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Independent Toxicological Review of Vapor Industrial Hygiene Program Chemicals of Potential Concern (COPC)

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SIGNATURE PAGE

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This report has been compiled by and approved by the Independent Toxicology Panel (ITP) members as indicated by their dated signatures below:

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Executive Summary:

The toxicology panel reviewed the methodology used by CH2M HILL and PNNL to develop the COPC List for CH2M HILL. Overall the methodology used to develop this list was appropriate and relevant. Valid sampling and analysis protocols for identifying chemicals in the tank headspace were established as well as tank identification. Recommendations for prioritization of chemicals based on toxicological characteristics and prevalence are provided.

While we are aware that there are a number of chemicals in the headspace that are potentially more harmful than others, the issue is not their presence but their potential to harm workers. Many of the chemicals identified may be potentially harmful, but are present at concentrations that would not be harmful. By the same token many chemicals are inherently less harmful, but occur at concentrations near occupational exposure limits (OEL). The degree of concern for each is the ratio of maximum headspace concentration to the lowest occupational exposure limit. Absolute concentration of a chemical in the headspace is less significant than the concentration in relation to the OEL. Recommendations are provided to establish an Industrial Hygiene Vapor Monitoring Program based upon the categorization and prioritization of carcinogens and non-carcinogens. The panel expressed all concentrations of chemicals in ppm units as a matter of convenience. When relevant OEL values were found in mg/m3 units they were converted to ppm. Chemicals considered to be “known” carcinogens or “probable” carcinogens by IARC or other regulatory/guidance agencies were given highest priorities for workspace sampling. “Possible” carcinogens were given a lower priority and will be examined as a function of their concentration and prevalence in a manner similar to the evaluation of non-carcinogens. Non-carcinogens have been prioritized for monitoring based upon the ratio of maximum concentration in ppm (MC) to Lowest Occupational Exposure Guideline (LOEG), and the prevalence in the tank farms This list of prioritized chemicals (that is, the known and probable carcinogens and non-carcinogens above 0.1 MC/LOEG and seen in > 10% of tanks) will require area and personal monitoring. Chemicals that are related to the petroleum hydrocarbon streams can be consolidated and separately evaluated. Chemicals that are listed as having an invalid CAS ending with “m” can be evaluated using the main chemical component of that mixture as the chemical species. All other mixtures with invalid CAS numbers are to be considered for evaluation and monitoring at a future date. Chemicals found only in one tank or only once in a tank and in low concentrations should be considered lower risk chemicals and prioritized for evaluation and monitoring at a future date, based on detection in more tanks and/or at higher concentrations. Chemicals that have no developed OEL must be evaluated and an OEL developed for each chemical using applicable methods of risk analysis. In the absence of published OEL values, experienced risk assessors, using existing toxicological data, conservative uncertainty factors and expert judgment can develop practical OEL values which will offer protection to the workers while also assuaging worker concerns regarding exposure and health effects.

Chemical concentrations in the tank headspace are not the concentrations that would be expected in the workspace outside the tank. However, chemicals identified in the headspace could be assumed to be present outside the tank if a release were to occur. In order to establish an effective Industrial Hygiene Monitoring program the chemicals escaping from the tank, duration of the escape, concentration of the chemicals that have escaped, and, the movement of the chemical geographically outside the tank must be determined. A three pronged monitoring program utilizing personal samples, detectors located at points where chemicals emanate from the tanks, and samplers strategically located about the workspace can provide a picture of worker probable exposure during the work shift. Provision should be made for long term sampling which can detect the presence of chemicals which because they are present in low concentrations will not be observed in short term sampling efforts. The combined determinations of vapor concentrations, the profile of chemicals in the air, the duration of exposure and the description of personnel work activity patterns will allow the development of a best practices Industrial Hygiene monitoring program. Once worker exposure has been appropriately characterized, decisions can be made regarding modification of PPE requirements. The current PPE requirement may be overly conservative since it was not based upon scientific data. CH2M HILL must make the decision regarding "appropriately characterized" based upon statistical analysis of the data and professional judgment.

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INTRODUCTION

1. Charge to the Panel:

This report is written under CH2M HILL contracts established individually with panel members using identical scopes of work titled "Independent Toxicological Review of Vapor Industrial Hygiene Program Chemicals of Potential Concern (COPC)."

The charge to the Independent Toxicological Review Panel was to review the COPC development methodology, recommend improvements to the development methodology, evaluate reasonableness of risks for basing the Industrial Hygiene program on the COPC List, review monitoring and PPE strategies, benchmark CH2M HILL methodology for COPC development and results against industry standards, and make recommendations for addressing chemicals with no occupational exposure limits.

2. Background:

In response to a report produced by the Government Accountability Program (GAP) addressing worker concerns at the Hanford Tank Farms, the Department of Energy (DOE) conducted an investigation of the allegations cited in the GAP report. The Office of Independent Oversight and Performance Assurance (OA) report repudiated the majority of allegations, but substantiated a number of deficiencies that CH2M HILL Group (CHG) Richland, Washington seeks to address. Foremost among these expressed concerns in the OA report is the need for a consolidated listing of total chemicals found in the tank farms that could be found in a vapor release. The OA report recommended that Department of Energy Office of River Protection (ORP) and/or CH2M HILL "develop a comprehensive strategy for characterization of tank vapor headspaces that can be used as a living document for developing industrial hygiene exposure assessments and sampling and monitoring plans". CH2M HILL engaged the Pacific Northwest National Laboratory (PNNL) to characterize the tank contents and provide a list of COPC. This list was to be delineated in terms of a number of criteria, i.e., concentration in the headspace, valid CAS number, established toxicological reference values, presence in the TWINS characterization database, and others. After characterization of the headspace, the OA report recommended that ORP and/or CH2M HILL "periodically perform toxicological evaluation of chemicals identified in headspaces", "implement specific, conservative worker exposure limits for vapors to include adopting or establishing local control limits … that are well below existing recommended or regulatory limits where such limits exist … establish local control limits (e.g., limits of detection) where regulatory or recommended limits do not exist and it is practical to do so". CH2M HILL engaged this independent toxicology panel to conduct a toxicological review of the vapor Industrial Hygiene Program chemicals of potential concern.

The CH2M HILL Hanford Tank Farms are located in Richland, Washington. The site occupies approximately 586 square miles in this southeastern part of Washington State and is juxtaposed to the Columbia River. The site contains 177 underground storage tanks: 149 single-shell tanks (SST) and 28 double-shell tanks (DST). These 177 underground tanks are organized into two geographically separated tank farms, designated 200 East and 200 West Areas. The carbon steel tanks have storage capacities ranging from 50,000 gallons to one million gallons and the number of tanks contained in each geographic area is approximately equal. These underground tanks store waste from the various processes that were conducted or are being conducted at the site. There are approximately 53 million gallons of radioactive waste stored in these tanks that resulted from plutonium and uranium processes carried out during the period of 1943-1989; production processes ceased in 1989. Tanks contain a mixture of both solid and liquid waste materials (saltcake and sludge respectively), which are radioactive and chemically toxic. An underground piping system that allows tank-to-tank connections and farm-to-farm connections connects tanks. All tanks are ventilated to prevent gas build-up from reaching an explosive level. The SSTs are passively ventilated through HEPA filters on a tank breather while the DSTs are actively ventilated. DSTs are also ventilated through a HEPA filter, but unlike the SSTs, both the headspace and the annulus are ventilated. These ventilation points represent vapor escape points and present a potential exposure concern to workers.

The concern lies with the SSTs, which are older tanks dating from the WWII period: 64 were constructed during WWII; 42 during the period 1947-1949; 18 during the period 1950-1952; 21 during the period 1953-1955; and, the last four SSTs were built during the period 1963-1964. The 28 DSTs were constructed post-1964. A major concern is the possibility of leakage from the SSTs. It has been estimated that approximately 66 of the SSTs have leaked; 55,000 gallons of liquid escaped in 1956 and approximately 115,000 gallons in 1973. The result of leaking tanks is primarily an environmental concern. The tanks leak underground because of the deterioration of the tank walls releasing the tank contents to the surrounding soil. The chemical vapors contained in the headspace of each tank are of particular concern regarding worker exposure. The release of these vapors from various point sources (e.g. pits, instrument penetrations, ventilation equipment, etc.) provides avenues of potential exposure to the tank farm workers.

The current operational mission of the CH2M HILL Tank Farms is to process the waste contained in the tanks. The overall process is to retrieve the SST tank waste to the DST system and ultimately move the waste through the process of vitrification to produced glass logs that can then be shipped to Yucca Mountain, Nevada for storage. The emptied SSTs will then be closed. Throughout the entire process of working in the vicinity of these tanks, concern is given to protecting the worker's health. External radiation, radiological contamination, hazardous chemicals and physical hazards exemplify hazards during this closure process.

3. Tank Characterization

PNNL scientists conducted tank headspace characterization. Data used by the PNNL scientists were obtained from the Tank Characterization Database (TCD) developed and maintained by PNNL. This database contains headspace characterization data from 1992 to current day. Data from only 109 SSTs are included in the TCD; however, each SST farm and all major waste streams are represented. Stock and Huckaby (1, 2) reported the results of vapors found in the headspaces of single-shell waste tanks.

