Hanford Concerns Council

June 30, 2008

Re: Review of the *Industrial Hygiene Chemical Vapor Technical Basis*

The Hanford Concerns Council (Council) facilitated the attached assessment at the joint request of CH2M HILL and Hanford Challenge. The impetus for this joint request stemmed from the development of CH2M HILL's *Industrial Hygiene Chemical Vapor Technical Basis*, which provides the foundation for worker protection practices in the Hanford tank farms. Hanford Challenge, an organization advocating for the safe, efficient and cost effective cleanup of the site, questioned the rigor of the *Technical Basis*, specifically whether it is sufficiently conservative to be protective of workers. In response to questioning about the *Technical Basis*, and reflecting on their mutual goals for cleanup of the site, CH2MHILL and Hanford Challenge jointly requested that the Council select and oversee an expert committee to examine the *Technical Basis* document. The three parties drafted a memorandum of understanding to provide initial agreed upon guidelines for this task.

The Council selected a committee of three experts, by consensus, after an extensive nationwide search in three areas of expertise - toxicology, industrial hygiene, and occupational medicine. Selection criteria included recognition as an expert in their respective fields through participation on relevant panels, industry associations, presentation of papers at conferences, relevant publication of books or articles, peer reviews and/or furnishing of expert testimonies. Other criteria included a balance of applied field experience, regulatory background and knowledge of nuclear sites, and ability to communicate to lay audiences.

The committee members are:

- Dr. Hanspeter Witschi, professor emeritus of Toxicology, University of California at Davis, Chair
- Dr. Alfred Franzblau, professor of occupational medicine, University of Michigan
- Dr. Patrick Breysse, professor of industrial hygiene, Johns Hopkins University
- Katherine Clark, Doctoral Candidate in Public Health under the direction of. Patrick Breysse, Johns Hopkins University

The committee was tasked with evaluating whether the methodology and supporting data used in developing the *Technical Basis* 1) were consistent with industry best practices for setting exposure limits based on the prescribed methodologies of organizations such as OSHA, NIOSH, and ACGIH, and 2) is sufficiently conservative to be protective of workers, particularly during waste disturbing activities. In order to select a finite task and time frame, the scope of the assessment was limited to a review of the *Industrial Hygiene Chemical Vapor Technical Basis* and supporting documents, and did not include an assessment of its ongoing implementation in the industrial hygiene program.

The committee met with technical representatives of CH2M HILL and Hanford Challenge, toured the Cold Test Facility and viewed tank farms from outside the fence. CH2M HILL provided additional documents supporting the *Technical Basis* at the request of committee members (a complete list of the documentation reviewed for this assessment can be found in Appendix A).

Committee members presented a draft of their findings to a subcommittee of the Hanford Concerns Council on April 4, 2008. The presentation was based on an initial draft of their assessment dated March 24, 2008, which was reviewed by both Hanford Challenge and CH2M HILL for factual accuracy. Both parties submitted factual-accuracy comments regarding to the expert committee, and the final version of the committee's assessment incorporates changes based on comments at the April 4 presentation as well as written comments. The committee's written response to the factual-accuracy comments is included as Appendix B.

The committee concluded that the methodology for developing the *Technical Basis* document is consistent with industry best practices for setting Acceptable Occupational Exposure Levels. However, the committee questioned whether the source and exposure sampling data which underlie the *Technical Basis* sufficiently reduce uncertainties about the variation and potential maximum concentrations of hazardous constituents in both tank headspaces and worker breathing zones. The committee suggested some possible strategies to reduce uncertainties, recognizing that their suggestions were not based on a detailed review of implementation of the *Technical Basis* document.

These suggestions touch on: 1) headspace and breathing space sampling and personnel monitoring strategies 2) the screening levels used to identify chemicals of potential concern 3) whether known or potential carcinogens identified in tank sampling should be included for monitoring by adding them to the list of chemicals of potential concern and 4) the company's strategy for ensuring that the *Technical Basis* remains a dynamic instrument which continues to incorporate new sampling data and developments in the relevant scientific and regulatory arenas.

The parties recognize that this assessment is not an end point, but a basis for ongoing efforts to ensure safe worker protection practices. This assessment will be relied upon to provide greater understanding to all parties about technical and scientific best practices as evaluated by mutually agreed experts. The assessment provides a basis for ongoing discussions between the parties about opportunities for improvement in worker protection practices at the Hanford tank farms. The Hanford Concerns Council remains willing to assist future efforts at the mutual request of the parties.

Signed,

Jon Brock, Chair Hanford Concerns Council	Max Power, Chair Council Technical Review Subcommittee

The Industrial Hygiene Chemical Vapor Technical Basis Review

June 2008

Patrick N. Breysse, PhD, Board Certified Industrial Hygienist

Katherine Clark, MHS, DrPH Candidate, Johns Hopkins University

Al Franzblau, MD, Board Certified Internal Medicine and Preventive and Occupational Medicine

Hanspeter Witschi, MD, Diplomate, American Board of Toxicology; Fellow, Academy of Toxicological Sciences

EXECUTIVE SUMMARY

This report describes the analysis and conclusions of an independent review of CH2M HILL's *Industrial Hygiene Chemical Vapor Technical Basis.* The review was commissioned by the Hanford Concerns Council and conducted by a committee representing three areas of expertise - toxicology, occupational medicine, and industrial hygiene. This report reflects a consensus assessment of the committee.

The purpose of the *Industrial Hygiene Chemical Technical Basis* "is to identify all chemicals within a waste vapor source that are potentially hazardous and might be released into worker breathing zones" (CH2M HILL Hanford Group, 2006a). It sets forth Acceptable Occupational Exposure Levels (AOELs) by using existing standards and setting exposure levels where none previously existed.

The review committee was charged with evaluating whether the methodology and supporting data for developing the *Technical Basis* were 1) consistent with industry best practices for setting exposure limits based on the prescribed methodologies of organizations such as OSHA, NIOSH, and ACGIH, and 2) are sufficiently conservative to be protective of workers, particularly during waste disturbing activities. In addressing this second question, it must be remembered that it is not possible to guarantee safety. It is also important to indicate that the Hanford Tank Farm is a very unique situation and there are not any readily comparable situations that can be used to benchmark safety and health practices. In its evaluation, the committee focused on whether the conservatism underlying the *Technical Basis* document was appropriate for the unique conditions existing at the Hanford Tank Farms.

In order to address these two larger questions, the committee focused on two primary assumptions which underlie the *Technical Basis* document, and then developed specific questions to explore the fundamental aspects of those assumptions. The committee's evaluation relied on CH2M HILL documents provided at the outset of the review and, where necessary, other documents available in the scientific literature.

