicated that chemical concentrations in the tank headspace were subjected to sufficient convection to maintain relatively constant concentrations throughout the headspace (Huckaby et al., 2004). The time-dependent variability in headspace concentrations from a survey of 42 SSTs was reported to be less than an order of magnitude (RPP-21972). Thus, no significant stratification of chemical species in the headspaces is expected, and there is high confidence that chemical identification of vapors in the tank headspace is not dependent on where samples are collected in the headspace.

Since the establishment of a COPC list of 52 chemicals by January, 2006 (Meacham et al., 2006), the list has been amended to now include 59 chemicals. The addition/deletion of compounds to the COPC list since publication of the IH Technical Basis document has occurred on an *ad hoc* basis, without a system being implemented for programmatic review and updating of the list. Indeed, one of the dose-response recommendations of the TVAT (DR2) was to, *“Conduct a rigorous review of the COPC list to ensure it is current, and develop a process to document the mechanisms used to ensure COPC updates and the basis for changes in the COPC list over time.”* A process is now being developed to systematize that review; WRPS has responded to the TVAT recommendation by developing and implementing the PNNL Health Process Plan (HPP), discussed in Section 6.2.

4.2 Health Process Plan Methods: FY16 and Beyond

In 2016, WRPS created the Health Process Plan (HPP) group of personnel from WRPS, PNNL, and DOE Office of River Protection (ORP). This group developed a work plan and began work on several tasks to launch an ongoing process to collect and examine the latest tank farm analytical data as well as toxicological information regarding individual vapor constituents and their mixtures. CTEH® reviewed the HPP group FY16 statement of work (PNNL SOW Requisition # 284283) and met with several members of the group to understand the strategy devised to develop the required system. First, the HPP defined their strategy and plan for accomplishing their task. The HPP recognized that information needed to be collected and considered for possible health effects from transient high concentration events and acute exposure to tank farm vapors in addition to chronic effects on which current OELs, Hanford AOELs, and ACLs are based. The group began development of a database to capture ongoing tank farm analytical data collection efforts so that recommendations for COPC list inclusion would be based on the most current tank vapor situation.

The HPP group also began development of a database as a central repository for health effects data of current and future candidate and selected COPCs. The database has been populated with toxicological information on the current 59 COPCs, focusing on information that informed current OELs derived by U.S. OSHA, NIOSH, and ACGIH. CTEH® understands that HPP group efforts in FY17 will include identifying and adding relevant information for effects from acute and transient high concentration exposures, as well as

data for COPC odor and sensory irritation characteristics and thresholds to the health effects database. Along with the initial database development, the HPP group began implementing a system whereby the publically-available toxicological literature is periodically reviewed to identify new health effects data for current and candidate COPCs, including data for transient and chronic health effects. The HPP group is scheduled to develop a system for external scientific peer review of health effects and odor threshold data as it is entered into the database.

4.3 CTEH® Observation: COPC Determination

The selection of Hanford COPCs to date has been based on assessments of screening values, existing and newly-derived OELs, and the appearance of chemicals in the tank headspace at levels approaching a fraction (10%) of the OELs that trigger further consideration. Using measured chemical levels of 10% of the OEL as a selection criterion for the COPC list does not suggest that a COPC is or will be present in the headspace or worker breathing zone at or above the OEL. Rather, it is used as a conservative, health-protective measure to identify chemicals more likely than others that may be present within an order of magnitude of the OEL. This process is adequately health protective and scientifically sound and has resulted in a manageable number of COPCs from over 1,200 possible tank vapor constituents. The new system of chemical evaluation and COPC candidate consideration that is being put into place by PNNL and the HPP group will provide a sound ongoing venue to process and interpret data to assure workers and the community that the proper chemicals are being monitored to adequately manage worker health and the tank farm vapor issues.

5.0 Assessing Actual Airborne Chemical Hazards to Tank Farm Workers

CTEH® examined the work environment to assess opportunities for workers to be exposed to tank vapors. The observations discussed in this section relate to correct identification of hazard sources (including non-waste tank sources) and organizational structure of work practices as they inform worker hazard exposures.

5.1 Tank Farm Work Patterns

During the period in which this evaluation was conducted, many of the routine tasks that are performed within the tank farms were not being conducted due to standing stop work orders. The tasks that were ongoing were construction based in nature. These tasks involved work groups conducting various construction activities in the farms.

A. Location, Frequency, and Duration of Work Tasks

Due to stop work orders affecting the site, observation of the locations, frequency and durations of routine work tasks could not be directly observed. Interviews with WRPS staff and contractors informed the opinion that in general, IHPs work from offices and remotely direct the activities of the IHTs who

perform the bulk of the IH monitoring on site, though a few of the IHPs interviewed stated that they were field IHPs and routinely worked in the field with their technicians.

B. Opportunities for Vapor Confinement (i.e., work tents)

Within the tank farms and the nearby associated buildings, there are areas in which the potential for odor confinement exists. The work tents where workers gather when not conducting work tasks while in the farms have the potential to confine vapors and contain odors that would otherwise dissipate and which could negatively affect workers occupying the spaces. Additionally, the nearby administrative buildings, whose proximity to the tank farms and intermittent downwind positioning, have the potential to have an odor containment within them. This potential could be exasperated by HVAC fresh air intakes which service the buildings. However, at the time of this evaluation, no reports of tank farm vapors within the nearby administrative buildings could be located, nor were any reports reported during the workforce interviews.

C. CTEH[®] Observations: Need for Job Hazard Matrix Development

A job hazard matrix is a tool used to ensure hazards, tasks, and controls related to specific job titles and serve as supporting documentation to a comprehensive IH program. Such a matrix is a “live” document that is updated and reassessed as work activities change and potential hazards are introduced to or eliminated from the work site. CTEH[®] was not able to determine whether or not a job hazard matrix existed and was in use in the tank vapors program. Whereas many of the IHTs were unaware of the concept of a job hazard matrix, several of the IHPs interviewed were aware of the concept and expressed the need for a robust and thorough matrix. None of the IHPs or IHTs interviewed were aware of the existence of a job hazard matrix in the Information Security Management System (ISMS).

Discussions with WRPS management regarding the need for a job hazard analysis led to the possible existence of a matrix within the ISMS. Attempts to locate the matrix were unsuccessful. If a current matrix exists, its visibility should be increased through training and communications so as to provide further information on the evaluated hazards associated with the different job tasks performed inside of the tank farms.

5.2 Fugitive Emissions From Tanks and Off-Farm Vapor Migration

The potential exposure points within the tank farms have been scrutinized to a great extent by many sources, both by WRPS, previous Hanford contractors, and third parties. Recently, in response to the recommendations put forth by the TVAT report, the IHT-Vapors group was formed. This internal group was designed to assess all of the tank farms for fugitive emission points and perform routine monitoring of identified emission points. Additionally, this group has been involved with testing and implementing new monitoring technologies. These new technologies, such as open-beam Fourier Transfer Infrared Spectroscopy (FTIR) and Forward Looking Infrared (FLIR) cameras are currently in the pilot-stage of deployment. Other tasks conducted by this team include cartridge testing to determine at what level

respirator cartridges used by air-purifying respirators will become saturated and lead to breakthrough. These efforts are part of a greater effort to reduce the stress on the workforce caused by the requirement of SCBA usage at any point that workers enter the tank farms.

Besides odors being generated by tank vapors, other potential fugitive emissions exist in the areas both within the tank farms and outside the tank farms where chemical waste may have historically been released to the ground. Chemicals and their associated odors may be come from outside of the tank farms, and may be re-entrained into the air during remediation work being conducted independent of tank farm operations.

WRPS has enlisted a mobile Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) van which conducts rounds throughout the tank farm areas monitoring and cataloging chemicals in the ambient atmosphere outside of the tank farms. The air monitoring capabilities of this equipment include the capability to detect chlorinated solvents, aromatic and polyaromatic hydrocarbon compounds, pesticides and agricultural emissions, furans, nitrosamines and acetonitriles. Additionally, the unit has the capability to monitor air on a continuous basis, in real time with detection levels in the parts per trillion level for many common volatile organic chemicals (VOCs).

5.3 WRPS Air Monitoring/Sampling Practices

Common air monitoring practices implemented at the Hanford tank farm are primarily based around the monitoring of ammonia as a sentinel or “leading indicator” compound. The concept of the use of a sentinel compound is based upon the relationship of the primary constituent compound in a headspace in comparison to other less prominent compounds. In the case of the Hanford tank farms, the most prominent chemical vapor in the headspace is ammonia. The assumption employed by the sentinel compound method is that when ammonia is detected through direct reading instrumentation, other vapors not easily detected by similar methods may also be present. Based on the relative abundance of these other compound in relation to ammonia, it is assumed that if ammonia concentrations do not exceed a defined action level, the concentrations of other COPCs will also be below their respective action levels. By using ammonia as a sentinel compound, detection of ammonia in the tank farms provides a process of worker protection in which the detection of ammonia triggers evacuation of the farms until further analytical methods can be used to determine whether or not additional chemical vapors are present.

Some sampling methods directly observed by CTEH® staff, or those in which photographic documentation was provided, are questionable. For example, IHTs have reportedly been observed by other Hanford workers using extensive lengths of tygon tubing were placed at points within the farms and attached to instrumentation outside of the farms to take samples from outside the fence line to avoid having to don SCBA, as currently required for inside tank farm activities. It is not known how widespread this practice is, but it demonstrates a lack of knowledge regarding the capabilities of the instruments. The primary issues with this methodology involve the decrease in the real time capability of the instrument by delaying

any vapor concentration readings from reaching the detector as they travel the length of the tubing. Other issues of concern include the tubing and whether the static pressure imparted on the tubing may cause it to collapse under suction, the excess strain placed on the pump reducing the life of the instrument or pump, any dilution or buildup of vapors due to kinks or bends in the length of tubing and potential contamination within the tubing which may cause incorrect readings.

A primary concern regarding this practice is the lack of dynamic sampling (sampling where the crews are working as they move throughout the farm(s)). In this case, the DRI is only checking a single location which may or may not accurately represent the ambient air that the work crews are working in. Additionally, anecdotal evidence was provided by multiple interviewees that in many cases the IHT will place the tubing attached to the DRI outside of the tank farms and leave the area while monitoring is in progress. While this prevents the IHT from having to don an SCBA to enter the farm and work, it prevents the IHT from accurately monitoring the work crews as they move throughout the farm. Additionally, by leaving the monitor unattended, they are not able to continuously monitor the levels near the work crews. Should a detection occur, the amount of time in which the IHT could react would be increased based on how far away they are from the meter, whether any noise is present that may prevent the IHT or others inside and outside of the fence line from detecting the meter's alarm, or any incapacitation which would prevent the IHT from responding to the meter's alarm.

5.4 Instrumentation Utilized to Assess Exposures

Various types of instrumentation are utilized by the IH group to monitor for chemical vapors within the tank farms. Typical monitoring is done through the use of DRI such as MultiRAE Pro multi-gas meters for ammonia, VOCs, ambient oxygen levels, carbon monoxide and flammable gas. Mercury vapors are monitored through the use of Ohio Lumex Portable Mercury Detectors.

Detection limits of direct reading instrumentation used within the tank farms are adequate to detect these typically sampled analytes at or below the site specific occupational exposure limits and associated action levels.

Analytical sampling is conducted using SKC personal air sampling pumps. Many of the (DRI) analytes are monitored through means of analytical sampling. While not instantaneous like direct read instrumentation, analytical monitoring allows for a more specific targeting of chemicals and lower limits of detection. Examples of the types of chemicals that WRPS tests for include nitrous oxides (NO_x), ammonia, nitrosamines, VOCs, and mercury vapor. All 59 of the COPC are monitored through the use of analytical air sampling and/or DRI monitoring.

A. AOP-15 Odor Response Protocol

The Abnormal Operating Procedure (TF-AOP-015) was established to provide a consistent approach to odor detection by tank farm workers. The process entails a standard for initiation of notification, intermediate action including air monitoring, a determination of severity, a standard for escalation or

resolution/all-clear notification, and a provision of an investigation and final report. The intent of the protocol is to be able to identify potentially hazardous vapor events that could impact the health of the workforce.

Unfortunately, in practice the TF-AOP-015 protocol implies that detecting an odor is abnormal and that actions should be taken, even though the document currently attempts to qualify the odors of concern as “*stronger than normal*,” it is entirely too subjective and leads to confusion in the workforce. This confusion leads to unnecessary work interruptions, time spent documenting and producing form A-6005-744 reports, and unneeded medical interventions. Many workers interviewed stated that the primary reason that they utilize the TF-AOP-015 process upon detecting an odor is so that the event is ‘documented’ for future needs, up to and including medical or health issues. Among some workers there is a perception that at some time in the future the DOE or other entity will make payments to persons who were exposed as was done under the Energy Employees' Occupational Illness Compensation Program (EEOICP). The implementation of this protocol has led to a situation where AOP-015s are entered into without respect to the criteria (odor detection by two or more workers or one worker experiencing symptoms of exposure such as a headache or a sore or scratchy throat), likely out of an abundance of caution or confusion as to what the triggering criteria are. The detection of an odor from person to person appears highly subjective and variable based on many variables.