Samples from the headspaces were collected either with triple sorbent traps (TSTs) or SUMMA canisters. Samples were analyzed using robust gas chromatograph/mass spectrometer (GC/MS) systems; 1230 tank headspace samples were analyzed using this technique. Approximately 41,000 results are recorded in the TCD using the GC/MS method for organic vapor analysis. Of the 1230 compounds identified in the headspaces of the total number of tanks sample, 445 compounds have a maximum concentration of less than 0.025 mg/m3. Based on chemical classification Stock and Huckaby identified the following organic and inorganic compounds: alkanes (200 compounds); cycloalkanes (150 compounds); alkenes (170 compounds); alkadienes; alkynes; arenes; halogen compounds; alcohols, phenols, and ethers (120 compounds); aldehydes; ketones (120 compounds); acids; esters; nitriles; amines; amides; nitroso compounds; nitro compounds; heterocycles (100 compounds); sulfur-containing compounds; silicon compounds; miscellaneous other organic compounds. Inorganic compounds identified included: hydrogen, carbon monoxide, carbon dioxide, nitrous oxide, nitric oxide, nitrogen dioxide, ammonia, sulfur oxides, carbonyl sulfide, and, carbon disulfide. In addition to the compounds identified by Stock and Huckaby, subsequent sampling of headspaces has revealed the presence of mercury, dimethyl mercury and formaldehyde. The Stock and Huckaby reports display results as follows: chemical compound, total number of observations, maximum concentration in mg/m3, MW, maximum concentration in ppbv, tank with maximum concentration, and TWINS2 (CAS) Number. Of pertinent note is that of the 1230 identified compounds, 553 of these compounds were observed only once.

B. Areas of Concern Addressed

1. Evaluation of Methodology for selecting the universe of chemicals

Without a doubt, CH2M HILL (CHG) has devoted considerable time, effort and expertise in developing and validating a methodology for characterizing the chemical composition of the potential toxic vapor associated with Hanford's underground tanks. These tanks store both liquid and solid waste. Such waste is composed of not only radioactive material but also contains known toxic chemicals. Several sources of the toxic chemicals include waste from weapons production, chemical products used in tank processes and substances from facility maintenance. By monitoring the headspace, CH2M HILL can characterize, identify and quantify those chemicals which are volatile enough to migrate to the headspace within each of the tanks. In addition, some source monitoring in the area and personal monitoring has also been conducted. CH2M HILL recognizes that the chemical composition within these tanks is complex. This is due not only to the wide variety of chemicals added to the tanks, but also because of the creation of new chemical compounds that is continually occurring in these tanks. Because of the dynamic chemical interaction within these tanks, they were designed with an adequate headspace for evolving gases. The tanks also require a ventilating system for the accumulating gases. Single shell tanks are passively ventilated while double shell tanks are actively ventilated. Human exposure could result when tank vapors are released from the tanks'ventilation systems, tank monitoring equipment and any other open system. Therefore, it is difficult to clearly identify potential health risks from exposure to such a mixture of tank vapors. In an effort to better identify and understand the potential health risks, CH2M HILL has developed a methodology for selecting the universe of chemicals using its "toxicological review criteria for identifying chemicals of potential concern" (COPC).

IDENTIFICATION OF VAPORS IN HEADSPACE: A strength of the COPC methodology is that CH2M HILL uses well established and valid means (GC/MS) for monitoring the chemicals in the headspace. Through COPC, CH2M HILL has been able to classify the chemicals into various categories of toxicological concern for inhalation occupational exposure. This database is of particular significance in: 1) identifying and classifying 1728 chemicals of potential concern (COPC) as target compounds; 2) providing an historical record of possible exposure levels for workers; 3) ensuring compliance with exposure guidelines; 4) evaluating and comparing exposure data in different work areas; 5) ranking the various tanks according to COPC; and 6) assessing the effectiveness of controls. Such a database is critical for supporting industrial hygiene/medical team efforts by documenting the maximum concentration at which individuals may have been potentially exposed.

USE OF VAPOR CHARACTERIZATION OF HEADSPACE FOR IDENTIFYING COPC:

1. CH2M HILL recognizes that the hundreds of chemicals identified in the headspace can be expected to be released or vented from the tanks and into the outside area surrounding the tanks. This represents a potential source of chemical exposure to workers, and is of primary concern to CH2M HILL.

Since the majority of the tanks are passively vented, the vapor releases are unpredictable. To accurately assess worker's potential exposure requires reliable human exposure data using recognized exposure methodologies. CH2M HILL's methodology in testing for chemicals in the headspace and subsequent classification appears to be well thought out and scientifically defensible. While the analysis of the tank vapor concentrations contained in the headspace provides an historical record for the Tank Waste Information Network Systems (TWINS) database (3), the use of such data to estimate human exposure emanating from the headspace may not be directly extrapolated. Headspace, source and personal monitoring should be performed especially when the tanks are being disturbed, possibly increasing or changing the chemical composition/concentration of the escaped vapors. Real-time personal exposure data should use sampling and analytical methods approved by NIOSH, OSHA or another validated method. Results of personal exposure assessment should be communicated to employees as well as to management. Personal exposure monitoring data can be compared to "OEL", when available, in order to determine compliance. One would expect that the area airborne concentrations would be less than the concentrations found in the headspace. Source monitoring can be of value in establishing or confirming emissions from areas where emissions could potentially expose workers.

Other recommendations for defining/improving exposure assessment can be found in this report

2. Chemicals listed as COPC include those compounds identified in tank headspace, some of which could have potentially adverse health effects. While CH2M HILL documents many of the chemicals listed, some of these chemicals that appear on the list seem unlikely to have been actually used. Indeed, one could infer that they might have been added to the list without clear identification of the specific chemical in the headspace. Improving the validity of the COPC list can be accomplished by crosschecking the chemical list with the original inventory. When the source of chemicals is in question, attempts should be made to determine if the material could result from substances used to maintain equipment (asbestos gaskets, lead shielding, paint, etc) or whether the chemistry indicates that they could have been formed "in situ". If no reasonable source can be found, arguably, such chemicals should be deleted from the list. Furthermore, in some cases, it appears that some chemicals were included on the COPC list merely because they appear on the State of California Air Toxics List. It seems that the chemicals selected from the California Air Toxics List were chosen as examples of the types of toxic substances that could be present in the atmosphere and have little or no

relevance to samples identified from headspace sampling or from any source or personal monitoring activities.

3. In determining human risk assessment of vapors and gases the proper unit of exposure should be expressed as ppm or ppb, not mg/m^3.

2. CH2M Hill Identification of Chemicals in Tank Headspace

The overall goal of this project was to categorize and develop a prioritized list of COPC from the activities at the Hanford Tank Farm. Chemicals to be considered are those that comprise the potential tank vapor emissions surrounding the tank farm workers. PNNL scientists characterized the tank headspace. Characterization included identifying chemicals present by GC/MS. After the headspace characterization was completed the list of chemicals present was used to develop the COPC list. This list included not only those chemicals identified in the headspace but also chemicals identified from the Data Quality Objective (DQO) Process, and a list of anticipated one- and two-carbon compounds. A list of 1728 compounds was provided to PNNL for development into the COPC list. PNNL toxicologists developed a methodology for identifying chemicals with the goal of classification of tank vapor chemicals into categories of toxicological concern for inhalation occupational exposures. Consequently, three major categories of chemicals were identified.

Chemicals with highest priority have valid CAS numbers, available peer reviewed occupational exposure reference values (PEL, TLV, REL, STEL, RfC, MRL, others), and have a measured concentration in the Tank Waste Information System (TWINS) database or have been identified as probably present based on tank waste chemistry. A valid CAS number refers to the chemicals that have CAS numbers defined by Chemical Abstract Service. A comparison was made between the measured concentration in the headspace and one or more occupational exposure reference values. The highest recorded headspace vapor concentration is equal to the maximum vapor concentration at 25 C. The vapor concentration was compared to the reference values based upon DOE G 440.1-3. 03-30-98 (Implementation Guide for Use with DOE Order 440.1: Occupational Exposure Assessment) guidance. This guidance states: “Usually, an ACL (administrative control limit) is set to one-tenth or possibly one-fourth the OEL when monitoring is initiated or when there are not yet sufficient data to generate a statistically valid exposure profile. If, in initial monitoring, the ACL is not exceeded, this is an indication that the actual exposures are acceptable with respect to the OEL and additional exposure monitoring many not be needed. .... Based on statistics, the probability of exceeding the OEL is less than 5% if initial, random “measured” exposures are less than one-tenth the OEL and if exposures are not highly variable.” (4) Therefore, based on this guidance a comparison was made to determine if the maximum vapor concentration of the chemical in the headspace at 25^o C was greater than 10% of the occupational exposure reference values. This comparison was carried out with the following occupational exposure reference values:

1) PEL (Permissible Exposure Limit), 8-hr TWA (time-weighted average)
2) PEL, acceptable ceiling concentration
3) PEL, maximum peak, 5 minutes in 4 hours
4) TLV (threshold limit value)
5) REL TWA, (recommended exposure limits based on 10 hour TWA)
6) STEL (short term exposure limit), 15 minute
7) Others, OEL (occupational exposure limit)-type criteria
8) RfC (reference concentration for inhalation)
9) MRLs (minimal risk level)

3. Rationale for prioritizing chemicals

The derivation of the lists of carcinogens and non-carcinogens in Table 1 was carried out in the following series of steps. Beginning with the COPC list of detectable chemical species generated from headspace sampling and other sources, those which could not be identified as specific chemical species were set aside for later examination. Inability to better identify them was in large measure the result of their presence in extremely low concentrations.