The committee found that the process for evaluating hazards at the Hanford site is conceptually similar to the four step risk assessment process employed by many federal agencies. In the process of risk assessment of sites with particularly hazardous and toxic materials, such as Hanford, special attention must be paid to unpredictable yet potentially critical events despite their low probability of occurring.

For this reason, it is important for the risk assessment process at the Hanford site to be sufficiently conservative, i.e., err on the side of being overly protective. Perhaps most important in the risk assessment process is the quality of the input data (i.e., sampling data). If the data used as the foundation of the risk assessment (e.g., head space concentration data) are inadequate then the resulting risk characterization can be incorrect. While the committee feels that the risk assessment process described in the *Technical Basis* is sound, there is concern about the adequacy of the data used to

implement the process and make decisions about worker health and safety. These inadequacies are discussed below.

The committee found that CH2M HILL has made substantial efforts to sample for chemicals in the tank headspaces as well as worker areas and breathing zones. The methods used to collect and analyze samples are consistent with and in many cases superior to industry best practices. However, the committee identified several areas where a more systematic approach to sampling would yield a more comprehensive assessment of tank head space chemicals and personal exposures. In many cases, there are not enough samples to characterize temporal or spatial variations in headspace or work area concentrations with a meaningful level of confidence.

For example, the fact that not all tanks have been sampled and less than 30% of the tanks have been sampled more than once suggests that there was not a systemic comprehensive strategy employed to characterize head space variability over time either during quiescent conditions or during waste disturbing activities. As a result, the committee is not convinced that the headspace characterization is truly conservative, i.e., that the upper ranges of headspace concentrations have been identified. This is important because these sampling data are key inputs to the risk assessment process with respect to selection of COPCs. The committee recommends a more systematic approach to sampling, both in the headspaces and in the work areas.

In general, the approach developed to screen chemicals detected in the headspace for potential to enter a worker's breathing zone at hazardous concentrations was sound. For chemicals with existing Occupational Exposure Limits, the committee recommends lowering the threshold for inclusion as Chemicals of Potential Concern (COPC) from 10% to 1%, in an effort to be more conservative. Further, the committee recommends including on the COPC list all carcinogens (IARC Groups 1 and 2) detected or known to be in the tanks. For those chemicals without existing Occupational Exposure Limits, the committee found the method of applying surrogates and safety factors in the development of screening levels to be consistent and conservative.

The committee finds that where toxicological data are available, the methodology for developing Acceptable Occupational Exposure Limits outlined in the *Technical Basis* document is generally consistent with industry best practices. An exception to this general assessment is the use of surrogate chemicals for setting exposure standards for chemicals for which adequate toxicological data do not exist. Surrogates have been used in other risk assessment situations where little toxicological data are available. However, the use of surrogates is not standard practice in setting occupational exposures standards by organizations such as NIOSH, ACGIH, or OSHA.

It is generally assumed that the TLV®s suggested by ACGIH are conservative enough for the protection of workers. However, they do not represent a fine line between a healthy versus an unhealthy work environment. Some individuals can experience discomfort or even more serious adverse health effects when exposed to chemicals at the TLV® or even at concentrations below the TLV® (ACGIH, 2007).

The issue of whether occupational exposure limits are protective under all conditions, including during waste-distributing activities, is a function of whether the occupational exposure limits were set appropriately and whether these limits were not exceeded, rather than the activity itself. As mentioned previously, the committee is not convinced that the headspace sampling data and subsequent screening of chemicals was done in a manner that represented the range of tank waste chemistry that may exist in the tanks farms.

When conducting risk assessments, it is difficult to evaluate complex mixtures and the possibility of toxicological interactions. To deal with the potential toxicity of highly complex mixtures, such as identified in the tank headspaces, the *Technical Basis* document has adopted the widely used "mixture rule". The basic premise for this rule stipulates that, in exposure to a mixture, the effects of chemicals with similar toxicities are additive. No inhalation hazard for a mixture can be anticipated, provided the sum of C1/T1 + C2/T2 + …….Cn/Tn is not bigger than 1 (C defining the atmospheric concentration and T the OEL of a given agent). To rely on the mixture rule as a default option is reasonable. The issue of toxicological interactions is not explicitly addressed in the *Technical Basis* document, but is appropriate to consider given the unique circumstances at Hanford. Since the current state of science relative to toxicology and risk assessment of mixtures and interactions is in flux, the committee does not have any immediate recommendations on how to better address these issues.

The *Technical Basis* document reviewed by the committee is the first revision of the original, and text within the document suggests it will be revised again as new data or methods become available. However, the committee would like to see a more specific timeline for seeking out and incorporating new data and toxicological guidance, such as a review every five years. Periodic review is required to assure that the document and corresponding industrial hygiene practices are informed by the most recent and up to date information.

In summary, with respect to the first question, the committee agrees that the methodology for developing Acceptable Occupational Exposure Levels as described in the *Technical Basis* is generally consistent with industry best practices.

With respect to the second question, the committee concludes that while the risk assessment process described in the *Technical Basis* document is generally sound, its implementation is limited by inadequately representative source and exposure data. As a result, the committee is unable to conclude that the protective measures are sufficiently conservative to protect worker health. There are several areas in the *Technical Basis* where there is significant uncertainty in sampling data. One area in particular deals with the impact of waste disturbing activities on the emission characteristics of a tank over time. The committee has identified several opportunities where the approach outlined in the *Technical Basis* document could be made more conservative, i.e., more protective of workers, by reducing uncertainty.

1. Re-evaluate the COPCs by implementing a more statistically representative tank head space sampling strategy
2. Reconsider the thresholds in the development of screening levels (1% not 10%);
3. Consider all carcinogens (IARC Groups 1 and 2) detected or known to be in waste tanks as COPCs;
4. Apply the revised COPC list to a systematic and statistically representative sample strategy to characterize area, source, and personal exposure across the tank farm.
5. Develop a timeline for future program reevaluation (including seeking out new information that would impact OEL setting);
6. In a continuing effort to reduce the inherent and existing uncertainties in dealing with complex mixtures, and the possibility of toxicological interactions, follow closely new developments suggested and adopted by the scientific community.

The goal of the *Technical Basis* Document - “to identify all chemicals within a waste vapor source that are potentially hazardous and might be released into worker breathing zones” - is an ambitious, laudable and appropriate goal. However given the limitations of input data the committee does not feel that this goal is currently being met.