A side effect of entering into a TF-AOP-015 is reinforcing the idea that tank vapor releases in the workplace are by definition of the process ‘*abnormal*’, and workers exposed to odors should be receive medical surveillance, IH monitoring of the odor is required to verify or measure the odor that was observed, and that a report should be generated for every odor event. Staff responses during interviews with CTEH® were highly skeptical of the TF-AOP-015 process, with stories and personal asides regarding perceived abuse of the process, the vague nature of entry condition criteria, as well as a broad dislike of the length of time to generate and return a report back to the field workers describing the findings of the event.

The determination of what is “abnormal” should not include odors that are a frequent occurrence within a work environment based on the process in which the odor is generated. For instance, in a food processing facility, peracetic acid is used to prevent microbial growth on organic material such as chicken. While peracetic acid does have a vinegar-like smell that is present throughout the process, a more pronounced smell experienced at some point throughout the day does not indicate that an abnormal condition is occurring. As such, these exposures would be well characterized by periodic monitoring of the process and peracetic acid levels and understood to not be harmful to the workforce. However, should an odor be present that is not associated with the operations occurring at the facility, such as hydrogen sulfide or chlorine, it should serve as a trigger that an abnormal condition has occurred.

Tank vapors should be understood to be the normal character of Hanford. Vapor spaces are continuously ventilated into the work area, either passively or actively, and this is the normal character of the work environment. Each tank farm should have a specific list of COPCs, odor characteristics, and concentrations

that are expected to be normal on that particular farm. Only odors that do not appear on the characteristics list should be considered abnormal.

Chemicals are found in the tanks, in the soil, and being produced by activities on site (painting, porta-john, herbicide, evaporator building, diesel generators, etc.) and the expectation is that an active IH program will be monitoring levels and workers to determine where additional controls are needed, if any.

B. Developing New Methods: The Pilot Study of a Vapor Monitoring and Detection System (VMDS)

These new technologies, such as open-beam Fourier Transfer Infrared Spectroscopy (FTIR) and Forward Looking Infrared (FLIR) cameras are currently in the pilot-stage of deployment. In addition to the known emission sources and fugitive emission sources located by the IHT-Vapors group, WRPS has also enlisted an RJ Lee mobile PTR-MS van which conducts rounds throughout the tank farm areas monitoring and cataloging chemicals in the ambient atmosphere outside of the tank farms.

5.5 Determining the Reasonable Maximum Exposure (RME) Concentration For Tank Farm Workers

A. Results of air dispersion modeling relevant to worker exposures and work patterns.

AERMOD and other modelling software such as INPUFF and ISC have been used on the Hanford site to inform the behavior of tank vapors with respect to the releases into the work environment (Droppo, 2004). PNNL-14767 describes a modelling study which tried to “understand the magnitudes and mechanics of potential exposures to people working in the immediate area downwind of the tank vents” with mixed results. (Droppo, 2004).

Whereas the models used are well accepted in the environmental industry, they do present some challenges when used to try and model potential workplace hazards. Environmental software is well suited to modeling the dispersion of vapor releases in the far-field, dozens and hundreds of meters from a source or sources, however most workplace exposures take place in very short distances from potential sources and there are IH modeling tools freely available that can better predict potential exposures at shorter distances in the workplace. Environmental software is not well suited to defining potential workplace exposures in the near or mid-field range without additional investigation. Even with these limitations the findings were favorable to limited exposures with distance, stating, *“Occasional short duration exposures of up to several seconds to relatively undiluted headspace air can be expected in the immediate vicinity of the tank vents. Average concentrations that represent diffusion, as well as spatial averaging, fall off rapidly with distance for the passive vents and to a lesser extent for the forced air stacks. The addition of the influence of the surface roughness elements on the tank farms will increase the rate at which concentration will decrease with distance”* (Droppo, 2004).

IHMOD, provided by the AIHA's Exposure Assessment Strategies Committee, is a collection of standard mathematical models designed specifically to assess potential worker exposures from point sources. The near and mid-field plume model in particular assesses potential exposures at distances of less than 100 meters. As much as 98% of dilution occurs within one meter of a point source, which is why near-field modeling is so critical to adequately modeling worker exposures. The importance of dilution to the exposure of a worker is described by this concluding statement, *"Thus air vented from the tanks will have a volume that a worker could, if the plume is undiluted, get a breath of mostly vented air. However, the volume of the downwind breathing space is much larger than these volumes and the intake of relatively undiluted air downwind of a vent will be a limited-occurrence, short-duration event. Even if the worker's mouth is very near to the vent, the initial dilution in the wake of the vent will make it difficult to get a steady supply of undiluted air from the vent. Thus, the vented volume of headspace air is too small to be a significant source of the air inhaled by a worker (Droppo, 2004).*

B. CTEH[®] Observation: Air Modeling

WRPS is currently working on having IH Mod approved as a tool for use by IH staff and should adopt it as soon as approval is received and use the model to inform decisions regarding exposures, worker protection areas, work activities and personal protective equipment considerations.

5.6 The TVAT Airborne Vapor Hazard Assessment

Appendix A provides a matrix of the technical issues discussed by the TVAT that are within the scope of CTEH[®]'s evaluation. This matrix also includes CTEH[®]'s position on these issues, many of which are in general agreement with the TVAT. However, a significant point of disagreement is in the formulation and support of the bolus release theory. This was one of the central issues raised by the TVAT report in critique of the tank farm IH program, which held the opinion that there was a lack of IH sampling or monitoring to address short-term (i.e., minutes or less) high concentration releases of tank headspace vapors which were termed *"bolus"* releases.

The TVAT report explored the disconnect between the lack of DRI or analytical data over the previous 30 years that would indicate injurious levels of COPCs in tank farm air, and worker reports of significant momentary odor exposures, some accompanied by alleged injuries. To explain this apparent disconnect, the TVAT developed the *"bolus"* theory of worker exposure. In essence, this theory posits that vapor exposures sufficiently high to cause the subjective adverse health effects reported by some tank farm workers, but not observed in any of the DRI or analytical data, must be the result of sudden venting of very high concentrations of tank vapors into the workers' breathing zone. Whereas bolus releases could occur in theory, extensive data exist that can be applied to test this theory, and the available data do not support the validity of the bolus release theory.

A. Bolus Release Theory

The TVAT defined the bolus exposure as vapor emissions from tanks in high concentration plumes that may last seconds to minutes and sporadically intersect the breathing zones of some workers. In its discussion of Overarching Recommendation 4 (OR 4), the TVAT opines that the current air monitoring and analysis program is *“incapable of detecting and quantifying this type of transient exposure event.”*

Appendix I of the TVAT report describes the potential impact of a bolus exposure, citing a particular air modeling plume simulation result that was published by PNNL in 2004 (Droppo, 2004). The simulation cited was selected from 240 different simulations of passively ventilated tanks to represent plume development from a hypothetical, worst-case meteorological condition. The simulated plume dilution over distance traveled from the vent resulted in a hypothetical diminution of just 19% at 10 feet from the vent, and 72% at 33 feet from the vent. The TVAT used these values to suggest that a vapor plume could maintain relatively high fractions of the source vapor concentrations at appreciable distances from the vent.

B. TVAT Justification for the Bolus Theory

The approach used by the TVAT to support the bolus theory was to assume, based on worker interviews, that tank farm workers have been exposed to near-source concentration levels of tank farm vapors resulting in severe upper respiratory irritation. The theory is supported by applying a worst-case mathematically-simulated exposure scenario [Huckaby et al., 1998; Droppo, 2004] to explain specific, severe health effects (which do not comport with the available medical findings). This is contrasted by, data from tracer gas studies in the tanks and bulk of the modeled simulations discussed below in Section 5.6 C, which indicate the TVAT worst-case scenario to be highly unlikely. When describing the concept of the bolus exposure, the TVAT did not provide perspective on the range of vapor concentrations that could make up the maximum or minimum values within a plume, but have assumed that relatively undiluted vapor concentrations similar or equal to headspace levels must exist in the workers' breathing zone at some time, even at considerable distances away from a source but within a tank farm. Indeed, the discussion in Appendix I of the TVAT report focused on the single simulation representing a worst-case scenario for vapor concentrations in the breathing zone. The TVAT dismissed more likely alternative cause-effect relationships, such as instantaneous emissions giving rise to plume vapor concentrations orders of magnitude lower than the worst-case simulation, above levels required for odor detection and sensory irritation, resulting in odor induced stress reactions. The principles whereby such conditions and worker reactions can occur are discussed in detail in Sections 6.5 H and I.

In Appendix C of the TVAT report, the bolus exposure theory was supported with a causation analysis based on the Hill Criteria of causation (Hill, 1965). These criteria have been in use for decades in epidemiology and toxicology to evaluate the adequacy of available data to associate exposure to a specific chemical and a specific health outcome. Toxicologists, epidemiologists, and physicians use the Hill Criteria as the first step of causation analysis, which is the determination as to whether or not an individual's exposure to a given toxic agent was capable of causing a specific adverse health condition or disease. In

order to establish that an alleged chemical exposure resulted in any particular adverse health condition, two separate analyses must be performed: a general and a specific causation analysis.

1. **General causation** is the scientific determination as to whether or not the chemical in question is capable of causing a particular condition in the general population at some specified dose. It is a determination of what toxicities the chemical is known to produce in humans.
2. **Specific causation** is a scientific determination as to whether a known or alleged chemical exposure an individual may have received was more likely than not the cause of the claimed injuries, symptoms, and/or diseases etc....

The objective methodology for proving general causation, as currently practiced, is a process that has undergone continual refinement for approximately the last 150 years. Probably the first effort to formalize this process occurred when scientists and physicians sought to establish the cause of diseases induced by infectious agents whose presence could not easily or readily be identified with the naked eye (Yerushalmy and Palmer, 1959; Evans, 1976). A similar process was instituted in the 1960s as scientists began to focus on diseases induced by chemicals associated with the workplace, our environment, or lifestyle choices like smoking (U.S. Dept. Health, Education, Welfare, 1964; Hill, 1965). At the present time, a number of different criteria have been proposed by scientists as the basis of the scientific method for establishing general causation (Hill, 1965; Evans, 1976; Hackney and Linn, 1979; Doll, 1984; Guidotti and Goldsmith, 1986; Susser, 1977, 1986, 1991). The criteria for general causation as outlined by Hill are:

- 1) The Strength of the human association;
- 2) The Consistency of the human association;
- 3) The Specificity of the human association;
- 4) Temporality (do biologically realistic temporal relationships exist);
- 5) Biological gradient (i.e., the principle of dose-response where within some range of doses the incidence of the response increases with increasing dose);
- 6) Biological plausibility (the response in humans is likely to be consistent with the observed response in animal tests, or would be predicted from the known animal toxicity and mechanism of action for that toxicity);
- 7) Coherence (there is an internal and external consistency to all of the evidence);
- 8) Experiment (the response decreases or increases with corresponding decreases or increases in exposure); and
- 9) Analogy (structure activity relationships with other chemicals suggest the chemical should be capable of producing the toxicity of interest).

It is well recognized within the scientific/medical community that the above criteria form the scientifically accepted method for establishing general causation. These or very similar criteria have been adopted by the World Health Organization (WHO, 1987), the International Agency for Research on Cancer (IARC) (2006), the United States Environmental Protection Agency (USEPA) (2005), and the ACGIH (2016). Numerous respected epidemiological texts adhere to the Hill criteria as the methodological basis for

evaluating causality (Mausner and Kramer, 1985; Monson, 1990; Hernberg, 1992). Casarett and Doull's Toxicology textbook, which is commonly used to teach toxicology to undergraduate, graduate, and medical students, presents these causation criteria for evaluating epidemiological data (Faustman and Omenn, 2013). And finally, a number of occupational medicine textbooks (Schenker, 1997; Eisen and Wegman, 1995) describe these criteria as the method by which epidemiological evidence is evaluated. Finally, this methodology is described in the Reference Manual on Scientific Evidence as the factors that guide judgments about causation (Federal Judicial Center, 2011). The fundamental issues of general causation are generally answered in the scientific literature, however, the fundamental nature of specific causation (i.e., whether the exposure incident in question caused a particular person's specific health effects) cannot be answered by the scientific literature alone. The mere fact that a chemical may be capable of producing various health effects does not mean that a particular person's specific adverse health effect is a direct result of the exposure incident.

The process for establishing specific causation has been established in the scientific literature for many years (Sackett et al., 1991; Sullivan and Krieger, 1992; Guzelian et al., 2005). Assuming that general causation has been established for a given chemical(s) and disease(s), the following additional steps are required to establish specific causation in an individual person:

1. The exposure was of sufficient magnitude (concentration and duration) to produce the alleged medical condition (satisfying the principle of dose-response).
2. The chemical exposure was temporally related to the onset of the alleged medical condition (satisfying the principle of temporality).
3. Potential alternate causes of the medical condition (confounders) can be adequately ruled out (eliminating alternative possible etiologies for the condition).
4. There is coherence and consistency in the evidence evaluated in this specific case (establishing that the evidence is consistent with all scientific facts and beliefs).

Using established and accepted methodology is critical in developing causal opinions as it limits the use of unacceptable methodology and/or faulty reasoning in establishing causation.