The remaining list was searched for species which could be classified as petroleum-related chemicals and they will be examined as components of complex mixtures akin to those often found in refinery streams. However, this is not part of this document.

The list of the remaining chemicals was screened with respect to the severity of their potential adverse effects, the maximum concentration (MC) at which they were found and the number of tanks in which they were found. Those chemicals classified by the International Agency for Research on Cancer (IARC) or regulatory/guidance agencies as “known” or “probable” carcinogens were all classified as “high priority” chemicals (5, 6, 7, 8, 9, 53). Those referenced as “possible” carcinogens were dealt with using the same criteria as those applied to the non-carcinogens. Using the criteria of maximum concentration/lowest occupational exposure guideline (MC/LOEG) values and frequency of finding them in the tanks, none of the “possible” carcinogens were advanced to the list of high priority chemicals.

For non-carcinogens the literature was searched for occupational exposure guidelines, e.g., PEL, TLV, WEEL, and others. A metric, defined as MC divided by the lowest occupational exposure guideline found (LOEG), i.e., MC/LOEG, was calculated for each chemical. “Possible” carcinogens were evaluated using the same criteria. As a first approximation those chemicals for which MC/LOEG was less than 0.1 were deferred from further consideration for the high priority list. These chemicals may be evaluated in workplace air at the discretion of the CH2M HILL Industrial Hygiene team. The resulting list was then evaluated for prevalence in the tanks. Chemicals found in less than 10% of the tanks were added to the deferred category. A group of chemicals remained for which no LOEG value could be discovered. LOEG values were estimated based on similarity to chemicals with known LOEG or derivation of estimated LOEG beginning with animal toxicity data. Based on these considerations three chemicals were added to the high priority list.

Table 1 shows the results of these analyses. Table1a. shows a list of 17 chemicals, the MC/LOEG values of which exceed 0.1 and were found in more that 10% of the tanks. Table 1b shows a list containing all of the “known” and “probable” carcinogens found in the tanks. Both lists are sorted from the top down by the number of tanks in which they were found.

Table 1a and 1b. Suggested chemicals for high priority monitoring

a. Non-carcinogens with >0.1 MC/LOEG in >10% of tanks			**b. Carcinogens (“known” and “probable”)**	
	No. Tanks	**% Tanks***		**No. Tanks**
Ammonia	96	64.4	***Benzene***	**69**
1-Butanol	89	59.7	Methylene chloride	60
Acetonitrile	84	56.4	Tetrachloroethylene	50
Methanol	72	48.3	Acetaldehyde	42
Nitrous oxide	69	46.3	Carbon Tetrachloride	38
Propanenitrile	67	45.0	Chloroform	26
Butanal	66	44.3	***N-Nitrosodimethylamine***	**19**
Butanenitrile	60	40.3	Trichloroethylene	18
2-Hexanone	59	39.6	1,3-Butadiene	14
Pentanenitrile***	57	38.0	Ethylene dibromide	13
Hexanenitrile***	57	38.0	1,4-Dioxane	10
2-Ethyl-1-hexanol,	38	25.5	***Vinyl chloride***	**8**
Propene	30	20.1	Formaldehyde	4**
Hexanal	28	18.8	1,2-Dichloroethane	6
Tributyl phosphate	27	18.1	Fluoroethene,	2
Nitrogen dioxide	15	10.1	***Ethylene oxide***	**1**
3-Hexanone***	15	10.1	4-Ethenyl-cyclohexene,	1
			2-Nitropropane,	1
			Bis(2-ethylhexyl)phthalate	1

*Assume 149 tanks (Single shell tanks)

**Limited sampling for formaldehyde, i.e., 4 tanks.

Bold = "known" carcinogens

***LOEG value calculated

A separate category was established for chemicals which were not detected in the tank headspace, but whose presence may have been missed due to analytical limitations. These are shown in Table 2 sorted from the highest to the lowest estimated LOEG. In many cases no LOEG values were found. The column headed "Surrogate Assumptions" refers to chemicals structurally and/or biologically related to the chemical of concern in the column headed Compounds. LOEG values for the surrogate chemicals were assembled and were used to estimate the LOEG of the chemicals in the Compound list.

Acetamide was not considered a hazard because the LD50 is in the range of 10g/kg in several species by various routes. Glycine, glycolic acid and glyoxylic acid were considered not relevant because they are endogenous metabolites and were found at exceedingly low concentrations.

Table 2. Compounds not reported in headspace but potentially present*

CAS#	Compound	Estimated LOEG (ppm)	Surrogate Assumption
624-91-9	Methyl nitrite	160	Ethyl nitrite
no CAS #	Ethyl peroxynitrite	25	Nitric oxide
no CAS #	Methyl peroxynitrite	25	Nitric oxide
75-12-7	Formamide	10	
123-39-7	N-Methyl formamide	10	Formamide
517-25-9	Trinitromethane	7	Nitromethane=20 ppm
625-76-3	Dinitromethane	7	Nitromethane=20 ppm
600-40-8	1,1-Dinitroethane	7	Nitromethane=20 ppm
64-18-6	Formic acid	5	
no CAS #	Isocyanic acid	4.7	Hydrogen cyanide
74-90-8	Hydrogen cyanide	4.7	
3031-74-1	Ethyl hydroperoxide	1	Hydrogen peroxide
3031-73-0	Methyl hydroperoxide	1	Hydrogen peroxide
151-56-4	Ethyleneimine	0.05	
75-17-2	Methanal oxime**	0.016	Formaldehyde
463-57-0	Methanal hydrate**	0.016	Formaldehyde
no CAS #	Ethanal hydrate**	25	Formaldehyde
107-29-9	Ethanal oxime**	25	Formaldehyde
60-35-5	Acetamide	not relevant	LD50=10 g/kg in several species by several routes
56-40-6	Glycine***	not relevant	
79-14-1	Glycolic acid***	not relevant	
298-76-3	Glyoxylic acid***	not relevant	

* It is not possible to accurately determine the number of tanks in which they might be found.
** Presumed probable carcinogens
*** Normal human endogenous metabolites not likely to reach concentrations harmful to workers.

In summary, the criteria used were:

- For non-carcinogens
    1. A ratio of maximum headspace concentration to the LOEG 0.1 or greater
    2. Present in at least 10% of the tanks
- For carcinogens
    1. Known and probable carcinogens
    2. Possible carcinogens were included with the non-carcinogens

Other identified chemicals are not likely to be present in the headspace, or additional evaluation is required.

The low priority category should contain chemicals that are of a lesser concern based on: (1) concentration; (2) frequency with which the chemical was observed (if the chemical was only measured once, concern is greatly reduced); (3) number of tanks in which the chemical was found; (4) correlation to the chemical inventory used during the production process for which the tank waste has been identified; and, (5) chemicals that have been identified as needed during maintenance and operation of the tank.

The term toxicological reference values should be renamed. The reference values being used for comparison are occupational exposure reference values with preference given to inhalation concerns. The term toxicological reference values should be replaced with the term Occupational Exposure Limits (OELs). The data used to establish OELs may be derived from studies of human exposure or may be extrapolations using data from animal bioassays (6, 7, 8, 9).

4. Methodologies for dealing with chemicals with incomplete toxicological data

For those chemicals for which there are no toxicity data available, it is recommended that structure similarity be used to estimate their toxicological characteristics. In other words assume that the toxicological characteristics will be the same for chemicals with similar structures, e.g. same chemical family. This would base the toxicity assessment for unstudied chemicals on those that have been studied and have similar structures. Structure analogy does have some pitfalls so the exercise should be conducted by personnel with a toxicology background.

A prerequisite for any exposure guideline list that is used is that it should be generated from a peer-reviewed database. The use of un-peer reviewed data in standard setting is not recommended unless there are no other data. EPA frequently uses industry reports when other data are not available and the National Academy Of Sciences Committee On Toxicology has approved their use. In selecting which exposure guideline is the most appropriate one to use in developing the COPC list, one must take into account the exposure profile that is encountered in the workplace. In other words, consider whether the potential exposure is acute or chronic in nature. If the exposure is sporadic in nature and of short duration, then the guidelines that address short term exposures would be the most appropriate. When spikes are common, as is the case in the tank farms, the use of STELs should be considered. If on the other hand, the exposure is likely to be consistent (even if some spikes are evident) over a longer period of time then guidelines that address Time Weighted Averages (TWA) over hours of exposure should be used.

Additionally, structure activity relationship (SAR) may be used to help establish OELs when none exist. The use of SARs however further perpetuates the uncertainty in the derivation. SAR is useful if the uncertainty associated with the technique is known. Chemicals of similar structure can be assumed to have similar endpoint effects. However, the fallacy with this assumption is that similar structure results in similar effects based strictly on chemical structure. In reality, the endpoint effects may be totally different. However, in the absence of laboratory data the assumption is reasonable from a professional standpoint and is commonly used.

The COPC List must be reviewed periodically and structured in a way that allows for the incorporation of new toxicological data, if and when these become available.

5. Methodologies for dealing with chemicals with no established OEL

There are 1053 chemicals with no established OELs. The first approach to the problem is to separate out the petroleum-related mixtures or compounds and compare with existing petroleum industry toxicological data. That leaves relatively few chemicals. For those the panel suggests that a search of HSDB (10) for animal toxicology studies to help derive Human Occupational Exposure Guidelines (HOEG) using accepted risk assessment approaches.