INTRODUCTION

The Hanford Concerns Council (HCC) provides a forum for resolving conflicts regarding workplace health and safety issues between workers and employers at the Hanford site. In 2007, the HCC commissioned a committee of experts in three areas of occupational health (toxicology, occupational medicine, and industrial hygiene) to evaluate the occupational health and safety evaluations conducted by CH2M HILL Hanford, as outlined in CH2M HILL Hanford's Industrial Hygiene Chemical Vapor Technical Basis, Rev. 1 (hereby referred to as the *Technical Basis* document).

The purpose of the review is to determine if the *Technical Basis* document is 1) consistent with industry best practices for setting exposure limits based on the prescribed methodologies of organizations such as OSHA, NIOSH, and ACGIH, and 2) is sufficiently conservative to be protective of workers, particularly during waste disturbing activities. The committee was asked to specifically focus on CH2M HILL Hanford's hazard evaluation outlined in the *Technical Basis* document and not on the subsequent implementation of risk management programs. This report is the product of the review by the committee.

The committee's main interface with CH2M HILL and worker advocates was through a subcommittee of the HCC, comprised of a balanced representation of independent members, company representatives, and worker advocates. In September 2007, the HCC subcommittee provided the expert committee with a package of documents that support or are relevant to the *Technical Basis* document (See Appendix A). On September 24, 2007, the committee met with members of the Hanford Concerns Council, CH2M HILL representatives and representatives of the Government Accountability Project (GAP) (now Hanford Challenge) in Kennewick, WA. The next day, committee members toured the Hanford Tank Farm site. During the next weeks, the committee discussed the project in several conference calls and developed an initial scope of work. This original scope was reviewed by a Council subcommittee as well as GAP and company representatives and further modified by the committee.

The final scope of work centers on two major assumptions identified by the committee that form the basis of the *Technical Basis* document; they are provided below. For each of the two major assumptions, the committee developed a series of questions that explored the fundamental aspects of the assumptions. The questions serve as a vehicle for responding to the task the committee was given – to evaluate whether the approach in the *Technical Basis* document is consistent with industry best practices for setting exposure limits, and whether these standards are sufficiently conservative to be protective of workers during a range of activities (e.g., waste-disturbing, quiescent, etc.).

The members of the committee then responded to the specific questions posed in the scope of work according to their professional expertise. During this process, committee members evaluated the CH2M HILL documents provided at the outset of the review and, where necessary, other documents available in the scientific literature. The following review reflects the consensus of the committee.

Based on the statement of work defining the scope of the committee's review, the following outlines the assumptions and corresponding questions related to the *Technical Basis* document.

Assumption No. 1:
The document has been developed under the premise that the results (database) of headspace sampling are adequate, reproducible and predictive of the universe of chemicals to which workers might potentially be exposed.

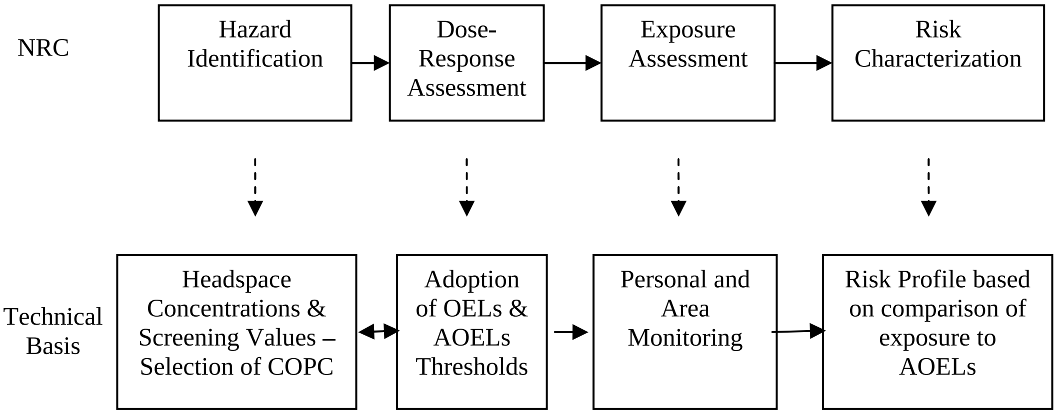
Assumption No. 2:
The document is based on the assumption that existing (available) TLVs®, PEL's etc., developed by national or international bodies (ACGIH, OSHA, NIOSH, MAK committee) are adequate or, where absent or no data are available, can be developed by interpretation of existing toxicological data or, where absent for specific agents, by using information on surrogate chemicals. In addition, the document appears to suggest that the monitoring of concentrations of chemicals released into the breathing zone of workers (under any circumstances), will provide the necessary data to estimate (or document) the absence or presence of hazard or risk of adverse health effects.

Background discussion

The stated purpose of the *Technical Basis* document is to "identify all tank vapor chemicals that are hazardous or might be hazardous in tank headspaces and could reasonably be postulated to be released into [tank farm] worker breathing zones." This is an appropriate and ambitious goal.

Conceptually, the *Technical Basis* document describes a risk assessment process that is similar to the four-step risk assessment process described by the National Academy of Sciences (and adopted by the Environmental Protection Agency and other agencies) for evaluating toxic substances in the environment (National Research Council, 1983). The *Technical Basis* document includes three of the four standard risk assessment steps: hazard identification (head space characterization and toxicity assessment), dose-response assessment (selection of exposure limits) and exposure assessment (area and personal sampling) (**Figure 1**). In a larger context, worker protection involves three components, risk assessment, risk management, and risk communication. A lesion in any of the three components can lead to inadequate worker protection. Risk assessment is a key component because all risk management and communication decisions are based on having a defensible risk assessment. While the committee focused on the risk assessment component of the process described in the *Technical Basis* document, it should be emphasized that a comprehensive review of worker health and safety would include an assessment of worker protection (risk management) and hazard communication.

Figure 1. Comparison of the National Research Council's (NRC) Risk Assessment Paradigm to the approach taken in the Technical Basis



The fourth step of the codified risk assessment process is risk characterization, which is the estimate of risk based on the three previous steps. Risk characterization is accomplished by comparing measured exposures to the exposure limit for each chemical. Risk management (controls and/or personal protective equipment) decisions are subsequently based on the results of the risk characterization. The *Technical Basis* document is intended to provide much of the underlying information needed for the risk characterization and subsequent risk management decisions. Figure 5-1, reproduced from the *Technical Basis* document on the following page, provides a decision making tree that outlines the detailed risk assessment process performed by CH2M HILL.