As mentioned above, the Hill Criteria are applied to the observed responses between exposure and disease in mechanistic studies, experimental animal studies, human volunteer studies, and epidemiology studies in order to ascertain whether or not a relationship exists in general between the alleged exposure and disease. This determination is known as general causation, and seeks to answer the following question: *"Has the chemical(s) in question been shown to cause the disease(s) in question in humans?"* In general, the more Hill criteria that are met to a reasonable degree of scientific confidence, the higher the likelihood that the specific adverse health effects in question are associated with a specific exposure scenario. The TVAT application of the following Hill criteria is unorthodox and scientifically questionable. Whereas the Hill Criteria can be validly applied to determine if a given COPC or mixture of COPCs could be capable of causing a given adverse health effect, the TVAT instead applied the Hill Criteria as to whether or not the hypothesized bolus release of vapors from waste tanks could result in the symptoms

complaints expressed by some tank farm workers. The TVAT did not conduct an analysis of the body of toxicology or epidemiology literature of any COPC chemical and any of the health effects being claimed by tank farm workers, but instead assumed general causation and erroneously attempted to apply the Hill Criteria to subjective complaints made by tank farm workers during interviews, which is in fact a specific causation question. This is not a proper application of the Hill Criteria, and as such, cannot form the basis for the conclusion that bolus vapor releases from tank headspaces are responsible for the workers' symptom complaints.

For example, the TVAT misapplies the Hill Criterion of dose response, and confuses it with the role of dose response in specific causation. In general causation, the Hill Criterion of dose response is applied to experimental studies, animal studies, or epidemiology studies under the premise that if a toxicological agent is causative of an adverse effect, the frequency or magnitude of the response should increase with increasing dose. In the realm of specific causation, the criterion of dose-response relates to the question of whether or not the dose received by the subject or subjects was sufficient to have caused the alleged adverse health effect. Instead of first determining the dose-response relationship for any of the tank vapor constituents and then ascertaining whether or not tank farm workers could have been exposed to concentrations sufficient to cause their complaints, the TVAT instead relied upon worker's complaints as evidence that the workers had been exposed to concentrations sufficient to have caused their symptoms.

First, it is argued that the existence of the claimed medical condition (e.g., a symptom or a diagnosed disease) demonstrates that sufficient antecedent exposure has occurred. Then, it is argued any exposure, even in the absence of evidence demonstrating significant exposure, provides the basis for explaining the cause of the claimed medical condition. In short, the symptoms essentially become the basis for explaining themselves. Such reasoning does not provide the proper foundation for a causation analysis (Rothman and Greenland, 1998; Federal Judicial Center, 2011). In essence, this reasoning provides the person using it with no way to single out the most probable cause of a medical condition, be it chemical or nonchemical. When establishing the dose and the dose-response relationship are no longer necessary components of the causation analysis, there is no longer scientific or reasonable basis for eliminating other known or suspected causes of the condition.

A more appropriate approach to the issue that the TVAT could have taken is a "lines of evidence" approach that lays out the linkage of the chain of events that would be necessary for the theorized bolus release and symptom reports. Once the lines of evidence have been established, each of these steps in the process can then be tested based on existing data or data generated in the course of the investigation, to determine if the causal chain of events can or did occur under a specific set of circumstances.

C. Evaluation of the Bolus Theory in relation to available air dispersion modeling and physical data

The bolus theory as presented in the TVAT report conflicts with the standard and accepted IH and field air dispersion plume models which show that most dilution (up to 98%) from a point source occurs within

one meter. These data do not support the bolus theory that a release can maintain 80% of its initial release concentration for dozens of meters and affect some workers but not others in close proximity. By comparing the modeling results in Table B.1 of PNNL-14767 (Droppo, 2004) [from which the TVAT worst-case scenario was taken], it is clear that maintaining a high percentage of a source's vapor concentration over a distance requires the unlikely combination of unusually high atmospheric stability (classes E, F, or G), minimal wind movement (1 m/s), and high vapor volume release (100 m³/hr). Changing any one of these three conditions results in a simulated plume that is far more dispersed from 1 meter onwards than in the scenario used by the TVAT. Further, data from tracer gas studies (Huckaby et al., 1998; Droppo, 2004) performed on multiple tanks in 1998 indicated very small vapor volume releases (most <6 m³/hr). Taken together, the physical data do not support the existence of conditions necessary for production of headspace-level vapor concentrations more than a few feet from the tank vent.

D. Evaluation of the Bolus Theory in relation to available tank farm air quality data

Area and personal air sampling and DRI data collected since 1992 do not indicate the existence of bolus vapor plumes at the tank farms. Over the 11 span of 1992-2003, thousands of area, personal air samples, DRI readings, and odor source survey measurements were collected. At no time were the breathing zone levels of ammonia, nitrous oxide, 1-butanol, or select VOCs above their respective OELs. CTEH[®] reviewed personal sampling data from May 2006 to July 2016, all reported as 8-hour TWAs. The highest concentration measured for any COPC was for nitrous oxide, with 3 of 3,361 samples found to be above (59-69 ppm) the OEL of 50 ppm. None of the 5,474 ammonia samples exceeded 15 ppm, and 1-butanol measured in 2,332 samples never exceeded 2 ppm.

E. CTEH[®] Observation: The Bolus Release Theory

The bolus exposure theory was developed based on the existence of odor complaints and subjective injuries in the absence of monitoring or air sampling data to support exposures necessary to cause injury. Years of air monitoring and sampling data and available modeling and tank dynamics studies have not supported the existence of bolus exposures that would impact worker health. The TVAT causation analysis was applied incorrectly and did not adequately consider the totality of available monitoring and sampling data in evaluating the dose-response criterion, nor does it consider the whole continuum of effects (odor ID and possible stress responses at low concentrations) when evaluating the dose response and plausibility criterion. There are insufficient data at this time to support the bolus exposure theory, but an alternative explanation of odor and low-level transient irritation induction of stress effects resulting in no objective medical finding cannot be ruled out.

CTEH has almost 20 years responding to hazardous materials events involving both pressurized and non-pressurized vessels, as well as extensive IH and response experience in chemical plants and refineries. It is our experience that the "bolus" release of chemicals occurs primarily within vessels that are not passively or actively vented to the atmosphere, as these vessel types allow for the buildup of pressure within the vessel. Such vessels are sealed to the atmosphere with some type of pressure relief device

(PRD) that will allow venting of the tank at a designated pressure to prevent tank failure in the event of pressure buildup. Even in vessels that are not considered “pressure” vessels, the PRD is designed to release at some pressure above ambient. For example, general service tank cars may carry pressures of up to 25 psi, and common highway tanker trucks may carry pressures of 3-15 psi (USDOT, 2016). If pressure within the vessel exceeds the operating pressure of the PRD, there is a resulting rapid release of pressure, resulting in the potential for a “bolus” release as described in the TVAT report. In closed systems, this process is often referred to a “burping” and occurs with temperature changes or a chemical reaction causes a sudden increase in tank pressure.

In contrast, the SSTs present in the Hanford Tank Farms are openly vented to the atmosphere through riser stacks. This prevents the buildup of significant pressure and allows for much more gradual equalization of pressure between the tank headspace and the atmosphere. As described in the Technical Basis document, the dynamics of the “breathing” of the SSTs is well studied and the available evidence does not indicate the occurrence of “bolus” exposures. The TVAT report provides a concentration graph from the tank SX-103 breather filter as an example of “...transient peaks in the release rate from tank vents.” Whereas this does show a transient increase in emission concentrations from the breather filter, there is no information regarding the rate or volume of the release, and it is therefore not possible to determine whether or not this provides evidence of a “bolus” release. In the absence of waste disturbing activities, one could posit two possible scenarios under which a relatively large amount of headspace vapors could be released in a short time from SST risers. These include 1) A rapid chemical reaction producing both heat and/or vapors at a rate sufficient to result in the release of a “bolus” of tank vapors, and 2) the buildup of a large amount of gas under tank sludge or some type of a surface crust that could suddenly be released, resulting in the displacement and subsequent release of a “bolus” of tank headspace vapors. As discussed in the Industrial Hygiene Chemical Vapor Technical Basis document (Meacham et al., 2006), tank chemistries and headspace dynamics are well studied and defined, and the data do not indicate that either of these conditions occur within SST under static (i.e. non-waste-disturbing) conditions.

5.7 Acceptable OEL Development

The Hanford tank farm COPC OELs are known as Acceptable OELs (AOELs), and a combination of OELs derived previously by regulatory and other scientific bodies, and OELs proposed by PNNL for COPCs that did not already have an OEL in 2006. The process of developing OELs has long been established in U.S. industry, and is constantly being adjusted to utilize the state-of-the-art in toxicology assessment, instrumentation, and IH practice. Briefly, OELs are based on quantitative data from human occupational exposure experiences, studies of volunteer exposures, laboratory animal studies, and leveraging of toxicology/safety data from compounds with ample data to chemically similar compounds that are likely to produce identical or similar physiological effects, albeit at possibly different exposure levels. The exposure concentration that has been observed to result in no appreciable risk of the most sensitive adverse effects in humans or lab animals (the critical effect) is modified by dividing by uncertainty factors to account for the unknowns arising from possible (but often unknown) differences in response between

humans and animals, differences in human response sensitivity, extrapolation of dose data from oral toxicity studies to occupational inhalation, and other sources of uncertainty.

The quality of an OEL to guide adequate protection of worker health without placing an unnecessary burden of resources depends, to a large extent, on the ability to minimize the level of uncertainty between a proposed exposure level and the actual level that would result in adverse health effects, including nuisance working conditions and injuries. These factors have been taken into account in the current list of COPC OELs. However, the OELs that are now guiding IH decisions in the Hanford tank farms are in need of expansion to appropriately guide the response to acute or momentary exposure to tank waste vapors in the worker breathing zone.

A. Current AOEL Derivation Process

The current COPC AOELs were derived by utilizing previously established OELs (OSHA PEL-TWA, ACGIH TLV-TWA, German MAK values, DOE WEELs) or emergency response planning guidance values (AIHA ERPGs), if such values existed at the time. For COPCs without a previously-established OEL available, Hanford-specific AOELs were derived by using established OELs for chemically-similar compounds, and applying uncertainty factors of typically 3 to 10, resulting in an AOEL that is typically 1/3 to 1/10 that of the OEL on which it is based. This application of uncertainty factors may be overly conservative if the adverse effect in question is point-of-contact irritation for which structurally-similar compounds are unlikely exhibit marked differences in toxic potency.

The majority of current AOELs are based on protection of workers from adverse health effects from chronic occupational exposures (i.e., daily exposures for a working lifetime), and may not be appropriate for acute or momentary breathing zone exposures. Some OELs are based on the critical effect of nuisance mucous membrane and upper respiratory tract irritation that may not result in objective pathology, but are sufficiently irritating to cause discomfort on most workers from constant exposures. Adverse health effects resulting from chronic occupational exposures, such as degenerative pulmonary diseases or cancer, are often quite different from effects seen following acute, momentary, and non-constant tank vapor exposures that are at issue in the tank farms. Critical effects of nuisance discomfort or acute neurological effects from acute exposures are appropriate bases for protection against effects presently reported by tank farm workers which have been related to very short-term and intermittent releases of tank headspace vapors.

B. AOEL Derivation for Momentary Exposures

The transient nature of tank farm vapors and odors in the worker breathing zone suggests that OELs based on acute, even momentary, exposures are more appropriate than those designed to protect from injury due to chronic exposures. Thus, there is a need to develop a parallel set of COPC AOELs that are based on known critical effects from acute or momentary exposures. Thus, AOELs for acute effects can guide to the interpretation of DRI measurements, while AOELs for chronic effects would continue to guide the interpretation of TWA sampling and analysis results.

C. CTEH[®] Observation: AOEL Development

The approach used to develop tank farm AOELs that are protective against effects from chronic exposures is based on sound toxicological and IH practice. The paucity of toxicological data for many of the existing COPCs requires leveraging of data from surrogate compounds, which has been done; however, the application of uncertainty factors in some cases may be overly conservative. Secondly, complementary AOELs need to be developed that are more applicable to acute, sometimes momentary vapor exposures that result in pungent, irritant, and sometimes unidentified odors. The process of developing acute OELs that are similar to ceiling or STEL values that is underway within the HPP group is toxicologically sound and should provide acute AOELs that are more germane to worker protection than the use of OELs based on chronic exposures.

5.8 Leading Indicators of Exposure

Because tank farm vapor and their associated odors are transient in nature, the best opportunity to assess the air quality is from instantaneous data collected using real-time air monitoring equipment. The number of analytes available for real-time monitoring are very limited, and are a small subset of the present COPCs. Thus, there exists a need to determine the level of confidence in the use of the available real-time analytes as Leading Indicators (LIs) to warn of presence of other COPCs at levels of acute health concerns.

A. Current Status: PNNL Draft Assessment

PNNL has drafted a rigorous framework for vetting of available analytical data, creating pairs of candidate LIs, and statistically examining the likelihood that any particular LI candidate airborne or headspace concentration will correlate well with the concentrations of other vapor constituents. In this framework, concentration data points for COPCs are paired with other COPC data points that were collected simultaneously in time and location to examine the relationship between COPC concentrations.