It is possible to use the procedures set out in the U.S. EPA National Advisory Committee’s Standing Operating Procedures (11) to help determine OELs for the Hanford Tank Farm vapor issues. While the derivation of these OELs is beyond the scope of this project, the panel has suggested certain approaches for the development of

OELs. To further alleviate the concerns of Hanford workers, these OELs should be derived and made available either in the open scientific literature or available to Hanford worker populations and should be reviewed by an independent panel.

A general approach for deriving HOEG involves the following equation (11, 12, 13, 14, 15, 16, 17, 18):

$$HOEG = \frac{NOEL\ (or\ LOEL)}{(UFA)(UFH)(UFL)(UFS)(UFD)(MF)}$$

Where:

NOEL- No observed effect level

LOEL- Lowest observed effect level

UFA- Uncertainty factor used in converting animals data to humans

UFH- Uncertainty factor used to account for most sensitive human

UFL- Uncertainty factor when extrapolating from LOEL to NOEL

UFS- Uncertainty factor used when extrapolating from sub-chronic to chronic studies

UFD- Uncertainty in the data base

MF- Modifying factor (1-10 based on collective professional judgment)

It is important to recognize that in most risk assessments many of these uncertainty factors are assigned a value of one. The key extrapolations involve going from an animal to a human and then to the most sensitive human. The range of uncertainty factors for most chemicals is either 3 or 10 from animal to human and 3 for extrapolation to the most sensitive human. Ordinarily, it will be unlikely that we will use uncertainty factors that total to more than 100 or 300.

In the absence of animal data one can examine standards set for structural analogues, and by making use of other uncertainty factors estimate HOEG values.

The compounds requiring further evaluation typically have been seen in the headspaces, but have not been evaluated to establish toxicological properties. Additional evaluation should include grouping into chemical families, use of empirical petroleum industry toxicology data for complex mixtures of organic molecules, and use of structural activity relationships to develop provisional OELs. In the development of these provisional OELs it is recommended that additional occupational exposure reference lists be scrutinized, such as Acute Exposure Guidelines [AEGLs (19)], Spacecraft Maximum Allowable Concentrations [SMACs (20)], Submarine Escape Action Levels [SEALs (21)], Emergency Response Planning Guidelines [ERPGs (22, 23, 24, 25)], Workplace Environmental Exposure Levels [WEELs (26)], Emergency Exposure Guidance Levels [EEGLs (27, 28)], Continuous Exposure Guidance Levels [CEGLs (28)], Community Emergency Exposure Levels [CEELs (29)] and Short-Term Public Emergency Guidance Levels [SPEGLs (28)]. These references are peer reviewed and with the exception of the ERPGs and WEELs, are reviewed by the National Academy of Sciences, National Research Council, Committee On Toxicology. The inclusion of other country reference values adds more credibility to the overall method for comparison because they widen the population database of reference values.

6. Benchmark CH2M HILL methodology, results, and proposed actions against industry standards

While many of the individual chemicals in the headspace vapors have occupational exposure limits (OEL), no OELs have been set for such a complex mixture of chemicals, which may escape from the tanks. CH2M HILL recognizes the shortcomings in its approach and concedes that other approaches need to be considered. Specifically, the CH2M HILL approach has been to consider existing published occupational regulatory standards/guidelines [for example, OSHA (8), ACGIH (7), EPA (32, 33, 34, 35), ATSDR (36), EEGLS (27, 28), NIOSH (30, 31) or CEGLs (28)] to protect workers from such exposures. While these are well-documented standards/guidelines for many workplace environments, the usefulness in CH2M HILL tank environment is minimal. A number of issues must be considered in utilizing such guidelines in order to determine acceptable limits for such unique exposures. It is difficult to use existing TLVs or other OELs without accounting for a number of factors. Important considerations include: 1) multiple sources of exposure to multiple agents, 2) very short duration but repeated exposure that may involve long-term effects, and 3) toxicity of complex mixtures.

While the toxicological principles used in establishing such limits can be useful, the application to specific exposure in these tank fields is questionable. TLV is for example for a “40 hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect”. Data would indicate that the duration of exposure associated with vapors from these tanks is expected to be of a very short-term, intermittent exposure. While the use of TLVs may be a starting point in deriving an appropriate safe level, other existing regulations may be more appropriate. A Short-Term Exposure Limit (STEL) could be considered for such exposures. While a STEL is usually a 15-minute time weighted average exposure that should not be exceeded at anytime during a workday, an averaging period other than 15 minutes may be used when warranted. A second approach to consider is the use of a ceiling value approach, where the concentration should not be exceeded during any part of the working day. Ceiling limits place a definite boundary that should not be exceeded. Finally, other approaches that may be appropriate are EEGLs since they differ from STELs in that STELS are generally for 15 minute limits to which a worker can be exposed to for many years and the EEGLs have been developed for both a 1-hour and 24-hour exposure (27, 28). While the number of chemicals with EEGLs is minimal, the concept/approach may be used by CH2M HILL. The EPA has also developed RfCs, for chronic inhalation exposures (32, 33, 34). These assume a 70-year exposure and may or may not be relevant for evaluating potential human health risk for the short term, intermittent exposure reported in the tank fields.

Even with such limitations, all published studies used to establish previous industrial or public exposure limits for airborne materials should be carefully reviewed for pertinent information before establishing acceptable levels in the fields. Clearly the purpose of this comparison is not to merely provide background information on how other agencies set guidance levels for workers in the tank fields. Rather, the purpose of this report is to determine if the levels are reasonable in light of the specific needs of CH2M HILL. The panel highly recommends CH2M HILL use weight of evidence methodology concerning the derivation of provisional OELs.

Special consideration must be given in assessing the health hazards that are associated with such mixtures. When two or more hazardous substances, which act upon the same organ system, are present, their combined effect, rather than an individual one, should be given primary consideration. The effects can be considered to be additive. This is discussed in further detail later in this report.

To conclude that a risk is acceptable, one must be able to identify and quantify it. This requires a profound knowledge of not only the relationship between exposure and the health effect, but also the relationship between exposure intensity and the prevalence of a defined adverse effect.

7. Evaluate reasonableness of risks for basing Industrial Hygiene Program on the proposed COPC List

Principal objectives of CH2M HILL's Industrial Hygiene (IH) program must be to (1) recognize the potential risks from chemical exposure associated with working in the tank farms; (2) to assess the magnitude of these risks; and (3) to implement controls that manage these risks to an acceptable level.

In addressing objective number two it must be recognized that the complexity of potential exposures in the tank farms dictates that a structured and disciplined approach to assessing risks be implemented. A critical component has to be a prioritization of the chemicals found in the tank farms to make this risk assessment exercise manageable.

The development of a COPC List has this as a goal. The panel suggests that the list, predominantly based on chemicals identified by GC/MS in the headspace of the storage tanks, identify the chemicals that have to be addressed and then through a series of decision points categorize the chemicals for monitoring prioritization as indicated above.

This categorization is critical input for the "Industrial Hygiene Exposure Assessment Strategy" in the design of an effective and efficient sampling/monitoring program for the tank farms. It ensures that the sampling effort is focused and that the chemicals of greatest health concern are evaluated first.

The adequacy of the COPC list is dependent on the comprehensiveness of the list of chemicals found in the tanks' headspace. It is, therefore, very important that the list from which the COPC list draws its chemicals be kept up to date. A recent example is the discovery of formaldehyde, mercury and dimethyl mercury in samples that previously had not been identified. Also, in many cases chemicals have been only identified once, and never detected again.

As new information becomes available on the chemicals the COPC List addresses, its impact on the decision logic and chemical categorization must be reassessed. As the COPC is revised, the Industrial Hygiene Exposure Assessment Strategy must be reviewed and modified as necessary.

The area of potentially greatest risk to the Industrial Hygiene Program is the large number of chemicals that do not have established OELs. Not knowing the potential adverse health effects from each chemical is a considerable risk to the program because sampling for each chemical with an unknown OEL may not be given the proper priority. Workers have the potential to be exposed to a highly toxic material and this hazard would not be known until the OEL has been developed. All chemicals have some effect; the dose will determine the degree of effect. OELs are developed based upon the effects of the chemical at different concentrations for different time periods.

Another area of risk concern deals with the various mixtures that have been encountered. Using SAR methodology has merit; however, chemical class similarity does not necessarily equate to health effect similarity. A good example is the difference in health effects between benzene, toluene, and xylene.

Lastly, chemical interactions must be considered (37, 38, 39). Very little is known about the interactions that can occur in such diverse mixtures as exist in the tank headspaces. Mixtures are the norm in the workplace, but are the hardest to study and have the least amount of data in the literature. There are techniques however to study mixtures. Chemicals that affect the same target organ can generally be considered to have additive effects. However, if each chemical in the mixture affects a different target organ they very well may have different interactive effects. This is a very real risk for the Industrial Hygiene monitoring program based upon the COPC List. However, chemical mixture concerns are not unique to these underground storage tanks.