In the process of risk assessment of sites with particularly hazardous and toxic materials, special attention must be paid to unpredictable yet potentially critical events despite their low probability of occurring. For this reason, it is important for the risk assessment process at the Hanford site to be sufficiently conservative, i.e., err on the side of being overly protective.

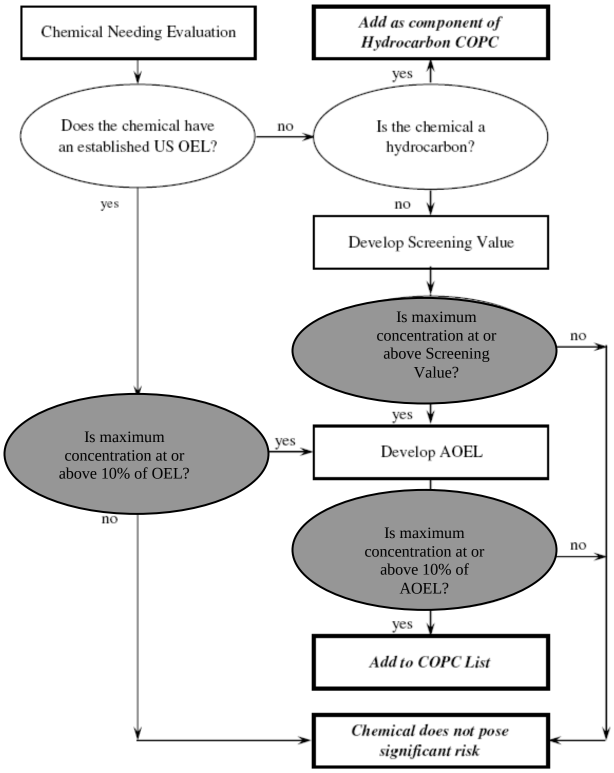
Hazard identification is a crucial first step in the risk assessment process. In this step, chemicals with the potential to cause adverse health effects are identified. If the risk characterization fails to identify the correct universe of chemicals, subsequent risk characterization will be incomplete and risk management decisions may be inappropriate. The process of evaluating the chemicals that are detected or may exist in the Hanford tanks for the potential to cause health effects is described in the *Technical Basis* document and is summarized in Figure 5-1 (reproduced on the following page).

The process summarized in Figure 5-1 is the cornerstone of the *Technical Basis* Document. The database of chemicals in the tank farm and their concentrations are used as the starting point to identify chemicals needing evaluation. The endpoint of the process is the list of Chemicals of Potential Concern (COPCs), chemicals with the greatest potential to enter a worker's breathing zone at hazardous levels; and a list of Acceptable

Occupational Exposure Limits. As mentioned above, the first step in CH2M HILL's approach was to use the results from tank headspace sampling to determine the universe of chemicals that a worker could be exposed to, i.e., chemicals that could potentially be released from the tanks.   Head space sampling in the tank farms presents numerous sampling and analytical technical challenges that are described in *Technical Basis* report as well as the supporting documents.

Briefly, samples were collected in the tank headspaces and analyzed for chemicals known or predicted to exist in the headspaces, as well as chemicals that are particularly hazardous (e.g., dimethyl mercury). Samples were collected using standard industrial hygiene methods, including SUMMA canisters, triple sorbent traps, and impingers. The analytical methods used by the analytical laboratories were usually gas chromatography coupled with mass spectrometry, which can detect a wide range of organic chemicals. For some chemicals that are not as well detected using the standard methods, particularly low molecular weight organics and metallic compounds, more targeted analyses were conducted (CH2M HILL Hanford Group, 2006a).

Figure 5-1. Toxicological Evaluation Logic Diagram



In their effort to identify all possible hazards in the tank farms, CH2M HILL started with a list of approximately 1800 chemicals that were detected or anticipated to exist in the tank headspaces. Critical analyses of sampling results and analytical methods reduced this list to approximately 1400. The chemicals removed from the list included duplicate entries, chemicals that were contaminants in the analytical methods, and chemicals with low probability of exposure. Sampling for all of the remaining chemicals in the breathing zones of workers would be prohibitively expensive and cumbersome. Thus, CH2M HILL used a screening approach to determine which chemicals could potentially enter the workers' breathing zone at hazardous levels. The headspace sampling data for each chemical was compared to a screening level developed for each chemical (discussed later in this report), which was either 10% of a United States Occupational Exposure Limit

(OEL)[1], 10% of a surrogate chemical's OEL that was modified (lowered) by safety factors, or, in cases where no appropriate surrogates existed, was based on a toxicologist's expert judgment (CH2M HILL Hanford Group, 2006a).

Chemicals that exceeded the screening level and did not already have a United States OEL were assigned an Acceptable Occupational Exposure Limit, (AOEL). Chemicals whose maximum headspace concentration exceeded 10% of the AOEL or OEL were deemed Chemicals of Potential Concern (COPC) and were targeted in industrial hygiene surveys and subsequent risk characterization (Figure 5-1).

Three key steps in Figure 5-1 are highlighted with shaded circles. These steps are key gatekeeper operations that are used to relegate chemicals to the COPC list or remove them from subsequent risk consideration. These boxes all state that a chemical will not be considered a COPC if the concentration is less than 10% of screening limit, OEL, or AOEL.

Assumption No. 1: The adequacy of the database

The following questions may be asked about Assumption 1:

- *Are the analytical results of the headspace sampling performed to date suitable to provide information on varying (random) conditions such as quiescent and waste disturbing activities?*

The *Technical Basis* document describes a great deal of effort dedicated to developing defensible sampling procedures. As a result, sampling and analytical biases are well characterized. In addition, there has been a large amount of head space sampling conducted over the last ~20 years. These data are extremely valuable for hazard identification purposes. It is not clear, however, if the range of possible head space concentrations have been identified.

The question of whether the sampling conditions are representative of varying conditions is directed at two important issues. The first issue is whether the samples represent the variations in tank waste chemistry (especially following waste disturbing activities) which may lead to changes in the chemicals found in the headspaces. Specific properties of chemicals (e.g., vapor pressure, specific gravity, reactivity, etc.) may influence the conditions under which they are volatilized. In addition, ambient temperature extremes may also impact volatility. Volatility can be greatly affected by the amount of water in each tank. For example, substances with low water solubility and

---

[1] In general, for this report, a United States OEL refers to an OEL issued by the American Conference for Governmental Industrial Hygienists (ACGIH), referred to as Threshold Limit Value (TLV®), or by the Occupational Safety and Health Administration (OSHA), referred to as a Permissible Exposure Limit. (PEL). In some cases, Workplace Environmental Exposure Limits (WEELs), issued by the American Industrial Hygiene Association (AIHA), have also been used.

specific gravity greater than 1.0 (like carbon tetrachloride and methylene chloride) will be largely capped by the water layer. As the water levels drops or if the water layer is disturbed, these and similar substances will be released at a greater rate. The second issue is whether the peak concentrations found during headspace sampling truly represent an upper limit to the concentrations, such that the comparison to a screening level is justified.