PNNL selected and evaluated a subset of TWINS headspace and IH data to identify candidate LI pair that are found in the same location at the same time. Two such pairs of data suggest a possible relationship; three or more increase the likelihood of such a relationship existing. The LI pairs are then evaluated to qualify the relationship to determine if the relationship exists only for certain identifiable conditions (e.g., tank-specific pairs, pairs appearing together due to work activity) or in a more general sense. If the OEL of the COPC in question is below the detection limit of the LI, then the possibility exists for the LI to be measured as a “non-detect” while the COPC may be present above its OEL. As such, this LI/COPC relationship would not be judged useful. The ratio of OELs for the candidate pairs is also evaluated. The higher the ratio, the more informative is the presence of the LI for guiding actions to take prior to COPC exposure at or above its OEL. A suitability analysis is then performed to determine if the candidate LI is also a bounding indicator, meaning it can be measured at a level that correlates with the OEL of the COPC. This predetermined bounding concentration is indicative of an absolute alert level requiring a response. A statistical correlation analysis is then performed to determine the extent of false alerts

determined for a particular data set, and the correlational relationship is quantified using multivariate analysis.

In the same framework report, PNNL also performed a pilot computational fluid dynamics (CFD) modeling exercise following the release of ammonia and isobutylene on the PNNL campus to investigate the utility of using CFD modeling to qualify LI determinations. The concentration correlations were shown to be time dependent, with stronger correlations being exhibited shorter times after release.

The PNNL authors note that the framework needs to be exercised more robustly with additional analytical data, including data that are being generated by the pilot VMDS project and the RJ Lee mobile laboratory. They believe that these future exercises of the framework will help to better define certain threshold conditions within the framework decision structure and provide a clearer indication of whether this approach can identify useful (and protective) LIs now and in the future as automated data stream processing is implemented.

B. CTEH[®] Observation: Development of Leading Indicators

The draft approach developed by PNNL to identify and validate selection of leading indicators of easily-measured COPCs is a scientifically-sound approach, and should continue to be developed to the point of validation with incoming new data, including those data that were developed by the VMDS mobile laboratory initiatives.

6.0 Controlling Hazards: WRPS IH Program Implementation

CTEH[®] examined procedures, and policies established by WRPS to ascertain their impact on the protection of workers from chemical hazards within the tank farms.

6.1 Hazard prevention and abatement

This section requires that hazards are prioritized and abatement actions implemented based on the risk to the workers and that hazard controls are based on the Hierarchy of Controls.

A comprehensive risk assessment needs to be created that lists all known hazards to the workforce, the potential health impact (both acute and chronic), the frequency or potential frequency of exposure, number of workers potentially impacted and engineering controls in place with an estimation of effectiveness.

A. Hierarchy of Controls

Elimination/Substitution Controls

While the preferred method for reducing exposures is the elimination or substitution of the hazardous agents in question, this is not applicable to WRPS, as working with the site waste products is precisely why

the project and workload exist. Work on the tank farm sites, by definition, includes working in and around hazardous agents.

Engineering Controls

Engineering controls that are in place include the storage tanks and associated equipment which are designed for the long-term storage of hazardous wastes. Passive and active ventilation use breather filters which are designed to prevent radiological contamination from being released through the breather filters.

Actively ventilated tanks also have exhaust stacks of varying height in tank farms where active work is taking place. The intent of the design is to elevate the point of dilution above the work area. In practice, due to the elevation of some farms, the tops of stacks are level with neighboring administrative buildings, and in particular the roof mounted HVAC units. The potential exists to cause an odor event inside an adjacent building when prevailing winds are traveling in a particular direction. While this would not represent a health impact, it could reinforce negative attitudes toward the tank farm operations.

Administrative Controls

Administrative controls are limited to signage and the vapor control zones located around tank vapor point sources with signage indicating the potential hazard. The requirement to wear SCBA inside the tank farm boundaries appears to render this administrative control redundant, except to indicate the sources of exposure. An opportunity exists for WRPS to augment the current administrative controls with work practice controls that limit workers' exposures, such as worker rotation, task time limits, or other policies that reduce exposure time before requiring PPE to be worn.

PPE

Personal Protective Equipment (PPE) refers to equipment worn to minimize exposure to a variety of hazards. Examples of PPE include gloves, foot, head and eye protection, hearing protection and respiratory protection. PPE is used only to be used when a hazard cannot be controlled by other means. PPE must be implemented only after all other attempts to eliminate or control the hazard have not sufficiently reduced the exposure to the workforce to an acceptable level. Care must also be taken to ensure that the use of PPE does not introduce new hazards to the workplace.

B. CTEH[®] Observations: Utilizing the Hierarchy of Controls

The Department of Energy regulation, 10 CFR 851 Subpart E Appendix A-*Worker Safety and Health Functional Areas*-(6) *Industrial Hygiene*, agrees broadly with the AIHA guidance in requiring that contractors;

...implement a comprehensive industrial hygiene program that includes at least the following elements:

(a) Initial or baseline surveys and periodic resurveys and/or exposure monitoring as appropriate of all work areas or operations to identify and evaluate potential worker health risks;

(b) Coordination with planning and design personnel to anticipate and control health hazards that proposed facilities and operations would introduce;

(c) Coordination with cognizant occupational medical, environmental, health physics, and work planning professionals;

(d) Policies and procedures to mitigate the risk from identified and potential occupational carcinogens;

(e) Professionally and technically qualified industrial hygienists to manage and implement the industrial hygiene program;

Within the tank farms, the IH technicians (IHTs) conduct monitoring of various analytes using direct reading instruments for ammonia and volatile organic compounds (VOCs). Additionally, due to the requirement that all workers conducting activities within the tank farm fence line wear self-contained breathing apparatuses (SCBA), the IHTs conducted physiological monitoring of workers in an effort to prevent heat-related injuries and illnesses.

All work conducted within the fence line requires that an IHT be present and conducting air monitoring. The specific air monitoring required is dictated by the job task sampling plan. These plans are developed by the IH professionals (IHPs) and implemented in the field by the IHTs. While the IHTs conduct the work within the tank farms, many of the IHPs are present to assist as needed. However, this is inconsistent across the various groups such as retrieval and closure, construction and production ops, with each group's IHPs having various levels of visibility within the farms as well as both IHTs and IHPs visibility within planning and pre-job meetings.

In addition to inconsistencies with visibility of the IHTs and IHPs in planning and pre-job meetings, there are inconsistencies with the execution of the work and sampling plans depending on the individuals conducting the work that day. The variation seems to be dependent on the group within which the IHT is embedded. For tasks in which additional IH support is required, call outs to other groups requesting additional IHTs may be filled by technicians from other groups who may conduct monitoring in a manner different from those normally associated with that work group. This inconsistency has resulted in a lack of workforce confidence in the IH group.

The implementation of the IH vapors program with respect to tank vapor exposure is in need of revision and integration into Hanford work planning process. This revision should be based on alignment with 10 CFR 851 - Worker Safety and Health Program.

6.2 Management responsibilities and worker rights and responsibilities

It was discussed with CTEH® representatives several times that workers have the statutory right to refuse to wear a monitoring device in support of the IH program. This does not appear to be the case in all except for a very narrow definition. 10 CFR 851.20 (a)(9) states that the contractor management has the responsibility to;

Establish procedures to permit workers to stop work or decline to perform an assigned task because of a reasonable belief that the task poses an imminent risk of death, serious physical harm, or other serious hazard to workers, in circumstances where the workers believe there is insufficient time to utilize normal hazard reporting and abatement procedures...

Only when a worker believes wearing a sampling device would pose a risk of death, serious physical harm, or other serious hazard to workers, can they refuse to wear the device. In addition, the refusal can only proceed if the worker believes there isn't enough time to handle the concern through the normal reporting process.

The WRPS stop work authority procedure should be modified accordingly and practices should be implemented to document and report visibly each case of refusal to participate in monitoring activities. Documentation of refusal should include the type of sampling requested, perceived hazard, the perceived timeframe issue, and a statement that the worker believes the refusal to be justified and reasonable.

For further reinforcement the section continues in 10 CFR 851.20 (b)(1),(b)(8) and (b)(9) that workers have the responsibility to;

...comply with the requirements of this part, including the worker safety and health program, which are applicable to their own actions and conduct..., Decline to perform an assigned task because of a reasonable belief that, under the circumstances, the task poses an imminent risk of death or serious physical harm to the worker coupled with a reasonable belief that there is insufficient time to seek effective redress through normal hazard reporting and abatement procedures..., and ...Stop work when the worker discovers employee exposures to imminently dangerous conditions or other serious hazards; provided that any stop work authority must be exercised in a justifiable and responsible manner in accordance with procedures established in the approved worker safety and health program. (emphasis added)

This section clearly articulates the workers' responsibility to comply with the approved safety and health program (including monitoring), and ONLY when two standards of reasonable belief are met may they decline to perform a task. When doing so it must only be done when an imminently dangerous condition or other serious hazard is identified and done in a justifiable and responsible manner in accordance with approved procedures.

In plain language, once DOE has signed off on procedures as meeting the requirements of 10 CFR 851 Subpart C, said procedures are binding on WRPS management and workers.

Steps should be taken to tighten up the refusal or stop work authority on worker exposure monitoring activities. When it comes to collecting worker exposure monitoring data, the only thing worse than not collecting data, is collecting data that are not representative of the actual exposure. The practice of having another person wear the monitoring device should cease immediately. The use of data that are not representative of actual worker exposures increases the risk of not properly characterizing exposures and ultimately making incorrect decisions about worker exposures.

6.3 Role of the Health Safety Security Environmental and Quality (HSSEQ) Groups

Several groups under the HSSEQ program are involved in the implementation of the IH program. The primary groups are the IHT, IHP, and the Hanford Atomic Metals Trade Council (HAMTC) Safety Representatives. Other groups are minimally involved, such as the Health Physics Technicians (HPT).

IHTs are responsible for carrying out monitoring and sampling of chemical vapors within the tank farms, compiling the results of sampling, ensuring the chain of custody (COC) forms are properly completed, scheduling of technicians for work groups, ensuring proper timekeeping, calibration of instrumentation, attending pre-job and planning meetings, and preparing equipment and media for daily monitoring.

IHPs are responsible for the communication and implementation of the IH program, providing technical expertise to the IHTs, managing the IHTs, evaluating and revising IH programs as necessary, attending planning and pre-job meetings, and providing technical expertise and knowledge to tank farm workers.

Hanford Atomic Metal Trades Council (HAMTC) Safety Representatives are responsible for the overall safety of all workers at Hanford. Their role in the IH program consists of providing health and safety expertise to the workforce, working with the IHT, IHP, and HPT (RADCON) groups to assimilate sampling data, and ensure the safe operation and safety of workers performing work in and outside of the tank farms.

A. Training and Competency

The current knowledge of the IHTs varies greatly depending on a number of factors. These factors include, but are not limited to, the level of hands on training received, the availability of senior technician mentoring, previous technical/chemical monitoring experience, educational background, professional development, personal investment in their role, fear of occupational illnesses arising from performing their role, the IHT group in which they are embedded, time in their role, time as an IHT, level of IHP support, trust in management, and level of foundational IH knowledge.

Many IHTs are highly knowledgeable with the challenges faced by the tank farm IH program, as well as the underlying fundamentals of IH. However, some have minimal interest in furthering their knowledge.

Observations of, and communications with, the IHTs show a varying level of knowledge and comprehension of IH. The training program for IHTs places a high level of focus on the operation of direct reading instrumentation (DRI) and the methods to which they are calibrated for use in the tank farms. Many of the technicians voiced concerns with the lack of training in the manner in which the instrumentation is used while in the field. The primary concern with training centered on the feeling of being pushed through training at a rapid pace in order to achieve rapid deployment to the field. Many were concerned that they did not receive adequate hands-on training with a more experienced senior technician, which led to them being unable to answer questions from the workforce regarding the methodology dictating how and why sampling was being done in a specific manner. 10 CFR 851 Subpart E Appendix A (6)(e) requires professionally trained and technically qualified industrial hygienists to manage and implement the industrial hygiene program.

Current efforts to train IHTs for deployment into the tank farms are centered on providing knowledge in use and calibration of current instrumentation. Additional knowledge on basic troubleshooting is also provided. Training, in relation to actual field conditions, does not seem to be the primary focus. Many technicians expressed concern that the training was focused on teaching them instrument operation rather than how the instrumentation would be used when performing their roles in the tank farms. They stated that their lack of knowledge of the practical application of their training has led to the tank farm workforce challenging their knowledge of the IH program, doubting the applicability of the analytes they monitor for, and questioning their integrity when reporting their instrumentation's readings.

Technicians also raised concerns about the lack of training regarding the interpretation of the instrumentation's readings. Many were unable to convey the meaning of an elevated reading from their instrumentation, as they had no prior experience with either air monitoring equipment, or IH, prior to their role with WRPS.