8. Methodology for Industrial Hygiene monitoring based on the COPC List and the appropriateness of CH2M HILL PPE strategies

The overriding goal of an Industrial Hygiene monitoring program is to prevent overexposure to chemicals in the workplace and thus protect workers' health (40). The approach is to (1) identify the contaminants potentially present; (2) assess the airborne concentration and compare this concentration to an exposure guideline; and, (3) implement controls where needed. Paramount to establishing a monitoring program is to determine vapor release points, reasonable vapor release durations, workers (this could be similarly exposed groups) associated with these release points and durations, and chemical identification. It is reasonable to assume that the chemicals identified in the tank headspace would be the same chemicals identified outside the tank in the vicinity of the tank workers. However, it is not reasonable to assume that the concentration found inside the tank would be comparable to the concentration found outside the tank; one would not expect it to be greater. To determine vapor release points, duration and concentration, a reasonable method to use is a continuous recorder with the probe positioned at the most likely release point. Along with this monitoring procedure would be the use of specialized sensors in relation to the vapor release points. The use of this type of continuous sampling would best be conducted for a period of minimally seven days and preferably 14 days. Correlation then of the continuously recorded results could be used to establish a personal worker monitoring strategy. The benefit of continuous recording is that duration times of vapor release and corresponding concentrations can be identified. Along with the actual number of vapor releases that occur over the sampling period these data are necessary to establish a viable and valid personal monitoring strategy for individual tank farm workers. Coupling these data with the specialized sensor data for worker movement and a much more accurate personal monitoring strategy can be devised. The continuous recorder will provide data suitable only as area samples and are not suitable for personal exposure values. Area samples can be taken from various geographical areas inside each tank enclosure area. These area samples can also be collected using a continuous recorder for a comparable period of time as that collected at the vapor release point. One strategy that could be used for the area samples is to divide the tank enclosure area into quadrants and sample each quadrant. This type of sampling will give a very good indication of vapor gradients as the vapor is released from each vapor release point. Meteorological conditions must be taken into consideration. This sampling strategy would be established for each highest priority chemical. Actual worker exposure assessment must be conducted, using either direct or indirect methodology, as illustrated in Figure 3, within the work area using best available technology..

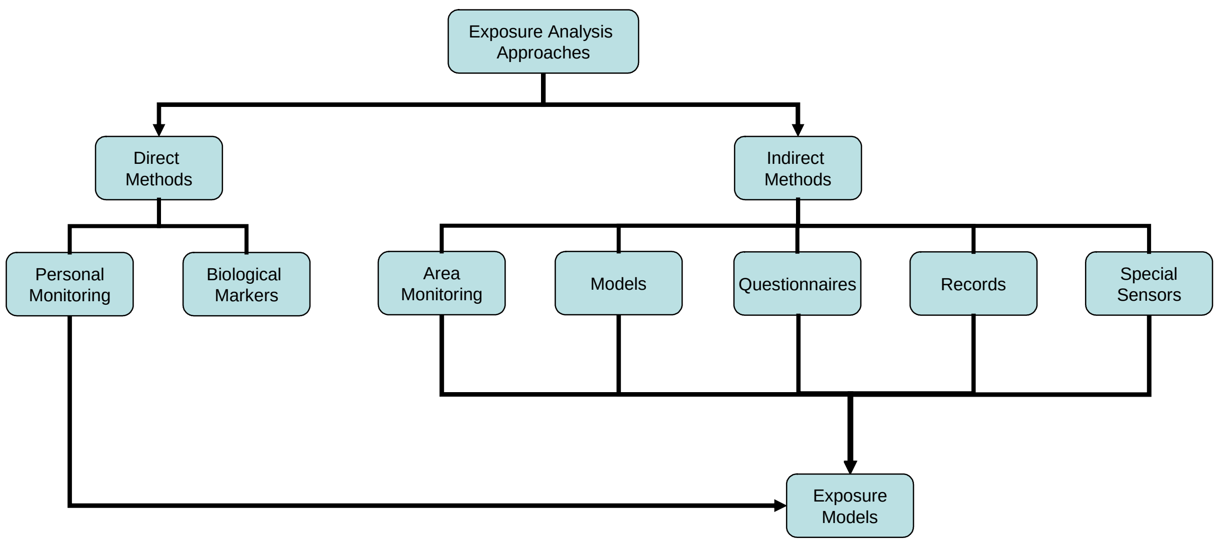

Figure 3. Possible approaches to measuring or estimating exposures

Estimating worker exposure to chemicals emanating in the tank farms during routine operations is complicated by the fact that the points at which chemicals leak from the tank are fixed but the workers move about these points in an apparently random fashion, depending upon the specific task with which they are charged. Exposure scenarios for workers involved in sampling headspace or emergency procedures will differ from those involved in routine operations, and will probably always involve use of supplied air. Routine job categories are divided into five different groups, which may result in five different exposure scenarios. In an attempt to develop an algorithm that would describe mean exposures we propose the following program:

a) A monitoring program involving fixed recording detectors at various locations around the tank head should be established. These detectors should be capable of acquiring data on intermittent releases as well as being capable of reporting integrated estimates of vapor concentrations. Note that intermittent short term measurements may not detect many chemicals but integrated data over weeks or months may show that they were present at lower, for short term samples, than detectable levels.

b) Workers in similar exposure groups should be monitored to detect the compounds listed in Table 1, including both carcinogens and non-carcinogens. Personal monitoring should monitor exposures during a complete work shift and are therefore capable of integrating data but not of measuring discrete emissions.

c) Through observation the movements of crews around the emission release points can be monitored during the course of a work shift.

d) Using these data an algorithm can be defined which describes the proximity of workers to the exhaust system in terms of time and distance during a work shift.

e) The result can be a method to estimate mean exposures, which can then be compared with recommended exposure criteria, such as TLV, PEL, or other OELs. Continuous recording instruments can determine frequency and magnitude of peaks for comparison with established STEL's. Detectability limits must be considered.

f) Care must be taken to calibrate measuring devices to ensure that the instruments can measure levels of chemicals which have low values for OELs, but exist at relatively high levels in the tank headspace. The Industrial Hygiene group might consider the utility of an alarm system focused on either specific chemicals of concern or on surrogates which would provide warning of excessively high releases.

g) The Industrial Hygiene chemical monitoring program should incorporate atmospheric conditions and gender as well as interact with the medical program to incorporate any medical condition that could be exacerbated by chemical exposure. The Industrial Hygienist should include any other conditions that are needed based upon their professional judgment.

h) Where indicated, the use of existing methods for biological monitoring to assess exposure is encouraged.

i) Where indicated, determine the probability of worker exposure by oral and dermal routes.

The industrial hygiene monitoring program must be designed to address three areas: first, the identification of contaminants actually present in the workplace and the nature of the potential exposure profile; second, assessment of worker exposure; and third the efficacy of implemented engineering controls.

Because of the consequences of overexposure, highest priority for Industrial Hygiene monitoring should go to assessing potential exposure to chemicals listed in Table 1. Area samples at the most likely source points to identify the contaminants present in the workplace and personal samples to assess potential exposure need to be taken starting with Table 1 chemicals. An alternative criterion for the noncarcinogens would be toxicological potency, that is assess those with the higher toxicological potency first. These area samples must be complemented by personal samples to better assess workers' potential exposure using the same prioritization scheme as that used for the area samples.

An attempt should also be made to characterize the exposure profile in the workplace. The nature of the operations leads one to believe that the profile will be one of "peaks" rather than a constant one over time. To verify, a direct reading instrument with continuous data recording profile showing concentration versus time could be positioned in the work area and let run over an extended period of time; recommendation is 7 to 14 days. If the contaminant airborne concentration is above the detectibility limit of the instrument, an exposure profile can be established.

Personal and area samples should initially be taken with a high frequency to assess exposure and identify Similarly Exposed Groups (SEG). The establishment of SEGs is an accepted Industrial Hygiene approach, and is supported for the tank farm vapor issue. While the SEGs do establish general profiles, they do not eliminate the need for personal monitoring of all individuals over time. The data collected must be statistically analyzed to determine the geometric mean and precision (degree of scatter). This allows one to statistically determine whether worker exposure is compliant with an Occupational Exposure Limit.

Until actual personal sample measurements have been collected the conservative approach to protection would be to use PPE based on recommendations stated for the OEL. This recommendation can be tempered with professional judgment as long as the rationale is documented. Professional judgment in the health sciences is an accepted methodology both in the scientific and legal arenas. Documentation for the judgment is mandatory for substantiation. Professional judgment however cannot be based on financial considerations, political ramifications, or time. Professional judgment must be based on science, statistics, and expertise of the individual. The conservative approach at this point in time would be to continue supplied air respirators (SAR) or self-contained breathing air (SCBA) respiratory protection and full body protective coveralls until representative personal breathing zone sampling has been completed for each similarly exposed group of workers for all chemicals in Table 1. Some chemicals may not require SCBA or SAR respiratory protection, depending on personal exposure assessment. The rationale for this recommendation is that placing all workers in maximum protection today has already set the precedent. Presently, the maximum protection being used is not warranted based on the science, but rather was implemented based on expressed worker concerns regarding the unknowns. Industrial Hygiene professional judgment in determining the level of respiratory protection required is widely accepted in the profession.

9. Discussion of "as low as reasonably achievable" (ALARA) for protection of workers

CH2M Hill has adopted the As Low As Reasonably Achievable (ALARA) principles for the control of workplace exposures (41, 42). Adoption of these principles acts as a driver for continuous improvement in the reduction of exposure to chemicals in the workplace; however, it also implies a zero-based exposure concept qualified by "reasonableness".