According to the *Technical Basis* document, headspace samples have been collected in 118 of the 149 single shell tanks (SSTs) since the 1990s (CH2M HILL Hanford Group, 2006a). Forty-four tanks have been sampled two or more times. The maximum number of times a tank headspace has been sampled was 10, with an average of 1.4 times across the 149 tanks. Neither the *Technical Basis* nor the supporting spreadsheet data provide a description of the condition of the tanks during sampling, or at what stage in the retrieval process they were (CH2M HILL Hanford Group, 2006a, 2007d). While it is likely that these samples were collected under a variety of conditions so as to support further waste chemistry analysis that has been conducted (e.g. Pacific Northwest National Laboratory, 2005), the sampling described in the *Technical Basis* document does not appear to have been conducted using a sampling strategy specifically designed to answer the question posed above. The fact that not all tanks have been sampled and less than 30% of the tanks have been sampled more than once suggests that there was not a systemic comprehensive strategy employed to characterize head space variability over time either during quiescent conditions or during waste disturbing activities.

Furthermore, although mixing and sharing of tank constituents and headspaces has occurred between tanks, many chemicals have only been identified (or tentatively identified) in one or a few tank headspaces (Pacific Northwest National Laboratory, 2004). Waste-disturbing activities have been shown to greatly impact headspace concentrations found in the tank (CH2M HILL Hanford Group, 2006d; Pacific Northwest National Laboratory, 2005). If the tanks are assumed to have similar chemistries, then the current headspace inventory may be adequate. However, sampling data suggest that they have differing chemistries, and the sampling that has been conducted may not capture all of the headspace constituents or the upper concentration range of headspace constituents.

In conclusion, a great deal of effort has been directed at characterizing the tank headspace concentrations. The analytical methodology used to identify and quantify chemicals in the samples is judged to be state-of-the-art. However, uncertainties with respect to the ability of the data to describe variability within and between tanks still exist. As a result, the committee is not convinced that the headspace characterization is truly conservative, i.e., that the upper range of headspace concentrations have been identified. This is important because these sampling data are key inputs to the risk assessment process with respect to selection of COPCs. Sampling results that under-report chemical concentrations in the tank head space will result in the inappropriate exclusion of a chemical from the COPC list.

A more conservative approach would address these uncertainties with a more comprehensive headspace sampling plan aimed at capturing the range of concentrations that may exist in the tanks over time and at different stages in the retrieval process (e.g., waste-disturbing conditions). Statistical calculations would be needed to determine the sample size needed to reach the desired confidence level and power. Additional analysis of the existing data (or future data) may support pooling data from tanks that are demonstrated to have similar chemistries, reducing the number of samples needed. However, the current revision of the *Technical Basis* does not provide any data supporting pooling tank data. The committee therefore recommends that a statistically justifiable tank head space sampling strategy be developed and implemented to characterize the variability of head-space concentrations within and between tanks. Particular attention should be paid to temporal changes within a tank after waste disturbing activities.

- *Do the current sampling data capture the right universe of chemicals for setting OEL's?*

When evaluating a site for hazardous vapors and gases, the best evaluations will determine which chemicals are to be included in the analysis *a priori*, such that sampling times, volumes, and standards can be selected that maximize the accuracy of the analysis. The waste present at the Hanford Tank Farms is known to be reactive, radioactive, and heterogeneous, making it difficult to predict the identities and quantities of the gases and vapors in the tanks with any degree of certainty. CH2M HILL (and their contractors) screened tank headspace gas and vapor concentrations to determine which chemicals may enter worker breathing zones at hazardous levels and then developed occupational exposures limits for those chemicals. They took several steps to maximize their ability to predict and measure headspace chemicals, which are outlined in detail in the *Technical Basis* document. The methodology that was adopted is reasonable in light of the uncertainty about what exists or may form in the tanks. In general, gas chromatography with mass spectrometry is the state-of-the-art method for detecting chemicals in a complex air sample.

There are two categories of error in sampling or interpretation that could lead to misidentification of the universe of gases and vapors inside the tanks that may be hazardous. One type of error would exist if some chemicals were not identified or were misidentified, resulting in the wrong universe of chemicals being evaluated in subsequent steps of the risk assessment process. An additional source of error would exist if the concentrations of chemicals were underestimated, such that some chemicals may be incorrectly assumed to be below screening levels and ultimately not included on the COPC list.

The first type of error (in identification of chemicals) is unlikely given the analytical methods employed. The second type of error may be more likely, since it is not clear, as discussed above, that the full range of possible headspace concentrations is known. Another reason for the underestimation may be due to sample handling and storage issues. For example, as noted in the NIOSH Health Hazard Evaluation, some samples were stored for weeks or months prior to analysis, which may have allowed time for some chemicals to breakdown or react (CH2M HILL Hanford Group, 2007a; National Institute for Occupational Safety and Health, 2004). Although these issues have been resolved since 2004, it is not clear how much of an effect sample storage issues may have on data quality and subsequent interpretation of samples collected prior to 2004, with respect to COPCs and other tank waste chemistry analyses.

In conclusion, the committee feels the technical aspects of sampling and analysis were appropriate. However, as discussed above, there is some concern that the quantities of some chemicals may have been underestimated, leading to their not being included on the COPC list. As a result, the committee is not confident that the current sampling data capture the right universe of chemicals for setting OEL's.

The previous section provides an outline of how increased certainty in the headspace concentrations could be achieved. It is expected that the sample handling issues have already been addressed by CH2M HILL following the issue of the NIOSH Health Hazard Evaluation (National Institute for Occupational Safety and Health, 2004) and other reviews of the industrial hygiene program. To determine whether and what effects delays in analysis (prior to 2004) may have caused on chemical measurement, it is recommended that identical samples be collected, analyzed at several time points (e.g., 1 day, 2 weeks, and 5 weeks), and the results compared to assess the impact of sample storage.

Further, similar to the suggestions above, the committee recommends that a statistically justifiable tank head space sampling strategy be developed and implemented. In addition, it is suggested that the COPC list be reconsidered as new sampling data become available.