Qualification cards are used as a mechanism for technicians to meet the requirements needed to operate the monitoring equipment to which the card refers. Many technicians raised concerns regarding qualification card sign offs by supervisors and trainers. Specifically, they raised concerns about some IHTs going to specific individuals who would simply sign off on the qualification card without verifying the IHT's knowledge of the instrument to which they were qualifying on. It was reported that this has led to IHTs not understanding the equipment used in the field, leading to the workforce raising questions about their competency. No tracking method for verification of this process could be located during the evaluation.

In addition, no continuing education, other than annual instrumentation qualifications, was noted among the IHT group. While the TVAT report suggests achieving parity of the IH program with the health physics program (RADCON) through an annual 40-hour certification training and testing, no attempt to implement this program was noted during the review. Additional training on Hanford and general process knowledge is offered at irregular intervals and it was not ascertained as to whether this training was mandatory or voluntary during the review.

B. Vertical Communication

Communication between the technician level and the management layers within the chain of command varies between the different subgroups within the IH program. Groups such as the production operations group described their access and communication as open and frequent, as they have close proximity to their supervisors and managers. Other groups such as retrieval closure and construction indicated that virtually no communication occurred on a regular basis and that supervisors and managers were rarely seen in the field or in pre-work tasks such as the planning and pre-job meetings.

Other communication concerns from the workforce are those surrounding transparency of data and analytical sampling results. Many workers expressed concerns regarding the location of data storage and its accessibility. Additionally, many expressed concerns about the availability of data. The length of time before the data are posted to publically accessible portals is inconsistent and intermittent. Many interviewed were unaware of the publically accessible databases available to them, as they had not received or could not recall any communication from either their direct line management or from WRPS senior management.

Additionally, a small group of IHTs interviewed expressed that there is a fear among the IHTs that asking questions regarding equipment and procedures will adversely affect their position within the group. They stated that the technicians are resistant to asking questions about something that they have been trained on, or even while in training, for fear of looking like they lack knowledge or are incompetent.

C. Workforce Opinions

In conversations with the HPTs, IHPs, and tank farm safety reps, many voiced concerns regarding the IHT's lack of knowledge with the subject matter. While many conceded that there were several IHTs who were very knowledgeable about what they were doing and why, there was a large portion of them who did not know, and in their opinion, did not care about the base knowledge that underlies their roles in the organization.

Communication of the IH work and sampling plans to the tank farm workers is frequently left to the IH technician (IHT) level staff. In many cases, the IHTs do not have the technical understanding behind the work and sampling plans to adequately address workforce concerns regarding sampling rationale, how an instrument operates or its capabilities, or to provide context to the action levels used by the IH vapors program. This damages the credibility of the IHTs in the field in the view of the tank farm workers. This, however, does not apply to the IH group as a whole. Many of the technicians are highly knowledgeable of both the instrumentation and the underlying technical basis on which the IH program is built. Many of these technicians are seen as leaders among the workforce, specifically, among the HPT and IHT groups.

HPTs were interviewed to gauge an outside perspective of the IH Vapors program and the AOP-015 process. The TVAT report suggested that the IH program needed to be brought up to par with the RADCON program which is used to manage radiological exposures. Some of the HPTs interviewed did have specific

criticisms of the IH vapors program and have performed research on potential issues with various COPCs. This group was very conversant in exotic COPCs such as nitrosamines and furans and questioned the capabilities of the IHTs and equipment used to test for tank vapor exposure.

Other HPTs were sympathetic to the plight of the IH team and the difficult nature of the IH Vapors program and voiced support for them. Still a third cohort of HPTs did not have an opinion either way or objected to the idea of being interviewed in the first place. However, interviews revealed quickly a very vocal subset of the HPTs is driving some of the criticism of the IH Vapors program, feeling that the IHTs don't know what they are doing, have experienced a negative experience with tank vapor exposure (felt ill effects from contact with vapors), or have a general distrust of present or past management of Hanford activities.

6.4 Risk Communication (RC) To Tank Farm Workers

Whereas communications to tank farm workers are made, this information is typically shared only briefly during morning meetings and is often read only as a formality. Conversations with field personnel revealed that rarely are the data discussed, and when this occurs, little or no context relating to the meaning of the data is conveyed to the workforce. Often, the data are referred to as a zero value when a chemical is not found above an instruments detection level. Many of those interviewed, in both the industrial hygiene group and non-industrial hygiene groups, have expressed their frustration with the use of the value 0, as it is not in keeping with sound industrial hygiene practice and should be reported as less than the detection level of the instrument used to collect the data.

Outcomes pertaining to AOP-15 investigations are shared only among those involved or through word of mouth amongst the workforce. In this case, much of the information shared is similar to that of a "he said/she said" situation. The data being shared pertains generally to the location in which the event occurred, what was done in response, and when the area was cleared. During the events, the only communication to the workforce is that of either the SOEN system, which is a voluntary text messaging system that sends out alerts when an event has occurred, or through two-way radio communication to those with such capability. No email communication or non-voluntary communication system is used to disseminate information to the workforce regarding vapor related events.

Many within the workforce were unaware of the existence of the multiple databases and websites employed by WRPS to share vapor monitoring data. Several workers complained of a lack of transparency in the collection of the data and its terminal location in which the data could be viewed. Those who were aware of these databases raised concerns regarding the length of time in which the data become available, though many understood the length of time required for assimilating the data into the databases based on the volume of data collected.

Information related to the chemicals that are onsite is provided in multiple locations and reports to the workforce. Only a small group of those interviewed were unaware of the list of COPCs located within the tank farm headspaces, as WRPS has been very forthcoming regarding the chemicals that have been found

within them. However, there is an atmosphere of distrust regarding the actual contents of the tanks due to anecdotal discussions on the unknown identity of chemicals disposed of in the tanks from classified materials brought into the site during the decades leading up to the facility's cessation of operations.

A. CTEH® Observation: Current Status of On-Site Tank Farm-Level Risk Communication

Risk communication within the tank farms is limited to morning, planning and pre-job meetings in which the IHTs and IHPs share information from the sampling plans developed for the task being conducted. Additionally, should a detection above an action level within the farm be discovered, the tank farms are cleared by the IHT's until further instructions are provided by the shift office, IHP's and field work supervisors. There exists a need to train workers in the conceptual differences between existence of a hazard and risk of and adverse effect. With this knowledge base in place, workers would greatly benefit from communication laying out the details of an odor/vapor exposure incident as well as information on relative risks of exposures to the chemicals at issue at concentrations that elicit odor detection and sensory irritation, but not necessarily toxicity.

6.5 Differentiating Hazard and Risk

In the collective experience of CTEH® health scientists, the majority of workers and members of the general public often do not make the distinction between a health hazard and a health risk. By definition, a chemical health hazard is an agent that has the potential to cause an adverse health effect if the exposure concentration is a sufficiently high and of sufficient duration to yield a toxic dose. Risk is the probability, or likelihood, that such an exposure might occur. Many people mistakenly believe that the mere presence of a hazard will inevitably result in an injury. This notion is, of course, not true, and does not comport with general principles of toxicology and epidemiology (Rodricks, 2007). If a person understands that exposures to chemicals may incur a risk of adverse health effects somewhere between zero and near certainty, then they will not mistakenly view an exposure to a hazard as an on/off switch that will deliver an injury simply by the hazard's presence in the person's environment.

A. Layman Toxicology: Dose-Response Knowledge

Toxicology is the science of the adverse effects of chemical or physical agents on living organisms. A toxicant is any agent that can adversely alter the normal function of healthy tissues and organ systems in the body. Toxicologists evaluate and attempt to measure or predict the extent of these effects and the intrinsic properties of the toxicants that produce them. An understanding and assessment of human health risks from such substances depends on an understanding of the magnitude and duration of exposure to these substances of concern.

Central to toxicology is the dose-response principle, which says that the higher the level and duration of exposure to a chemical, the more likely it is that an individual will experience an adverse effect. From the dose-response principle comes the concept of the adverse effect threshold dose (or exposure). This is the

exposure level below which no adverse effect will occur, and above which adverse effects begin and increase in intensity as exposure level or duration increases. These principles are true for all substances, and was first recorded by the Swiss philosopher, Paracelsus, who stated:

All substances are poisons; there is none which is not a poison. The right dose differentiates a poison from a remedy. (Klaassen, 2013)

This principle can be illustrated by the dose-response of familiar compounds. Common aspirin is non-toxic (and beneficial to human health) when taken daily at doses of 1 mg/kg of body weight in adults, but is acutely toxic at 150 mg/kg (Chyka et al., 2006). Table salt (sodium chloride) ingestion is recommended to be about 4 g/day in adults, with an upper tolerable limit of twice that (Drake, 2008). However, rapid ingestion of a single dose of 1000 g in 600 ml of water may be lethal due to respiratory distress (HSDB, 2106a). Even water, which is essential to life, is toxic when consumed in liter quantities before and during long-endurance athletic competitions, such as marathons, causing a dangerous drop in required blood sodium levels (hyponatremia) [HSDB, 2016b]. For many compounds, the safe exposure level may be hundreds or thousands of times lower than the toxic exposure level. Further, different effects have different threshold levels. For example, respiratory irritation from inhaling an irritant gas may have a very different (and lower) threshold concentration than neurological dysfunction. When considering whether a specific exposure situation will result in an adverse effect, one must consider the whole spectrum of exposures ranging from very low (which may produce no or even beneficial effects) and low levels (causing mild irritation) to exposures above the dose threshold for adverse effects.

Toxicologists may sometimes use epidemiology studies to describe the dose-response of a chemical in humans. However, most epidemiology studies cannot account for many other factors in the studied population that may play a role in the adverse health effect. Thus, controlled animal tests are often conducted to evaluate the toxicity of chemicals. This type of testing is common in the field of toxicology, as controlled laboratory studies allow for the evaluation of the potency, and dose-response relationship chemicals have on living organisms. The dose-response relationship accounts for toxicant presence in target tissues at sufficient concentrations and for a sufficient period of time to elicit an adverse effect. Typically, a range of doses is included in a study in order to capture the full range of response, which ranges from the No Observed Adverse Effects Level (NOAEL – the highest dose tested that doesn't elicit an adverse effect), the Lowest Observed Adverse Effects Level (LOAEL – the lowest dose tested that elicits an adverse effect), and a maximal effect or response (MTD – Maximally Tolerated Dose).

B. Acute vs Chronic or Delayed Effects

The adverse effects from exposure to chemicals above the toxicity threshold will vary depending on the exposure duration. Adverse effects from acute exposures that last seconds to minutes occur because the compound is a point-of-contact toxicant (causing an immediate irritation reaction to exposed skin or mucous membranes of the eyes, mouth, and respiratory tract) or is rapidly taken up, absorbed into the blood, and delivered to the central nervous system, where its effect occurs. Conversely, chronic effects

occur from repeated exposures delivering internal doses of a toxicant to tissues, which, over time, interferes with some biochemical system in the tissue sufficiently to cause that tissue to fail or grow in an uncontrolled manner (i.e., cancer). A single acute exposure that does not produce almost immediate tissue damage that can be medically observed will typically not result in a chronic, long-term adverse health effect.

C. OELs, ACLs, and Bright Line Toxicity Thresholds

As discussed previously, Hanford COPC AOELs and the regulatory/scientific body OELs that underpin many of them, were derived by identifying the NOAEL or LOAEL from a human or lab animal study, and adjusting it downwards (i.e., err on the side of caution) to account for uncertainties of possible, but not observed, higher sensitivity of humans compared to animals and unusually susceptible persons compared to the general workforce to the adverse effects of a given chemical. That being the case, AOELs, or their ACLs (10% of the AOEL) should never be confused with a bright line toxicity threshold for that compound. Exposures at AOEL levels or lower should be considered safe for the entire workforce; however, exceedances of an AOEL, even by an order of magnitude in most cases, is not and should not be suggestive of a likely risk for injury (Rodricks, 2007).

D. Odor Threshold, Sensory Irritation, and Perceived Injury vs Actual Toxicity

Many chemical compounds, including many of the COPCs, and especially irritant compounds may be detected by human chemosensory (sense of irritancy) and olfactory (sense of smell) detection at airborne concentrations that may be orders of magnitude lower than levels required to cause injury. Application of these phenomena is applied daily in the practice of toxicology, but is not well understood by a significant segment of the U.S. workforce and public (ref). An understanding by tank farm workers of basic toxicological odor biology principles discussed herein may help to put into proper perspective their experiences with detected or “felt” odors, compared to data provided by available air monitoring instrumentation, and air levels that truly represent risk of injury.

An *odorant* or *chemosensory irritant* is a substance (often one in the same) capable of eliciting an olfactory or sensory irritation response; an *odor* is the sensation of the olfactory response. Thousands of chemicals have unique odors that allow an individual to detect their airborne presence, however the detection of an odor does not imply a medically significant exposure to the chemical. The same applies to chemosensory irritants. The following sections provide discussion on the biology of odor perception and its relationship to adverse health effects.

An odor is sensed by the human olfactory system in the nose when an interaction occurs at the molecular level between odorous chemicals and the olfactory epithelium tissue within the nasal cavity. Upon interaction, cellular changes in the olfactory sensor structures lead to a set of neural signals that travel to the brain, where interpretation of complex signals results in the detection and identification of an odor (Amoore and Hautala, 1983; Engen, 1986). Likewise, irritant chemicals trigger chemosensory structures

in the skin, eyes, mouth, nose, and upper/lower respiratory system to send neurological signals to the brain that is interpreted consciously as discomfort and/or pain (Ballantyne, 2009).