Minimizing exposures can be achieved by a combination of controls. The preferred method is engineering controls. When engineering controls are neither feasible nor effective, the control strategy can be supplemented with administrative controls and the use of personal protective equipment.

It is recommended that CH2M HILL continue its review and installation of engineering controls to reduce contaminant airborne concentration in the workplace. Specifically, the program to install elevated stacks at the HEPA filters exit of the single shell tanks is endorsed. Elevating the stacks will remove the contaminants released when the tank "breathes" away from the workers' breathing zone and discharge them at a higher elevation that will dilute their concentration before coming back to ground. Panel recommends that CH2M HILL evaluate the stack height for effectiveness of dispersion, and whether additional deployments or modifications are warranted to maximally reduce workers exposure potential.

It is also recommended that CH2M HILL institute an aggressive program of leak detection and repair. Direct reading instruments can be used effectively to identify leaks which should be repaired, if at all possible, thus eliminating another source of potential exposure.

Results of the air monitoring program must be frequently reviewed to determine the effectiveness of the control programs with Industrial Hygiene concurrence. This review must not limit itself to determining whether the airborne concentration levels are meeting exposure goals, but also to identify trends so corrective action can be taken prior to exceeding goals.

It is recommended that periodically CH2M HILL conduct a comprehensive review, by an outside knowledgeable panel, of the air monitoring program results and control programs from an ALARA perspective. The objective of such a review would be to determine whether the ALARA principle is being implemented in the air monitoring program.

10. Assessment of exposure to chemical mixtures

In handling mixtures, for which there is no exposure guideline, the key determinant is whether the components have the same target organ or different ones. Should the target organs be different, each component is compared to its own exposure guideline. Should the target organs be the same, then their effect must be treated as additive and the following formula can be used in determining whether the airborne concentration is acceptable or not:

$$C_1/EG_1 + C_2/EG_2 + \ldots\ldots + C_n/EG_n =$$

Where:

C is the component's concentration
EG is the component's exposure guideline

If the sum is ≤ 1, the mixture is compliant with the exposure guideline
If the sum is > 1, the mixture is not compliant with the exposure guideline
Even though the exposure may not exceed the individual exposure guideline, the allowable total may be exceeded and exposure to the mixture must be reduced.

There may be some instances, not common, where the toxicological effect is synergistic, i.e. the effect is greater than the sum of the individual components. If that were to be the case this information must be taken into account in setting acceptable levels.

Ambient monitoring at the tank farm, rather than headspace analyses, must be used for the above calculation. Headspace values could vastly exceed the exposure guideline.

The panel also recommends that CH2M HILL work with experts in the petroleum industry, and determine if toxicological data collected for mixtures can be utilized to establish realistic OELs.

11. Evaluation of odor as an indicator of toxicity

As indicated in the number of Problem Evaluation Requests (PER) complaints submitted at CH2M HILL, odor is a worker perceived indicator of chemical exposure (43, 44). Odors were described as foul, strong tank vapors, medicine, sweet, ammonia-like, musty, dead animals and non-specific (smelled something). Upon investigation the source of the odor was usually identified and in some cases was not associated with tank vapors at all. For example, the dead animal odor on one occasion was traced to an area of a septic tank pump station and on a second occasion to a dead animal carcass in an area adjacent to the tank farm area; the strong tank vapor odors were usually associated with organic vapors in the ppb range. As previously stated, odor is an indicator of chemical presence, but it is not an indicator of toxicity.

The National Academy of Science/National Research Council has developed acute exposure guideline levels (AEGLs) that represent threshold exposure limits (exposure levels below which adverse health effects are not likely to occur) for the general population ranging from 10 minutes to 8 hours. Three levels—AEGL 1, AEGL 2, and AEGL 3—were developed and are distinguished by varying degrees of severity of toxic effects. In the derivation of AEGL-1 values, the SOP guidelines indicate that discomfort becomes likely above the AEGL-1 value (11). However, below the AEGL-1 value "exposure insufficient to cause discomfort or adverse health effects may be perceived nevertheless by means of smell, taste, or sensations (mild sensory irritation) that are not uncomfortable. The awareness of exposure may lead to anxiety and complaints and constitutes what is termed detectability." (11, pp 40) As defined in this reference, "AEGL-1 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure." The general public therefore might perceive an unhealthy exposure to chemicals if an odor is detected, even though the concentration of the chemical is well below the level at which adverse health effects might occur although they may be annoying and may cause discomfort. The detection of odor is one parameter that is useful to Industrial Hygienists as an indicator of chemical presence (45, 46, 47, 48, 49). However, the individual susceptibility of odor detection makes the reliance upon odor as an indicator of over-exposure questionable. There are a number of factors that make the use of odor unreliable as an exposure indicator: genetic variation among individuals; olfactory fatigue; odorless chemicals; high concentrations of some chemicals results in the loss of the characteristic odor at lower concentrations (example, hydrogen sulfide); and the absence of the ability to smell by individuals. 2-Heptanone has a sweet mushroom odor characteristic, which could be described as musty; butanol smells like alcohol which could be perceived as medicine; cyclohexane, acetaldehyde, and octanone are described as pungent; whereas carbon dioxide and propane are odorless. However, when odor threshold values are correlated with OELs, the detection of the odor is usually many times lower than the OEL. The high headspace concentrations of ketones and ammonia could easily account for the ammonia-like and sweet odors reported by individuals near identified point sources of vapor escape. AIHA 1986 (50), AIHA 1993 (51) and The Journal of Applied Toxicology (52) provide a wealth of information on odors and odor thresholds. Dalton (48) and Ruijten (49) provide additional information on the use of odors for chemical effects and recognition.

The presence of an odor in an area where odors are not to be expected is an indication of a chemical presence. In the tank farm areas, the presence of odors is indicative of vapor escapes. The chemicals associated with these odors can be sampled and a concentration determined. Industrial Hygienists can use the presence of odors as an indicator of potential exposure. The chemicals in the headspace can be characterized by odor and a correlation of odor and symptoms can be drawn. A literature search for odor thresholds should be conducted for the chemicals that are present in the tank headspaces along with the characteristic odor for the chemicals. A correlation between odor threshold and OEL can then be drawn. Because odor is indicative of the presence of a chemical or chemical mixture, the use of odor should be used in establishing the sampling protocol by Industrial Hygiene. For those chemicals identified in Table 1 if an odor has been identified with the chemical, then odor in correlation with the MC/LOEG should be considered when establishing the sampling priority. Odor should be considered a primary indicator of chemical presence keeping in mind that odor is not an indicator of toxicity of the chemical. Furthermore, the odor may be from an individual chemical or a mixture of chemicals. Odors need to be characterized for chemicals and thresholds determined. If the threshold is exceeded, this indicates the presence of the chemical and can be used by the Industrial Hygienist as one indicator for sampling/monitoring. For individuals, odor is the perception of something bad, whether it is or not. This then becomes a risk communication issue

C. Summary of Panel Recommendations

Section 1. Evaluating the methodologies used in the selection of chemicals of concern is an on-going process requiring:

a. Identifying, characterizing and quantifying those chemicals in the headspace
b. The assessment of the effectiveness of engineering controls
c. Only NIOSH or OSHA approved sampling and monitoring methods or other validated methods
d. Ranking the various tanks according to COPC
e. Personal monitoring should be performed especially when the tanks are disturbed and data compared to OELs
f. Chemicals identified in the headspaces should be correlated with the initial chemical inventory
g. The proper unit of exposure should be ppm/ppb and not mg/m^3
h. Periodically monitor for lower priority chemicals to assure that they do not appear at concentrations that merit placing them in higher priority.

Section 2. The term toxicological reference should be replaced with the term occupational exposure standards.

Section 3.

a. The Industrial Hygiene team should develop a monitoring strategy which involves measurement of the chemicals in Table 1 within the breathing zone of tank farm workers with regular frequency.
b. A second level plan to search for the chemicals in Table 2 should be developed.
c. An additional plan should be developed to seek chemicals which were deferred based on low MC/LOES values and detection in fewer than 10% of tanks. These might be focused on specific chemicals which may be deemed significant but found in only few tanks
d. A "continuous recording" approach to measuring as many chemicals as feasible over extended time periods should be developed.

Section 4.

a. Consider structural SAR to estimate toxicological characteristics of chemical compounds
b. Use peer-reviewed data, unless not available, for provisional OEL development
c. Developed provisional OELs must be peer reviewed by toxicology experts
d. The COPC list needs to be periodically reviewed and updated

Section 5.

a. For chemicals identified as needing further evaluation, group petroleum hydrocarbons into groups of mixtures that have been previously toxicologically characterized. This would allow priority ranking of each group rather than individual compounds.

b. A search of HSDB for animal toxicology studies is recommended to help derive Human Occupational Exposure Guidelines using accepted risk assessment approaches
c. Derived peer-reviewed OELs should be made available either in the open scientific literature or available to Hanford worker populations
d. In the absence of data for development of HOEGs, the uncertainty factor approach can be considered. In the absence of animal data, structural analogs may be appropriate.

Section 6.

a. Relevant published industrial and public exposure limits for airborne material should be considered in establishing LOEG
b. Consider using EEGL approach in establishing LOEGs
c. The panel highly recommends CH2M HILL use weight of evidence methodology concerning the derivation of provisional OELs.