- *Does the technical basis provide adequate evidence that the tank "exhalations" are fully characterized or negligible?*

CH2M HILL has performed several evaluations to address the potential for tank exhalations. For the most part, these evaluations have suggested that the tanks exchange vapors and gases with the atmosphere, which, under steady state tank conditions, is due to meteorological factors (wind, barometric pressure, and buoyancy forces). Investigations of the causes of large gas releases in the tanks have suggested that large releases are unlikely in the absence of waste disturbing activities.

Sampling during the A- and S- Prefix Tank Farm vapor characterization surveys were conducted while the tanks were exhaling, such that the samples collected are assumed to correlate with what is expected during typical tank exhalations. The magnitude and duration of tank exhalations could presumably vary over a wide range. In the final pages of the A- and S- Prefix Tank Farm vapor characterization surveys, readouts from direct reading instruments suggest that VOC concentrations can vary by orders of magnitude at the breather filter. Tracer gas measurements, collected over days to weeks, have also been used to characterize tank exhalation.

The tank farm sampling reports (CH2M HILL Hanford Group, 2006b, 2007c) describe a sound sampling strategy for characterizing tank exhalations and relating them to breathing zone concentrations. It is not clear from the data presented however, how many samples have been collected and how often the sampling has been repeated (see next question). Thus, without more supporting information, it is not clear whether the tank exhalations are truly characterized.

Similar to the head-space sampling discussion, the technical methods employed to characterize exhalation scenarios (both their existence and resultant chemical concentrations) are rigorous and state-of-the-art. However, this area, like others, lacks a clear sampling strategy that includes sample size calculations as well as temporal and spatial sampling plans. The fact that tanks are not always exhaling, and that the extent of exhalation varies, makes such sampling difficult, however not impossible.

The committee recommends that a statistically justifiable sampling strategy be developed and employed to fully characterize the range of concentrations during tank exhalation.

- *What is the proposed sampling strategy? Will it (or has it already) provide(d) adequate data for statistically meaningful estimates of worker exposures?*

The industrial hygiene data are comprised of several elements including source, area and personal measures. The sampling data are presented in the *Technical Basis* document by time periods. While it is clear that a large amount of data were collected, it is difficult to ascertain the representativeness of the sampling in terms of source, area or personal measurements. It is comforting to note that the data suggest there are not consistent patterns of elevated personal exposures. In some cases, the *Technical Basis* report refers to sampling without mention of location making a global interpretation of the sampling results difficult.

More recent data from the A- and S- Prefix Tank Farms are more readily interpretable. The results from area sampling in the A- and S- Prefix Tank Farms indicate that workers are not exposed to COPCs in concentrations in excess of the ACLs (Administrative Control Limits) outside of the Vapor Control Zone. (It should be noted that no personal samples were collected in these two exposure assessments). While the general strategy with respect to the types of samples to be collected is sound, the data from the A- and S-Prefix tank farms (CH2M HILL Hanford Group, 2006b, 2007c) do not contain a statistical justification for the number of locations to be sampled, or the number of repeat measures to be collected. For example, the A-farm report indicated 3-breather filters were sampled at a distance of 5 feet on one occasion each. Between the A- and S-farms, it appears that samples were collected at one time in a 5 foot radius for five breather filters out of 18. Limited statistical inference can be garnered from these data in terms of average, ranges or other measures of variability.

Area and breathing zone concentrations during waste-disturbing activities were not evaluated in this review. According to CH2M HILL, workers wear high-level respiratory protective equipment during waste-disturbing activities (e.g., supplied air), therefore, assuming the equipment is used properly, respiratory exposures can be expected to be minimal or non-existent during these activities. However, waste disturbing activities may change the profile of chemicals exiting the breather filter over time. It is therefore important to recognize that disturbing activities are not static events and can result in changes to the physicochemical properties of the chemical mixtures that might result in gradual changes in exhalation chemical profiles over time. Sampling should be conducted during waste disturbing activities to assess the concentrations during these activities and for a period of day's afterward to assess any changes over time.

In conclusion, the source, area, and personal monitoring represent a technically defensible approach to estimating worker exposures. A more systematic evaluation is needed to characterize the variability of concentrations that may exist spatially and temporally. This could be accomplished by collecting additional samples at several sites and at more time points, with the goal of characterizing all of the tank farms. Another limitation is derived from the discussion above with respect to COPCs. If the initial hazard assessment failed to identity the appropriate universe of COPCs, then the sampling strategy will have the same limitation.

Inadequate head space and breather filter concentration databases can result in an incomplete list of COPCs. While the committee feels that the risk assessment process described in the *Technical Basis* is sound, there is concern about the adequacy of the data used to implement the process and make decisions about worker health and safety. The committee recommends that a statistically justifiable strategy that includes area, source, and personal monitoring be created and implemented. The strategy should include any new COPCs that are identified.

- *What are the implications of a sensitivity analysis on the predicted levels of chemicals and mixtures? Is a cut-off of 10% of the screening level adequate?*

In the *Technical Basis* document, CH2M HILL used a threshold approach to determine which chemicals would be included on the updated COPC list. The original COPC list of 52 chemicals was re-evaluated and about 1400 chemicals detected in headspaces that were in need of further evaluation (CNFEs) were considered for inclusion in the updated COPC list. Of these, about 700 were hydrocarbons and were assessed as a mixture, per recommendation by a toxicologist specializing in hydrocarbons.

Some of the original 52 COPCs were removed from the COPC list because their maximum reported headspace concentrations were below 10% of their OEL. Many of these had originally been included because they were carcinogens; upon toxicological evaluation, the established OELs were deemed protective for cancer effects and the 10% threshold was applied. For the CNFEs that did have United States OELs, a threshold of 10% of the appropriate United States OEL was used to determine whether each chemical should be added to the COPC list. There were 131 CNFEs detected in the tank for which United States OELs were available (WEELs, TLVs®, PELs) (CH2M HILL Hanford Group, 2006a see Appendix C). The chart below (**Table 1**) provides an analysis of how the number of chemicals exceeding the threshold increases as the screening level (fraction of the OEL) is lowered.