E. Role of Low-Order Odor Detection in Humans to Protect Health

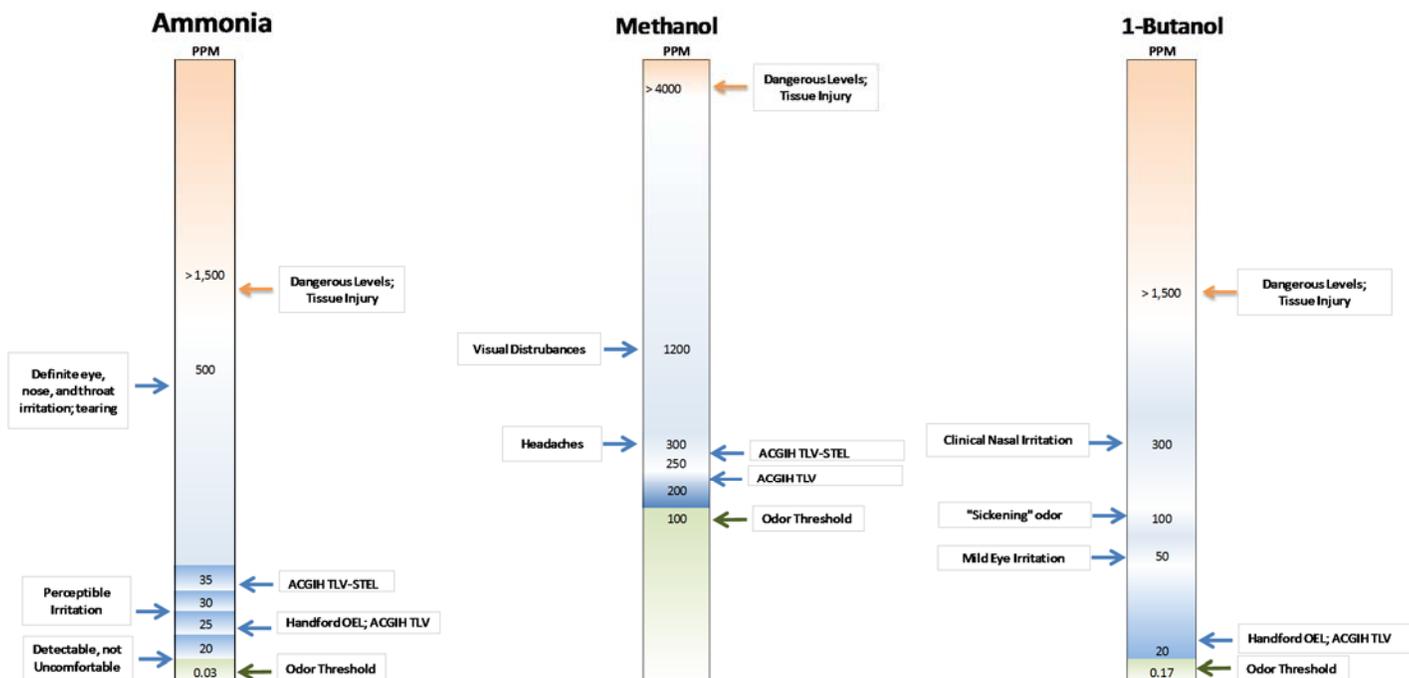
The odor threshold is the lowest airborne concentration of a chemical that can be smelled by most people. Many chemicals have an odor threshold that is lower, many times orders of magnitude, than the concentration that is hazardous. Chemosensory receptors in the body also have the ability to detect chemical irritants at airborne levels far lower than those required to cause frank irritation injuries to exposed tissues. For these chemicals, odor and sensory irritation is a good warning property to help humans avoid nearby areas where higher, and possibly dangerous, chemical levels exist (Ballantyne, 2009).

It is well recognized in the scientific and medical communities that odor perception is not an acceptable measurement of exposure severity. Greenberg et al. (2013) examined the many factors that affect olfactory perception. These include genetics gender, age, medical conditions, and alcoholism and smoking. Greenberg et al. concluded *“Attempts to verify exposure and intensity based on the report of a perceived odor is unreliable and has no useful application in legitimate exposure assessment paradigms. Detection of an odor does not imply a medically significant exposure to a toxicant and, due to subject bias the difficulty of detecting individual odorants and mixtures, may not constitute an exposure to the purported substance.”* (Greenberg et al., 2013) Thus, one must rely on actual or estimated airborne concentrations of a chemical, not odor reports, to make health and safety decisions.

F. Continuum of Effects: Odor to Irritation to Toxicity

One of the human body’s primary defense and survival characteristics is the ability to detect the presence of a chemical health hazard before a sufficient amount of that chemical makes contact with skin and susceptible internal tissues and organ systems at levels that are capable of producing damage. Specific nervous system structures residing in the eyes, nose, mouth, and throat are tasked with alerting the individual to a potential chemical danger in time for that person to take immediate action as simple as blinking, coughing, or reducing air intake or as drastic as egressing from the area as quickly as possible. Examples of the continuum of some COPC-induced effects, from triggering of odor detection to actual injury, are shown in Figure 1. These examples illustrate the vast increase in concentration over odor thresholds that must occur before actual injury is likely.

Figure 1: Continuum of Select COPC-induced effects



The ability to detect a potential hazard at a level that is similar to or not much lower than the level producing tissue injury and illness is not much of an advantage for human survival and self-preservation. Thus, the human body is capable of sustaining exposures to almost all, if not all, chemical compounds at levels triggering a recognition response and subsequent reaction or decision to mitigate the exposure. In most cases, as the exposure concentration and, sometimes, duration increases, the protective systems of the body signal increasingly more potent reactions to motivate the individual to take protective actions.

The recognition of an odor and occurrence of an instantaneous injury are not typical occurrence in biology except in the case of immediate exposure to a dangerous chemical environment. Nevertheless, some people believe that sensory detection of an irritating or unpleasant odor is itself an indicator of injury. Many people often confuse specific physiological stress responses designed to aid in escape with signs of onset of a toxic, injurious reaction.

G. Odor Recognition: Individual Variability

The capacity to detect odors varies across the population, due to multiple factors that can influence the process of olfaction. Factors that have been shown to influence odor detection include lifestyle habits (i.e., smoking/alcohol), age, health status (i.e., upper respiratory tract infections, neurodegenerative diseases), genetics and even personality (i.e., assertiveness, impulsiveness) [Doty et al., 1984; Doty et al., 1985; Doty, 1989; Hoshika et al., 1993; Hummel, 2000; Kaneda et al., 2000; Larsson et al., 2000; Lehrner et al., 1997; Meshulam et al., 1998; Murphy et al., 2003; Simchen et al., 2006].

H. Physiology of Odor-Induced Stress Reactions

Human exposures to adverse odors have been shown to cause measureable changes in autonomic nervous system functions. The autonomic nervous system is the portion of the central nervous system that controls involuntary functions of the body, such as breathing, heart rate, blood pressure, and digestive processes.

Odor and chemosensory irritation intensity have been shown to be strongly influenced by suggestion. Behavioral responses to environmental odors can vary, both over time for a single individual, and among individuals exposed to the same odor. These responses are largely dependent on the situational or contextual perspective in which odors are detected. It is the individual's cognitive evaluation of the olfactory cue that determines whether an odor is perceived as an annoyance or a pleasant experience, particularly when the sensory information sent to the brain is weak or ambiguous. Whereas individual biological factors can influence this perception, research also demonstrates that environmental effects are prominent factors underlying the variation in odor perception (Knaapila et al., 2008b), such that the connotation surrounding an odor strongly influences its intensity perception, as well as hedonic tone (i.e., pleasantness or unpleasantness of an odor) [Dalton, 1996; Andersson et al., 2013].

The detection of odors in the environment is often associated with adverse health consequences by workers and the general public. Furthermore, risk perception is often attributed to the assumption that environmental odor presence will result in a health hazard. Several studies have demonstrated that symptom complaints are a striking indicator of how readily people will attribute health problems to an ambient odor that they believe is hazardous (Dalton, 1996; Rosenkranz and Cunningham, 2003). In addition, a correlation between self-ratings of olfactory function and odor annoyance has been observed, where individuals who rate their sense of smell as better than average, tend to be more annoyed by environmental odors (Knaapila et al., 2008a).

In a study evaluating the influence of cognition and personality on odor identification ability, Larsson et al. (2000) showed that cognition and personality style were potent predictors for successful odor identification after accounting for confounders such as age, gender, and education. The study, consisting of 532 participants, showed that those who had higher scores in impulsivity and lack of assertiveness performed more poorly on odor identification tests ($p < 0.001$). Alternatively, individuals who rated higher in "*openness to experience*" identified more odors than those who rated lower in the openness to experience domain (Larsson et al., 2000).

Cognitive factors can greatly impact odor perception. O'Mahony et al. (1978) showed increases in odor reporting among television viewers who were told that a tone played on TV would create air vibrations at the same frequency of vibration of an odorous substance, and therefore, would lead to odor experiences. The same results were observed when the experiment was repeated for radio listeners. While several explanations were discussed by the study authors as possible suggestive mechanisms (i.e., criterion change by suggestion, chemosensory signal generation by suggestion, and suggestion of verbal

framework), the findings from this study indicate that suggestive power can play a strong role influencing odor perception (O'Mahony et al., 1978).

The context under which an odor is perceived affects odor perception, and this has been shown through different influences, such as the verbal labeling associated with an odor. Herz and von Clef (2001) showed that an individual's perception of the same odor varied, depending on whether or not it was given a positive label such as "*Christmas tree*" or a negative label such as "*spray disinfectant*."

In a study performed by Dalton (1996), it was shown that inter-individual variability in odor perception can result from the assumption that an odor is beneficial (i.e., derived from a natural extract), or potentially hazardous. For example, when subjects were exposed to isobornyl acetate, an odorant considered to be "*perceptually malleable*," adaptation responses varied as a result of the information given to the study subjects about the odorant prior to exposure. Subjects were exposed to a constant concentration of isobornyl acetate throughout a 20-minute period, during which subjects rated the perceived intensity of the odorant. Prior to exposure, they were told that the intensity could vary throughout the session, or could stay the same. While the concentration of the odorant was the same for all subjects, the information given about the odorant varied across the 3 experimental groups. The first group (positive bias) was told that the odorant was a natural extract from balsam trees commonly used for aromatherapy, and had been reported to have positive effects on mood and health. The second group (negative bias) was told that the odorant was an industrial solvent, which following long-term exposures had been reported to cause problems with health and cognitive function. The third group (neutral bias) was told that the odorant was a standard odorant approved for olfactory research. Results from this study demonstrated that the positive bias group showed typical adaptation to the odorant, as evidenced by a decline in perceived intensity rating over time. In contrast, halfway through the exposure, the negative bias group began rating the odor as intensifying, whereas the neutral bias group showed a final degree of adaptation to the odor that was intermediate between the negative and positive groups.

Variation in odor perception has also been shown in relation to distress level when a health risk is perceived from exposure to those odors. In a study conducted by Andersson et al. (2013), 40 nonsmoking participants were divided into high-stress and low-stress groups based on responses from completion of the Symptom Checklist-90 (SCL-90) inventory – a widely used questionnaire for the evaluation of stress symptoms. To manipulate health risk perception, subjects were told that the odorant (n-butanol) was either an industrial solvent (negative bias), or a natural extract (positive bias). The results obtained showed that high stress-type individuals who received negative bias rated odors as significantly more unpleasant than low stress-type individuals. In addition, individuals under relatively higher stress reported higher symptom intensity (eye, nose, skin, and throat irritation, nausea, etc.) than individuals in the low stress group (Andersson et al., 2013).

In a study evaluating 180 healthy individuals, Dalton (1999) demonstrated that positive, negative, and neutral bias could be reflected in the way participants scored odor and irritation intensity, as well as in the way they reported health symptoms. To create bias, test individuals were told that they would be

exposed to either natural extracts with relaxing effects (positive bias), industrial solvents (negative bias), or simply odorants used and approved for olfactory research (neutral bias). Individuals in the negative bias group consistently reported higher odor intensity values than those of the neutral or positive bias groups, and reported substantially more symptoms than the neutral or positive bias groups. Dalton (1999) concluded that people's responses to ambient odors may be determined less by the sensory qualities of the odor, and more by the context that is provided prior to exposure. Thus, there are a multitude of factors that may affect one's perception and response to an unknown or unfamiliar odor.

I. CTEH[®] Observation: Worker Odor-Induced Injuries In Light of Scientific Literature on Human Odor and Chemosensory Perception.

Whereas the detection of odors may evoke emotional responses that may be pleasant or unpleasant, depending on the individual (Croy et al., 2013; Haze et al., 2002), these responses and sensory irritation may induce a variety of involuntary systemic responses, such as very rapid changes in systolic blood pressure and heart rate, increase/decrease in gastrointestinal activity, and taste interpretation (Ballantyne, 2009; Croy et al., 2013). The role of these rapid changes as a primal defense mechanism is discussed below. However, these changes can result in symptoms including lightheadedness, headache, and breathlessness (resulting in the “going down” sensation described by some tank farm workers), as well as nausea.