Section 7.

a. Panel concurs with the methodology and decision making as described in the technical report; recommend continuation
b. The COPC list, methodology and decision making needs to be periodically reviewed and updated
c. Biological system effects from chemical mixtures and biological interactions need to be evaluated.

Section 8.

a. Use of continuous recorder to determine vapor release points, duration and concentration
b. Continuous recorder monitoring should be no less than 7 days and optimally 14 days
c. Use of specialized sensors as monitoring techniques should be considered to identify work patterns and possibly patterns of vapor releases
d. Correlate results of monitoring from (b) and (c) as outlined above.
e. Area samples should be taken for various geographical locations and compared to one another and OELs
f. Actual worker exposure assessment must be conducted using either direct or indirect methodology within the work area using best available technology.
g. Panel recommends that an exposure monitoring scenario be setup as follows:
    - A monitoring program involving fixed recording detectors at various locations around the tank head should be established. These detectors should be capable of acquiring data on intermittent releases as well as being capable of reporting integrated estimates of vapor concentrations
    - Workers in similar exposure groups should be monitored to detect the compounds listed in Table 1. Personal monitoring should be conducted for an entire work shift
    - Use special sensors to characterize worker movement; correlate with continuous detector data

- The correlated data from continuous and special sensors should be compared with OELs
- Ensure appropriate calibration of all sampling equipment in accordance with manufacturer's recommendations.
- The Industrial Hygiene group should consider the utility of an alarm system focused on either specific chemicals of concern or on surrogates which would provide warning of excessively high releases
- The Industrial Hygiene chemical monitoring program should incorporate atmospheric conditions and gender as well as interact with the medical program to incorporate any medical condition that could be exacerbated by chemical exposure
- Where indicated, the use of existing methods for biological monitoring to assess exposure is encouraged.
- Where indicated determine the probability of worker exposure by oral and dermal routes

h. The Industrial Hygiene chemical vapor monitoring program must include contaminant identification, worker exposure assessment and efficacy of engineering controls
i. The Industrial Hygiene chemical vapor monitoring program must characterize the exposure profile in the workplace
j. The panel supports CH2M Hill's implementation of a SEG program
k. The panel recommends statistical analysis of Industrial Hygiene vapor monitoring data
l. Industrial Hygiene professional judgment is a commonly accepted methodology but documentation of decision criteria is required

Section 9.

a. The Panel recommends CH2M HILL continue installation of engineering controls to control chemical vapor releases from tanks
b. The Panel recommends that CH2M HILL evaluate the stack height for effectiveness of dispersion, and whether additional deployments or modifications are warranted to maximally reduce workers exposure potential
c. The Panel recommends an aggressive program of leak detection and repair
d. Results of the air monitoring program must be frequently reviewed to determine the effectiveness of the control programs with Industrial Hygiene concurrence.

Section 10.

a. Additive effects from mixtures should be considered unless otherwise indicated
b. CH2M HILL should work with experts in the petroleum industry to determine if toxicological data collected for petroleum-stream mixtures can be utilized to establish realistic OELs for tank vapor exposures

Section 11.

a. CH2M HILL Industrial Hygiene should use odor as an indicator of chemical presence, however odor is unreliable as an indicator of toxicity

b. CH2M HILL Industrial Hygiene must consider that the absence of odor does not indicate the absence of chemical vapors
c. CH2M HILL establish a table of odor thresholds for COPCs

D. Intertox 2000 Report Review

While the computer-based Toxicological Significance Information Model, developed to aid CH2MHILL in the selection of chemicals of potential concern, was comprehensive and provided an approach for organizing COPC there are limitations to the report. Many of the problems stems from using concentrations expressed in mg/m3 and the failure to justify some of their decisions.

1. The use of mg/m3 fails to take into consideration the differences in molecular weights (MW) of the various chemicals. Calculations show that this could make a significant difference in calculated concentration.
2. Using concentration expressed as parts per million (ppm) also allows one to more accurately compare one chemical with another and to be able to compare toxicity of different chemicals.
3. There was no justification provided for their recommendation of a 0.025 mg/m3 de minimus concentration.
4. Their proposed Decision Tree based on use of structural activity relationship (SAR) seems like an acceptable approach.
5. Their suggestion for Literature Toxicity Information is similar to ours and is reasonable. While they propose to search two databases (Toxline and PubMed) there are a number of other databases that would provide useful information.

The Intertox 2000 approach is of interest and certainly worthwhile for our panel to review but our understanding of the solution/approach for CH2M HILL COPC does not support the Intertox proposed methodologies. It is recommended that, perhaps after our document is finalized, a more extensive review of these two approaches would be appropriate. For example, it might be interesting, when we finish our document, to see how the various categories compare… ppm vs. mg/m3.

E. Tech Basis Document Review

The draft tech basis document received on 08 September 2004 was reviewed by the ITP. Chapter 5 needs to be revised to incorporate recommendations outlined in the ITP report. The ITP should have the opportunity to comment on the final draft of the tech basis document before publication. Comments will be provided under separate cover.

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G. Personnel Interviewed

1. Tom Anderson, PhD, CH2M HILL Environmental Health Director
2. Amoret Bunn, PhD , PNNL Research Scientist
3. Nancy Butler, Consultant to CH2M HILL IH Programs
4. Donald Camaioni, PhD, PNNL Staff scientist
5. Bob Cash, PhD, Consultant to CH2M HILL Technical Basis Task Team
6. James Droppo, PhD, PNNL Staff Scientist
7. Joel Eacker, CH2M HILL Vice President, Project Delivery
8. Susan Eberlein, PhD, CH2M HILL Long Term Health Impact Studies Project Lead
9. Richard Higgins, CH2M HILL Vice president, Environment, Safety, Health and Quality (Acting)
10. Jim Honeyman, CH2M HILL Senior Technical Specialist, Technical Basis Task Lead
11. Jim Huckaby, PhD, PNNL Staff Engineer
12. J.W. Jabara, CH2M HILL Industrial Hygienist
13. Laurie Johns-Andersch, CH2M HILL Industrial Hygiene Program Technical Advisor
14. Terry Mast, PhD, PNNL Staff Scientist
15. Joe Meacham, CH2M HILL Process Engineer
16. Nadia Moore, PNNL Senior Research Scientist
17. Terry Moore, CH2M HILL Deputy to Vice President, Project Delivery
18. Bob Popielarczyk, CH2M HILL Vice President, Engineering/Chief Engineer
19. Addanki Sastry, Consultant to CH2M HILL Technical Basis Task Team
20. Robert Stenner, PhD, PNNL Staff Scientist

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I. Acronyms:

ACGIH	American Conference of Governmental Industrial Hygienists
AEGLs	Acute Exposure Guidelines
AIHA	American Industrial Hygiene Association
ALARA	As Low As Reasonably Achievable
AMZ	Air Monitoring Zone
ATSDR	Agency for Toxic Substances and Disease Registry
CAM	Continuous Air Monitor
CAS	Chemical Abstracts Service
CDC	Centers for Disease Control and Prevention
CEELs	Community Emergency Exposure Levels
CEGLs	Continuous Exposure Guidance Levels
CFR	Code of Federal Regulations
COPC	Chemicals of Potential Concern
COT	Committee on Toxicology
CY	Calendar Year
DOD	Department of Defense
DOE	U.S. Department of Energy
DRI	Direct Reading Instrument
DST	Double-Shell Tank
EEGLs	Emergency Exposure Guidance Level
EG	Exposure guideline
ERPG	Emergency Response Planning Guideline
FY	Fiscal Year
GAP	Government Accountability Project
HASP	Health and Safety Program
HEAST	Health Effects Assessment Tables
HEPA	High Efficiency Particulate Air Filter
HOEG	Human occupational exposure guideline
HSDB	Hazardous Substance Data Base
IARC	International Agency for Research on Cancer
IDLH	Immediately Dangerous to Life and Health
IPCS	International Programme for Chemical Safety
IRIS	Integrated Risk Information System
JHA	Job Hazards Analysis
JSA	Job Safety Analysis
LOAEL	Lowest observed adverse effect level
LOEG	Lowest occupational exposure guideline
MF	Modifying factor
MRL	Minimal Risk Level
NAS	National Academy of Sciences

NOAEL	No observed adverse effect level
NIOSH	National Institute for Occupational Safety and Health
NRC	National Research Council
NTP	National Toxicology Program
OA	Office of Independent Oversight and Performance Assurance
OECD	Organization for Economic Cooperation and Development
OEL	Occupational Exposure Limit
ORP	DOE Office of River Protection
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
PEL-STEL	Permissible exposure limit-short-term exposure limit (OSHA)
PEL-TWA	Permissible exposure limit-time-weighted average (OSHA)
PER	Problem Evaluation Request
PNNL	Pacific Northwest National Laboratory
ppb	Parts Per Billion
ppbv	Parts per billion by volume
PPE	Personal Protective Equipment
ppm	Parts Per Million
RfC	Reference Concentration
RfD	Reference Dose
REL	Recommended Exposure Limits
REL-STEL	Recommended exposure limit-short-term exposure limit (NIOSH)
REL-TWA	Recommended exposure limit-time-weighted average (NIOSH)
RL	DOE Richland Operations Office
RTECS	Registry of the Toxic Effects of Chemical Substances
SEALs	Submarine Escape Action Levels
SHIMS	Safety and Health Information Management System
SMACs	Spacecraft Maximum Allowable Concentration
SPEGLs	Short-Term Public Emergency Guidance Level
SST	Single-Shell Tank
STEL	Short-Term Exposure Limit
TEEL	Temporary Emergency Exposure Limit
TCD	Tank Chacterization Database
TST	Triple Sorbent Tubes
TLV	Threshold Limit Value
TLV-STEL	Threshold limit value-short-term exposure limit (ACGIH)
TLV-TWA	Threshold limit value-time-weighted average (ACGIH)
TWA	Time-Weighted Average
TWINS	Tank Waste Information Network System
TWINS2	Tank waste information network system 2
UF	Uncertainty factor
WEELs	Workplace Environmental Exposure Levels