Table 1. *Sensitivity analysis for chemicals with OELs (WEEL, TLV®, PEL)*

Cutoff (% of OEL)	**Number of Chemicals Greater Than Cutoff**
10	2
7.5	4
5	10
2.5	20
1	40

Using 10% of the OEL as a threshold for inclusion of chemicals on the COPC list is not as conservative as using 1% of the OEL, since there are 38 chemicals whose headspace concentrations are between 1% and 10%. Factors of 10 are frequently used in risk assessment to account for uncertainty and are considered a conservative approach. They are usually assigned for a specific type of uncertainty (e.g., inadequate data, variability in response between individuals, etc.). For one calculation, several factors of 10 may be applied, resulting in a net 100 or 1000 fold reduction in exposure limits (Hattis et al., 2002). The application of uncertainty factors is one of the controversial areas of risk assessment, with proponents on both sides of the issue: some argue that using several factors of 10 is unreasonably conservative (e.g., not having a scientific basis), while others argue that humans vary by more than a factor of 10 in response to environmental agents. In general, the greater the uncertainty, the greater the health concerns and the greater the value of uncertainty factors applied.

As previously stated, a conservative risk assessment will err on the side of being overly protective as a precautionary principle. The analysis presented in this section indicates that the selection of COPCs is highly sensitive to the selection of the screening level, as demonstrated in Table 1 above. For those chemicals with U.S. OELs, lowering the threshold for inclusion on the COPC list from 10% to 1% of the U.S. OEL is recommended, effectively adding 38 chemicals to the COPC list. This increase in the number of COPCs included in exposure and risk assessment is consistent with a more conservative approach.

Finally, as a conservative approach, it is recommended that all known or suspected human carcinogens (IARC Groups 1 and 2) detected in tank headspace sampling be included in the list of COPCs regardless of screening level or measured concentration. This is not only a more conservative approach; it will allow CH2M HILL to document the level or absence of exposure to these chemicals for purposes of medical monitoring or informing workers.

Overall conclusion for Assumption 1.

Although the technical methodologies employed in the development of the *Technical Basis* are sound, there are several areas where the approach presented in the *Technical Basis* can be made more conservative. These are:

- Re-evaluate the COPCs by implementing a more statistically representative tank head space sampling strategy;
- Reconsider the thresholds in the development of screening levels;
- Apply the revised COPC list to a systematic and statistically representative sample strategy to characterize area, source, and personal exposure across the tank farms;
- Develop a framework for periodically updating the *Technical Basis* document to reflect new data, as well as the interpretation of the new data.

Assumption No. 2: The adequacy of the methodology for setting exposure standards

The following questions can be asked:

- *Is the acceptance and application of existing TLVs®, OELs etc. consistent with regulatory requirements and industry best practices?*

The *Technical Basis* document (CH2M HILL Hanford Group, 2006a) provides a list of 48 chemicals of potential concern (COPC Table 5-1, p. 40). COPCs have been defined as chemicals whose concentration, measured in tank headspaces, exceeds administrative control limits (ACL), i.e. a concentration that calls for an appropriate monitoring procedure. ACLs have generally been set at 10% of an occupational exposure limit. This procedure follows established DOE implementation procedures.

Table 5-1, page 40 in the *Technical Basis*, lists the COPCs (or classes of COPCs), the proposed Tank Farm Occupational Exposure Limits (OELs) and the sources on which these values are based. Out of 48 listed compounds, the OELs for 17 agents, including some carcinogens (e.g., benzene, formaldehyde) have been set according to TLVs® or ceiling values developed by ACGIH, while the OEL for 1,3-butadiene represents the OSHA PEL. For another 13 agents, OELs have been derived by looking up existing TLVs® (developed by ACGIH) of compounds that might serve as reasonable surrogates for the agent in question (e.g. butyl nitrate, chlorinated biphenyls or methyl nitrite). The surrogates that were selected usually had a robust toxicological data base. In addition, all available toxicity data for the compounds that did not have an established TLV were scrutinized. Based on this analysis, the TLVs derived from the surrogate compounds were modified by additional safety factors

For 10 agents, threshold values have been taken from standards set by other bodies, such as NIOSH (RELs), the American Industrial Hygiene Association (WEELs), DOE or the German MAK Commission (e.g., butanal, heptanenitril). For one rather large group of agents, collectively labeled as "hydrocarbons", the AOEL is set identical with the TLV® (ACGIH) for kerosene. For 3 carcinogenic nitrosamines, AOELs have been developed by a consultant, using established EPA or CalEPA information and methodology and assuming an acceptable risk of 10^{-4} (Ch2M HILL Hanford Group, 2005; Intertox, 2006). AOELs for furan were set by taking into account the results of a NTP bioassay. The data used for determining COPC exposure limits can be summarized as follows (the numbers correspond to the individual agents listed in table 5.1., page 40, in the *Technical Basis*)

Table 2

Existing TLVs® (ACGIH or [1)]OSHA)	**AOEL based on existing TLV® taken as surrogate**	**OEL developed by other bodies (MAK, WEEL)**	**Others (Hydrocarbons, some carcinogens)**
1**, 2** [1)], 5, 10, 14, 18, 19, 20, 21, 28, 29, 30, 31, 37, 38, 39, 41, 47, 48	3, 4, 9, 11, 13, 15, 16, 17, 24, 25, 26, 27, 40	6, 7, 8, 12, 22, 23, 34, 35, 45, 46	32, 33, 36, 42, 43, 44

The process of establishing the AOELs has been clearly outlined and the submitted documentation is a thorough and well written document. The proposed AOELs in Table 5-1, with the exception for furan, have all been derived from numbers developed by thorough analysis of primary data and their interpretation through deliberations of committees. The recommendations of these committees (e.g. the ACGIH TLV® Committee, the German MAK Commission) are widely accepted and followed by industry. Adherence to these standards reflects best practice in Industry.

- *Are the exposure limits (standards) sufficiently conservative to be protective of workers?*

- *Has it been taken into consideration that certain TLVs® may have been developed some time ago and that there might be new information which could lead to a modification of the existing values?*

It is generally assumed that the TLVs suggested by ACGIH are conservative enough for the protection of workers. However, they do not represent a fine line between a healthy versus an unhealthy work environment. Some individuals can experience discomfort or even more serious adverse health effects when exposed to chemicals at the TLV® or even at concentrations below the TLV® (ACGIH, 2007). Also, as discussed by Roach and Rappaport (1990) and Rappaport and Kupper (2008), when the TLVs that are followed are actually based on human data (such as "industrial experience" or experimental human studies), often a surprisingly high percentage of workers may experience adverse health risks.

It is generally known that some TLVs® have been developed some time ago and that existing values might need modification whenever new toxicological information becomes available. The ACGIH TLV® committee attempts to do this on a regular basis, although intervals between revisions can be quite long. For example, an analysis of the 1991-1992 TLVs® showed a median age of 16.8 years (Rappaport, 1993). It is also notable that OSHA does not lower PELs except under extreme circumstances. Nevertheless, the activities of standard developing bodies should be followed closely for such updates and the toxicological experts involved in the development of the COPC list should be regularly consulted for eventual updates.