It would be of great benefit for workers to have a basic, conceptual education and understanding of the principles of toxicology and health risk discussed in this section. Such an understanding as it relates to tank farm vapors would help many workers put into context the seeming inconsistencies between odor detection and sensory irritation, non-detection DRI readings, and air sampling data indicating very low levels of vapors in tank farm air. In the hundreds of discussions that CTEH[®] toxicologists and industrial hygienists have had with workers reporting odors and odor-related illnesses, conveying an understanding of these concepts has more often than not helped to allay fears of the unknown and provide the worker with sound information with which to better understand to health ramifications (or lack thereof) of the current and future odor exposure incidences.

7.0 Conclusions

CTEH[®] evaluated the technical basis of the WRPS Hanford tank farm IH program as well as its implementation. Overall, the technical basis is sound from both a toxicological and industrial hygiene standpoint. The leveraging of tank chemistry and IH data that have been collected through the years of tank farm operations has resulted in a sound strategy for determining COPCs and developing and implementing AOELs to guide in-field decision making to minimize worker exposures that would be of concern for adverse health effects. CTEH[®] believes that the current concerns related to tank vapor exposure and health impacts relate to acute, sometimes momentary exposures to airborne chemicals present at odiferous and possibly irritant levels. To date odor investigations have focused on tank farm emissions, however, a comprehensive library of odor-generating locations outside of the tank farms

related to other site remediation tasks should be compiled to aid in source identification for future complaints. Further, a set of AOELs for acute effects, primarily respiratory irritant and neurological effects, needs to be developed and introduced into the IH program in order to be responsive to short-term vapor exposures. Because of the nature of physiological odor and irritant responses in humans, particularly at non-toxic exposure concentrations, CTEH® believes that training in these basic concepts would help workers to better discriminate toxic versus non-toxic exposures, and to better interpret results from real-time and analytical air monitoring and sampling results. Specific observations and recommendations are discussed in the following sections. CTEH® has noted in this report and in Appendix A that multiple initiatives suggested by the TVAT and launched by WRPS in the past year appear to be on track to systematically improve the ability of IH workers to characterize and respond to odor-related exposure issues more effectively

7.1 Observations of what is working well (IH Vapors Implementation)

The industrial hygiene group is well integrated into the various work groups that operate inside the farms. During planning meetings, the various crafts onsite are cognizant to include the requirement that the IHTs be included as part of the workgroup. Sampling plans have been developed for the various tasks that occur within the tank farms. Sampling for a particular task is determined prior to the commencement of operations. This allows for the IHTs to have prior knowledge of the equipment and media requirements for the task at hand. Sampling data is collected and vetted by a robust quality control process. This process requires the gathering of descriptive data, (location, activities, time, date, etc) by IHTs to inform the analytical or realtime sampling results. These data are then reviewed by IHPs before being finalized in the SWIDS database. This is a time consuming activity but the value to the dataset is high and should be continued.

Individual employee job task analyses (EJTA) are in place for workers that describe the various medical surveillance programs to which each worker is required. These include physicals, and battery tests such as beryllium program monitoring. Workers interviewed seemed to be aware of the purpose of the EJTA were able to explain how it was relevant to their work and well-being.

7.2 IH Vapors Program Implementation Recommendations

A comprehensive risk assessment is one of the key steps in hazard assessment. CTEH® recommends that this process be implemented to consider at a minimum, the following information; all known hazards to the workforce, the potential health impact (both acute and chronic), the frequency or potential frequency of exposure, number of workers potentially impacted and engineering controls in place with an estimation of effectiveness. This assessment should include all CEHAs currently in place and other applicable documentation of exposure risk and then serve as the basis for revising all JHAs, CEHAs, TVIS, Similar Exposure Groups, and Sampling Plans. Because a current job hazard matrix could not be located in ISMS it was difficult to determine if all potential exposures had been considered. Therefore, a new matrix should be developed to encompass all job tasks associated with IH work and site work in general. This matrix would serve as a basis for revising the similar exposure groups. If a matrix was previously

developed, it should be communicated to the workforce through a combination of training and communications. Additionally, as the IH program continually improves, steps should be taken to ensure that the matrix is reviewed and updated to reflect those changes.

Worker education regarding odor issues also represents an area for improvement. The workforce needs to be educated as to the nature of the tank vapor odors and the measures being taken to protect them from over exposures to tank vapor chemicals. Workers should not expect an odor-free environment, and this is not the case or expectation in other industries associated with the manufacture, handling, or use of chemicals. In these industries workers rely on safety and health professionals to protect them from over exposure to chemical hazards. They trust these protective measures and are not concerned by routine odors. The workforce should be educated to understand that occasional odors from tank vapors or other sources are part of a normal industrial operation and do not automatically represent a health risk. Each Tank farm should have a specific list of COPCs and odor characteristics that are expected to be encountered on that particular farm. Only odors that do not appear on the characteristics list should be considered abnormal. These chemicals along with odor characteristics should be posted at each site and reviewed in pre-job briefings so workers know what to expect. Chemical odor sources not related to tank vapor activities (i.e., painting, porta-johns, herbicides, evaporator building, diesel generators, etc.) must also be characterized and presented to the workforce as normal parts of industrial operations that do not carry and adverse health risk.

Improvement can also be achieved through better defining roles and responsibilities within the IH program. Ownership of roles described in industrial hygiene program documents must be detailed such that the person or persons intended to manage said roles is aware of, and held accountable for, the execution of their described duties. An example of this is presented in the TFC-PLN-34, Industrial Hygiene Exposure Assessment Strategy document. This document specifies that an “*IH Program Exposure Assessment Strategy Technical Authority (IH-EAS-TA)*” be established, who according to the document, has the sole responsibility for the exposure assessment program, establishing staff competencies, qualitative assessments, predictive modelling, monitoring programs, and overseeing data quality among a total list of 14 specified responsibilities in TFC-PLN-34. In addition, the responsibility of reviewing and signing off on updated CEHA and TVIS falls to the IH-EAS-TA. CTEH® could not establish who in the WRPS organization was acting as the IH-EAS-TA.

Continual improvement is a key component of all safety and health programs. An active IH vapors program will be monitoring levels and workers to determine where additional controls are needed, if any. Data generated by this program should be assessed and fed back into the comprehensive risk assessment at least annually. This will provide confidence that the program is being continually improved as tank farm or other working conditions change.

7.3 Air Monitoring and Air Sampling Improvements

In general, all real-time and analytical sampling methods should follow conventional sampling practices and any variations must be vetted for effectiveness before being implemented. Although not recommended, if circumstances dictate real-time air monitoring practices utilizing long lengths of tubing running from inside the tank farms to the outside fence, these configurations must be vetted through practical testing and discussions with the equipment manufacturer to assure that the process is sound and that the results obtained are representative of the actual work area. At a minimum it must be determined if the pump on each type of equipment is designed for such use and testing should be established to determine the time it takes to draw a sample from the sample point all the way through to the instrument.

7.4 Vapor/Odor Exposure Education Improvements

As discussed above, odor perception lies at the heart of many of the perceived issues with the tank vapors IH program. Some members of the workforce do not have a solid conceptual understanding that detection of odors by humans often occurs at airborne chemical concentrations that are far too low to cause toxicity. Providing workers with face-to-face training of these concepts will reduce fear and stress associated with detections of odors that are unknown and have pungent or sensory irritating effects. Further training will help workers to understand why some odor events are associated with instrumentation non-detections of COPCs, and will aid in the building of trust in instrumentation results.

CTEH® recommends a comprehensive course such as AIHA Fundamentals of IH for those with no formal IH background (from Program Leader to IHTs). This provides 100 hours of technical education and creates a knowledge foundation critical to understanding the science of IH.

The concept of “*exposed but protected*”, needs to be explained to the contractor workforce in detail so there is a fundamental understanding of the Assigned Protection Factors for respiratory protection classifications. The use of supplied air, including SCBA, implies that there is an expectation of exposure above and beyond what is legally acceptable for a worker without respiratory protection. The detection of a chemical at an action level should be expected when working in SCBA and not an indication that the work site needs to be evacuated. Action levels are used to indicate the opportunity to take action for individuals who have no protection from further exposure. A worker can safely work for more than eight hours in an environment where a chemical concentration exceeds an action level but remains below the permissible exposure level.

7.5 TF-AOP-015 Improvements

The Abnormal Operating Procedure (TF-AOP-015) process needs to be revised to remove implication that an odor is abnormal and that actions need to be taken when odors are encountered. Even though the document currently attempts to qualify odors of concern as “*stronger than normal*,” it is entirely too subjective and leads to confusion in the workforce.

Reporting the result of a TF-AOP-015 investigation back to the workforce is reported to take as long as 30 days or more. This breeds distrust, as the workers think they have been impacted by the event and are not getting results in a timely fashion. Consider creating a short event report that is quickly published and then proceed with whatever investigation is required.

7.6 SCBA Use Reassessment

WRPS has a duty to ensure that PPE used by workers and contractors does not over protect, or protect above and beyond an exposure, unnecessarily, as other hazards can be created for the worker by the use of the PPE itself. SCBA usage can contribute to serious ergonomic issues for the wearer, contribute to slips, trips and falls, and exacerbate injuries from falling. PPE can also present serious health hazards in the form of an added thermal burden on the body (heat stress) and an added burden on the respiratory system.

There is no indication that surface tank farm work can result in a low oxygen conditions and therefore an acceptable response to a potentially hazardous vapor event would be for each worker to carry a single use disposable escape hood rated for high hazard events. That would permit the workers time to get up wind of any potential threat. The use of SCBA should be reserved for line breaking, breather filter replacement, opening of vaults or cabinets, or any other opportunity for tank vapors to accumulate or be released in an uncontrolled manner in the immediate breathing zone of a worker. Vapor control zones should continue to be utilized to minimize exposure to workers not wearing respiratory protection.

7.7 IHT Education Improvements

Education forms the foundation for the competence in which IH technicians conduct their job duties. Unfortunately, IHTs represent the least trained and competent group for the work they are asked to perform. The education requirement is low and has provisions for being waived, via TFC-BSM-TQ-STD-01 and TFC-BSM-TQ-MGT-C-01. Employment as an IHT should require an intensive and on-going training, mentoring, and oversight process following hiring. Education requirements should be maintained to prevent excessive retraining of personnel. The expectation is not that the IHTs have the same level of educational background as an IHP, but rather a consistent and thorough level of technical ability. Consideration should be made to having an annual recertification process for IHTs that is comparable to the RADCON program to ensure the maintenance of the knowledge base.

7.8 Need for Worker Training on Select Toxicology, Odor, and Injury Concepts Germane to the Current Issues and Hanford

U.S. workers and members of the general public often tend to not make the distinction between a health hazard and a health risk. Many people mistakenly believe that the mere presence of a hazard will inevitably result in an injury. CTEH® believes that an understanding by tank farm workers of basic toxicological odor biology principles discussed in this report may help to put into proper perspective their experiences with detected or “*felt*” odors, data provided by available air monitoring instrumentation, and

air levels that truly represent risk of injury. Exposures at AOEL levels or lower should be considered safe for the entire workforce; however, exceedances of an AOEL, even by an order of magnitude in many cases, is not and should not be suggestive of a likely risk for injury.

The recognition of an odor and occurrence of an instantaneous injury are not typical in biology except in the case of immediate exposure to a dangerous, high-concentration chemical environment. Many people often confuse specific physiological stress responses, designed to aid in escape, with signs of onset of a toxic, injurious reaction. The role of these rapid changes as a primal defense mechanism is discussed in this report. Human exposure to adverse odors has been shown to cause measureable changes in breathing, heart rate, blood pressure, and digestive processes. However, these changes can result in symptoms including lightheadedness, headache, and breathlessness, as well as nausea and, in some cases, nose bleeds. Such understanding of these concepts as they relate to tank farm vapors would likely put into context the seeming inconsistencies between odor detection and sensory irritation. In the thousands of discussions that CTEH® toxicologists and industrial hygienists have had with workers reporting odors and odor-related illnesses in various industries, understanding of these concepts has more often than not helped to allay fears of the unknown and provide the worker with sound information with which to better understand the health ramifications of the current and future odor exposure incidences.