J. BIOGRAPHICAL INFORMATION OF INDEPENDENT TOXICOLOGICAL PANEL MEMBERS

Dr. Kenneth R. Still, Chair

Dr. Still is currently Senior Director, Safety and Occupational Health for the U.S. Navy's Pacific Fleet. He has held senior positions involving toxicology, industrial hygiene, occupational safety and health, research and major program development. During this time, he also held adjunct faculty professorships at several universities including the University of Hawaii John Burns School of Medicine; Johns Hopkins University School of Public Health; Wright State University School of Medicine; Uniform Services University of Health Sciences; Eastern Virginia Medical School; Wright State University Institute of Environmental Quality; and the Air Force Institute of Technology School of Engineering and Environmental Management.

Dr. Still's expertise and experience includes toxicology research program development; toxicology and occupational health program development and management; interpretation of toxicological data; hazard identification; human health and ecological risk assessment; exposure control and prevention; communication and interpretation of occupational health, environmental, preventive medicine and toxicological data; exposure assessment characterization; toxicology, occupational health, risk assessment training; research laboratory management and organization; Chemical/Biological/Radiological/Nuclear defense vulnerability assessments; and confined space characterization.

Dr. Still's research interests are in biochemical toxicology, occupational exposure level development, human health risk assessment, ecological risk assessment, reproductive/developmental effects of depleted uranium, health effects of jet propulsion fuels, submarine atmosphere contaminants and escape mechanisms, PCB control and health effects, chemical hormesis, chemical warfare agent exposure effects, and occupational toxicology. He has over 240 publications to his credit and is currently working on his third book. .

Dr. Still is a National Research Council Post Graduate Advisor in biochemical and occupational toxicology. He has served or is serving on over 25 government and industry committees related to toxicology, occupational health and industrial hygiene, including seven different sub committees of the National Academy of Sciences, National Research Council, Committee on Toxicology; National Advisory Committee, Environmental Protection Agency, on Acute Exposure Guidelines; American Industrial Hygiene Association (AIHA), current Chair of Toxicology Committee; AIHA Emergency Response Planning Guidelines Committee; AIHA Workplace Environmental Exposure Level Committee; American Conference of Governmental Industrial Hygienists

(ACGIH), past Board Member; Permanent Conference Committee ACGIH/AIHA, Chair; Bureau of Medicine and Surgery Closed Living and Working Space Environmental Working Group and Industrial Hygiene Officer Advisory Board; Navy, Army, Air Force Tri-Service Toxicology Consortium Executive Management Council Chair; and Department of Defense Committee on Low Dose Exposure to Chemical Warfare Agents. He is a Certified Industrial Hygienist; Certified Environmental Auditor; Certified Safety Professional; Certified Hazardous Materials Manager, Master Level; Registered Environmental Manager; and Registered Environmental Property Assessor.

Dr. Still holds a PhD in Chemical/Physiological Ecology from Oklahoma State University and has received advanced training in toxicology and risk assessment from Harvard, Johns Hopkins, MIT, and University of Cincinnati.

Dr. Donald E. Gardner

Dr. Gardner has over forty years of experience in the field of toxicology. He received a B.S. and M.S. degree from Creighton University with majors in biology, chemistry and medical microbiology, and holds a PhD in Environmental Health from the University of Cincinnati.

Dr. Gardner's past employment includes 20 years at the U.S. Environmental Protection Agency/U.S. Public Health Service. While at the EPA he served as the Director, Inhalation Toxicology Division, where he was responsible for both the animal and human toxicology program that addressed the potential health risks associated with exposure to environmental chemicals. Following retirement from the EPA, Dr. Gardner joined Northrop/ManTech Corporation as Vice-President and Chief Scientist. At the present time he is President of Inhalation Toxicology Associates, Inc., a company that provides consulting services to several government agencies and private industry including U.S. EPA, NIEHS, NIH, NASA, WHO, and private law firms.

Dr. Gardner has served on numerous advisory panels in the area of environmental health and toxicology. He has been on the National Academy of Science, National Research Council since 1989 and has been Vice-Chairman of the Committee on Toxicology. Dr. Gardner has served as Chairman for eight NAS/NRC COT subcommittees, including the subcommittee on Guidelines for Space Maximum Allowable Concentration for Space Station Contaminants and Acute Exposure Guideline Levels for Selected Airborne Chemicals. He is presently on the Editorial Board of Toxic Substances Journal, the Environmental and Nutritional Interactions Journal, the Journal of Immunotoxicology, Toxicology Mechanisms and Methods, and New Perspectives: Toxicology. He is co-Editor of the Target Organ Toxicology Series (15 volumes) and Toxicology of the Lung (four editions). Throughout his career he has published over 250 manuscripts. He is the founding Editor and Editor-in-Chief of the Journal of Inhalation Toxicology.

He has been designated Lifetime National Associate Member of the National Academy of Sciences in "recognition as advisor to the Nation in matters of science, engineering, and health". He has received the lifetime outstanding achievement award from the Society of Toxicology Specialty Sections in both inhalation toxicology and in immunotoxicology, several EPA Scientific and Technological Achievement Awards and the Meritorious Service Award from the US Public Health Service. Dr. Gardner was awarded the NASA Outstanding Public Service Award in recognition for guiding NASA toward a safer environment to enhance future exploration of space. He has held numerous elected positions in toxicology organizations, including President and Vice-president of three Society of Toxicology Specialty Sections including Metals, Inhalation Toxicology, and Immunology. He also served as President of the North Carolina Chapter of the Society of Toxicology and as President of the Academy of Toxicological Sciences.

Dr. Gardner is a Board Certified Fellow of the Academy of Toxicological Sciences and has served as adjunct professor at seven academic institutions including Duke University, North Carolina State University and the University of Massachusetts

Dr. Gardner's fields of specialization include occupational and environmental health, toxicology of confined space, U.S. EPA Programs and Policies, assessment of health effects associated with tobacco smoke, and NASA's ISS Program.

Dr. Robert Snyder

Dr. Snyder is Professor of Pharmacology and Toxicology, Rutgers Ernest Mario School of Pharmacy, Professor of Toxicology, Rutgers, The State University of New Jersey and has 40 years of academic experience in toxicology and pharmacology. He also holds visiting professorships at various European universities including Nueherberg, Germany and University of Tubingen. Dr. Snyder was the Director, Joint Graduate Program in Toxicology and Robert Wood Johnson Medical School, University of Medicine and Dentistry of New Jersey; Chairman, Department of Pharmacology and Toxicology, Rutgers Ernest Mario School of Pharmacy; Director, Division of Toxicology, Environmental and Occupational Health Sciences Institute; Acting Director, Environmental and Occupational Health Sciences Institute; and, Associate Director for Research, Ernest Mario School of Pharmacy.

He has conducted numerous seminars and lectures on toxicology at over 100 national and international universities, seminars, conferences and industries. He has edited, reviewed or written chapters on over 25 books and co-authored over 70 research reports related to toxicology.

He received Rutgers University Board of Trustees Award for Excellence in Research and twice received Humboldt Research Award for U.S. Scientists. He is or has been a member of the National Academy of Sciences Committee on Toxicology and six different sub committees of this committee; Board of Toxicology, National Academy of Sciences; Chairman, NAS-NRC Committee on Alkylbenzenes; and witness on several OSHA Hearings on Benzene. He has been a member of the editorial board of Toxicology and Applied Pharmacology Journal and is currently on the editorial board of Journal of Applied Toxicology and the International Journal of Toxicology.

Dr. Snyder currently serves as the President of the American College of Toxicology.

Dr. Snyder's research involves solvent toxicology, chemically induced bone marrow depression, liver toxicity, chemical carcinogenesis, drug metabolism, mixed function oxidase, cytochrome P-450, biological reactive intermediates, enzyme isolation and purification, and biomarkers for exposure to chemicals.

Dr. Snyder is board certified by the Academy of Toxicological Sciences. He holds a PhD in Biochemistry from State University of New York.

Dr. Jorge C. Olguin

Dr. Olguin has 35 years of experience with DuPont Company in several facets of industrial hygiene, including regulatory compliance; development of corporate safety and health guidelines; coordination of occupational health programs; and acting as company's regulatory resource on TSCA and OSHA regulations. Dr. Olguin is the Principal Consultant for DuPont Safety Resources and previously was the Principal Occupational Health Consultant and Senior Occupational Health Fellow for the DuPont Nylon Strategic Business Unit.

Dr. Olguin is a past Diplomate of the American Board of Industrial Hygiene and received certification in the Comprehensive Practice of Industrial Hygiene.

Dr. Olguin holds a PhD in Analytical Chemistry from Kansas State University.