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Appendix A

TVAT Technical Issues Matrix with CTEH® Assessment

| TVAT RECOMMENDATION | TVAT RECOMMENDATION | CTEH® OBSERVATIONS | SUPPORTING DOCUMENTATION |
|---------------------|---|--|---|
| TVAT 1 – SC1 | Develop a prioritized program to sample and characterize tank head space composition and stratification during quiescent as well as disturbed conditions. | Several studies involving numerical modeling (4) and actual observation (4), including use of tracer gases, have been performed and show that the headspace is in constant convection and rapidly equilibrates, making headspace gradients negligible. | PNNL-11391 PNNL-11640 FAI/95-63 PNNL-11640 |
| TVAT 3 – SC3 | Implement technologies to assess fugitive sources of emissions that are not connected to tank head spaces and characterize the emissions for each non-head space fugitive source. | <ul style="list-style-type: none"> CTEH® agrees that non-tank vapor fugitive gas/odor sources should be systematically characterized and sampled to create a “library” of chemical signatures associated with fugitive sources. This can be accomplished in part with the analytical capabilities of the RJ Lee van and its PCR-MS | WRPS VMDS presentation TFC-ESHQ-S IH-C-48 |
| TVAT 4 – SC4 | Identify and implement new technologies to detect, locate and quantify fugitive and episodic releases. | CTEH® agrees and has observed that WRPS has developed and implemented (on a pilot scale) a system of new detection technologies capable of monitoring movement into, out of, and across a tank farm. | WRPS VMDS presentation |
| TVAT 5 – SC5 | Identify and implement new technologies to quantify stack and vent emissions with suitable local alarms so that workers can respond in a timely fashion. | | |
| TVAT 6 – EA1 | Continue the development and expedite deployment of new techniques for real-time response and appropriate sampling for short duration intermittent releases. | | |
| TVAT 8 – EA3 | Use modeling, including computational fluid dynamics methods, to determine the potential locations, conditions, and next steps in attempting to measure sporadic exposure events. | WRPS is currently generating data for tank vapor and other fugitive emission movement across tank farms; PNNL is developing CFD modeling capability to simulate such conditions. | PNNL-25533 (DRAFT) |
| TVAT 9 – DR1 | Conduct an additional review and re-prioritization of COPCs under tank-disturbing conditions to provide adequate emission characterizations, OEL development, and worker exposure surveillance. | PNNL HPP group is developing a system accept incoming tank headspace chemical data and periodically and systematically evaluate it for consideration in revising the COPC list. | Meetings with HPP scientists and managers |

| TVAT RECOMMENDATION | TVAT RECOMMENDATION | CTEH® OBSERVATIONS | SUPPORTING DOCUMENTATION |
|---------------------|---|--|--|
| TVAT 10 – DR2 | Conduct a rigorous review of the COPC list to ensure it is current, and develop a process to document the mechanisms used to ensure COPC updates and the basis for changes in the COPC list over time. | PNNL HPP group is developing a system accept incoming tank headspace chemical data and periodically and systematically evaluate it for consideration in revising the COPC list. | Meetings with HPP scientists and managers |
| TVAT 11 – DR3 | Conduct additional evaluations of COPC toxicological studies to provide insight into the sensory and pathophysiological irritation response, including the role of mixture interactions and the potential need for additional toxicological evaluation. | <ul style="list-style-type: none"> • CTEH® agrees that these alternative acute effects need to be identified for all of the COPCs (or valid surrogates). • PNNL HPP group is working on this. | Meetings with HPP scientists and managers PNNL SOW Req # 284283 |
| TVAT 12 – DR4 | Perform a comprehensive evaluation of acute odor thresholds and toxicity effect levels for each COPC to facilitate the establishment of action levels based upon the relationship between odor and toxicity thresholds. | <ul style="list-style-type: none"> • CTEH® agrees. PNNL is adding odor threshold data to their developing database. • Odor threshold data from the old Vaportox database is being integrated into the PNNL COPC database. | Meetings with HPP scientists and managers |
| TVAT 13 – DR5 | Continue to evaluate COPC OELs within the context of observed symptomatology versus 10% of the irritations thresholds and develop a "new" acute OEL list. | <ul style="list-style-type: none"> • CTEH® agrees that OELs representing acute effects (OEL-C) need to be developed. • PNNL is in the process of developing these new OELs in FY17. | Meetings with HPP scientists and managers PNNL SOW Req # 284283 |
| TVAT 14 – DR6 | Maintain a robust health surveillance program that follows up with exposed workers to evaluate short- and long-term consequences from vapor exposures. | <ul style="list-style-type: none"> • CTEH® agrees that follow-up is important to get workers clear and useful information to help them understand the basis of short-term effects that they may have experienced, and long-term effect, if any. • Follow-up may be in the form of materials explaining possible exposure levels in the context of actual toxic exposure levels and relative to common consumer products exposures. | Not Applicable |

| TVAT RECOMMENDATION | TVAT RECOMMENDATION | CTEH® OBSERVATIONS | SUPPORTING DOCUMENTATION |
|---------------------|---|---|--|
| TVAT 16 – DR8 | Develop an overall IH strategy for aerosol evaluations that focus on analytical quantifications, the evaluation of chemical aerosols for inclusion in the COPC list, as well as the establishment of appropriate aerosol OELs. | CTEH® agrees that continued interaction between WRPS and PNNL should continue to leverage the toxicological expertise already present at the laboratory. | Meetings with HPP scientists and managers PNNL SOW Req # 284283 |
| TVAT 18 – RCH1 | Identify an Occupational Exposure Limit – Ceiling Limit – (OEL-C) for each analyte in Hanford tank head spaces. | <ul style="list-style-type: none"> CTEH® agrees that an OEL-C should be derived for each COPC. PNNL is pursuing this issue in FY2017. | Meetings with HPP scientists and managers PNNL SOW Req # 284283 |
| TVAT 19 – RCH2 | Classify and conduct toxicological testing on a reasonable number of distinct types of Hanford tank head space vapors (e.g., potential classes of tank vapor types such as ammonia rich, ammonia poor, and nitrosamine rich). | CTEH® agrees that using acute OEL-C values for individual components of mixtures will provide useful information for protecting against mixtures irritant effects from potential mixtures. | Not Applicable |
| TVAT 20 – RCH3 | Use the OEL-C from analysis or subsequent toxicological testing to characterize the hazard index and risk from the tank vapor mixtures. | <ul style="list-style-type: none"> The IH Technical Basis document already addresses the grouping of hydrocarbon mixture concentrations for comparison to an OEL based on petroleum stream OELs. Once OEL-C values are derived, COPCs with irritant properties may be treated as additive for irritancy (see response to RCH2 above). | IH Technical Basis, Section 5.3.2 and Appendix C2.3.2 |
| TVAT 21 – RCH4a | (Chronic) The WRPS IH program has in place procedures for evaluating chronic chemical exposures [based on Time Weighted Average (TWA)]; it is recommended that more periodic follow-up monitoring be conducted and documented to provide needed data for the industrial hygienist to verify that worker chronic exposures have not changed with time. | Data for TWA exposure concentrations continue to be collected and are useful for examining chronic health risks. | TFC-ESHQ-S IH-C-48 |

| TVAT RECOMMENDATION | TVAT RECOMMENDATION | CTEH® OBSERVATIONS | SUPPORTING DOCUMENTATION |
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| TVAT 22 – RCH4b | (Acute) Transient vapor/gas exposures (i.e., high dose rate) are substantially greater than what is currently measured as a TWA; alternative strategies for evaluating transient plume-like vapor exposures are recommended and adherence to excursion limit principles must be implemented (5 times OEL). | <ul style="list-style-type: none"> • CTEH® has not seen data to suggest that exposures “substantially greater than what is currently measured as a TWA” actually exist. • The new technologies being implemented under the VMDS program should aid in confirming the actual existence of vapor plumes. | WRPS VMDS presentation |
| TVAT 23 – RCH4c | (Medical Surveillance) Routine medical surveillance is a key workplace evaluation tool needed to predict health impairment from vapor exposures; appropriately designed epidemiology studies focused on tank farm workers are recommended to evaluate the potential long-term health consequences. | <ul style="list-style-type: none"> • The usefulness of medical surveillance related to tank vapor exposure is questionable. • Exposure data from VMDS technologies would aid in determining the type, if any of medical surveillance tools that should be brought to bear on odor-related health complaints. | Not Applicable |
| TVAT 24 – RM1a-d | Provide and manage IH professional and technician staffing levels to properly characterize and assess worker vapor exposure in the tank farms, and properly recommend and evaluate the effectiveness of work practices, PPE and engineering controls. | WRPS has increased staffing IH staffing levels. | |
| TVAT 32 – RM5 | Redefine unacceptable chemical exposure risk to include short-term, episodic exposure to chemicals that can result in adverse health impacts. | This recommendation is addressed already in TVAT 13 – DR5. | Meetings with HPP scientists and managers PNNL SOW Req # 284283 |
| TVAT 33 – RM6 | Investigate and implement best available technologies to detect and control vapor plumes from fugitive sources as well as from vents and stacks. | New technologies to detect and characterize the existence and nature of vapor plumes are already deployed on a pilot study scale | WRPS VMDS presentation |
| TVAT 34 – RM7a | Establish a more effective methodology for designating Vapor Control Zones (VCZs) and Vapor Reduction Zones (VRZs). | Data from newly deployed monitoring technology should be used to inform the steps for delineating VCZs and VRZs | |

| TVAT RECOMMENDATION | TVAT RECOMMENDATION | CTEH® OBSERVATIONS | SUPPORTING DOCUMENTATION |
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| TVAT 35 – RM7b | Confirm that air-purifying respiratory protective equipment is effective in reducing exposure to tank vapors below acceptable levels. | There exists a CVST task group that is evaluating new APR technologies and are communicating their findings to the CVST. | CVST meeting presentations |
| TVAT 36 – RM8 | Modify the medical case evaluation process and reporting procedures to recognize the appropriate uses and limitations of the available monitoring data and other potential exposure information when evaluations are made regarding vapor exposures. | <p>Issues related to these TVAT recommendations are founded on lines of communication within WRPS management and workers.</p> <p>Working to educate the workforce, starting with the IHTs, on principles of the exposure and toxicology dose-response continuum from odor to toxicity, implications of real-time instrument detection limits of detection, and status of the VMDS technologies should validate WRPS management’s commitment to worker safety</p> | Not Applicable |
| TVAT 37 – RM9 | Verify that all programs associated with vapor controls are properly vetted, evaluated, communicated and tracked to ensure timely completion. | | |
| TVAT 38 – RM10 | All levels of line management demonstrate that they are committed to reducing the potential for tank farm vapors releases and continuously improving management systems to assure all workers are properly protected. | | |
| TVAT 39 – RC1 | Develop more routine and transparent communications, which offer unsolicited information to the Hanford Challenge, Hanford Concern’s Council, and other interested community groups regarding potential health impacts, health and safety risks, and WRPS/DOE efforts to reduce risk to employees and the community. | <ul style="list-style-type: none"> WRPS already provides useful information to the community via the HAB, which has representation from multiple community stakeholders. Efforts are ongoing to improve the publically-accessible Hanford Vapors website in terms of content and functionality. | Not applicable |

| TVAT RECOMMENDATION | TVAT RECOMMENDATION | CTEH® OBSERVATIONS | SUPPORTING DOCUMENTATION |
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| TVAT 40 – RC2 | Improve the EJTA process to include opportunities for worker engagement and buy-in into the process and protective measures assuring the health and safety of the worker. | WRPS has already addressed this process. | CVST meeting presentations |
| TVAT 41 – RC3 | Improve the degree of employee involvement in and ultimate acceptance of all teams and programs that are associated with tank farm vapor issues (e.g., PERs, CVST). | CTEH® believes that personnel training in general concepts of dose-response and the continuum of effects from odor detection to toxicity will help tank farm employees and IHPs/IHTs better understand the health impacts. | See Sections 6.4 and 6.5 of this report |
| TVAT 42 – RC4 | Revise the content of the employee monitoring notification letters to include more relevant information regarding the capabilities and limitations of technology used to collect and analyze samples, which should include clear definitions for concepts such as “ND” vs. “<LOQ” vs. “<RQL.” | CTEH® agrees that adding elements to the notification letters to bring perspective to the reported values, including non-detects, would provide a stronger foundation for conclusions regarding health impacts. | |
| TVAT 43 – RC5 | Establish a greater IH technician and professional presence in the tank farms and undergo specific risk communication training and improve their ability to deliver effective risk communications to employees. | <ul style="list-style-type: none"> • WRPS has increased the number of IH personnel working in the tank farm areas. • CTEH® believes that dose-response-relative risk training of IHPs/IHTs would provide needed skills and knowledge to better communicate significant or insignificant risks to the tank farm workers. | See Sections 6.4 and 6.5 of this report |
| TVAT 44 – RC6 | Perform an alternatives assessment for the current Shift Office Event Notification (SOEN) process to identify other methods to assure that all workers potentially impacted by vapor events (i.e., WRPS, MSA, visitors) are immediately alerted of a vapor event and understand what mitigating actions they must take to avoid possible health or safety impacts | <ul style="list-style-type: none"> • WRPS has begun the process of evaluating different options for communication of events related to significant vapor presence in the tank farm air. • CTEH® agrees that WRPS should consider the non-tank fugitive odors data as it is developed to inform the need and level of protective measures if any. | TF-AOP-015 |

| TVAT RECOMMENDATION | TVAT RECOMMENDATION | CTEH® OBSERVATIONS | SUPPORTING DOCUMENTATION |
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| RC8 | Communicate in a timely fashion to all employees the results of incident investigations, including a description of event, results of any samples taken, lessons learned, and corrective actions planned and completed. | <ul style="list-style-type: none"> • CTEH® agrees that communication of air monitoring and sampling results related to a suspected vapor release is a vitally important step in the vapor/odor evaluation process. • Communication of these data should be presented with data for the full spectrum of biological effects (sensory detection, odor detection, OEL (acute), and toxic effects level). | Not applicable |