In conclusion, acceptance of existing TLVs® and PELs generally reflects current industry's best practices. The existing standards on permissible exposure levels are generally considered to be health protective of workers. It must be emphasized, though, that many standards have been developed several years ago and actually could be out of date. As more information will eventually become available, new developments will need to be considered. This will require that continuous attention is paid to all updates issued by ACGIH or other standard setting bodies or pertinent new toxicological information and to make corrections or modifications to the *Technical Basis*.

- *Is the mixture rule set forth by OSHA and other bodies (e.g., Committee on Toxicology, NRC) really applicable? Given the large number of identified chemicals in headspace vapors, are these standards applicable relative to the tank farms at Hanford?*

In general, exposure standards for the public at large (e.g. for common air pollutants such as ozone or nitrogen dioxide) or for industrial exposures (e.g., benzene, formaldehyde) are developed based on available toxicological data from animals and, preferably, human data. On occasion, they are backed up by toxicokinetic and toxicodynamic considerations, and, where appropriate, supplemented by mechanistic information. In reality, the general population is exposed to mixtures, such as "air pollution" or environmental tobacco smoke and, in the case of the Hanford workers, to atmospheres of a mixture of a large number of potentially toxic agents.

The question of how to deal with mixtures is one that toxicologists have grappled with for some time. From an experimental standpoint, it is very difficult to design studies with several agents. Such experiments can become very complex very quickly and impractical to do. For example, to properly study a quaternary mixture (4 agents and this at one dose and for one exposure time only), a total of 16 experimental groups would be required to cover all possible combinations. In practice, this means that animal experiments assessing the toxicity of mixtures are often conducted with the mixture itself (e.g., cigarette smoke, diesel exhaust emissions). For setting general population and workers exposure levels, rules have been developed based on general assumptions and/or detailed knowledge of dose-responses and mechanisms of action. A key concept, as formulated by the US EPA in 2000 is "additivity", used "when the effect of the combination of chemicals can be estimated directly from the sum of scaled exposure levels (dose addition) or the individual components" (quoted in Boekelheide, 2007).

The concept of additivity has essentially been adopted in the OSHA "mixture rule," as explained in the document "Industrial Hygiene Exposure Assessment Strategy"(CH2M HILL Hanford Group, 2007b). Essentially, this rule embraces the concept of additivity by postulating that if the sum of C1/T1 + C2/T2 + ……..Cn/Tn is not bigger than 1 (C defining observed atmospheric concentration and T indicating the corresponding OEL), then an OEL has not been exceeded. The additivity rule applies to chemicals with similar organ system toxicity. This has been adopted in the CH2M HILL documents. It should be noted, however, that for headspace measurements the mixture rule, thanks to the large number of chemicals, is easily exceeded. For example, in the document "Proposed Approach to Establishing Limits of Exposure to Hydrocarbon Vapors…..(United States Department of Energy, 2006), verification of the mixture rule for Table 1 alone shows a value considerably greater than unity (i.e. 8.45). However, it must be emphasized that these are headspace concentrations, not necessarily reflecting breathing zone conditions.

In addition to the US EPA and OSHA, the concept of additivity has also been endorsed and/or used in the NRC Report "Complex Mixtures," (National Research Council, 1988) the Presidential/Congressional Commission on Risk Assessment and Risk Management (National Research Council, 1997) and NASA (NASA Toxicology Group, 1999) in setting maximum allowable concentrations for airborne contaminants in spacecraft (SMACS). NASA explicitly applies the same formula as the OSHA rule.

It is impossible to ascertain that adherence to the mixture rule will be protective, given the high number of chemicals. One (if not the only one) study that dealt experimentally with exposure of animals to a mixture of 9 chemicals (Groten et al., 1997) concluded that "simultaneous exposure to these 9 chemicals does not constitute an evidently increased hazard compared to exposure to each of these chemicals separately, **provided the exposure level of each chemical in the mixture is at most similar or lower than its own NOAEL"** (emphasis added). Relative to the conditions at the Hanford Tank Farms, it can easily be calculated that, at least in headspace atmospheres, it is possible to reach values above unity. However, CH2M HILL fully acknowledges the problem and has identified 7 S-Tanks sources whose mixture occupational exposure limit is equal or greater than 0.5. These vapor sources are to be considered vapor hazards within 5 feet of the source.(CH2M HILL Hanford Group, 2007c).

A group of toxicologists associated with the TNO Nutrition and Food Research Institute in the Netherlands postulated in 1995 that a challenge for toxicology would be to gradually substitute mixture-oriented (real life-oriented) standard setting for (unrealistic) single chemical-oriented standard setting (Feron et al., 1995). Twelve years later it was pointed out that mixture toxicology would require "big science" where projects at first would be highly descriptive, a large amount of background information and resources would need to be available over a considerable period of time (Boekelheide, 2007). Given this situation, application of the mixture rule by CH2M HILL at present seems justified as a default option. It must be noted, however, that currently the ACGIH is in the process of developing a somewhat different mixture rule, based essentially on a paper published by McKee et al. (2005).

In conclusion, the mixture rule can be accepted as a default procedure. Therefore, its utilization in the *Technical Basis* is consistent with current best practices, but may require modification based on some new ACGIH suggestions which presently are open for comment (ACGIH, 2008)

- *Is the use of surrogates in setting OELs and screening levels appropriate in this situation?*

Surrogates have been extensively used in the setting of screening levels (Pacific Northwest National Laboratory, 2006). Surrogate compounds are either agents that have an established OEL, or agents without an established OEL but that have toxicological data deemed useful in setting one. Using a surrogate to establish exposure standards requires professional judgment in the rationale for selection of surrogates. The following comments are based on the assumption that screening values are set at 10% of an existing OEL. Screening values serve to trigger additional investigation for potential adverse effects if the screening value measured for any given agent in the tank headspace is exceeded.

It was postulated that screening values should be 10% of permissible occupational exposure levels, although the sensitivity analysis in Table 1 above strongly suggests that perhaps a lower cut-off point would be more conservative (see page 15) Screening values were developed for many chemicals identified in tank headspace that had no established OEL (either by the TLV® committee or similar bodies), nor was there toxicological information available. Accordingly, screening values often had to be developed by using data from surrogate compounds, i.e. chemicals with similar structures or with similar toxicity.

The rationale for setting these values is explained for each compound (Pacific Northwest National Laboratory, 2006). When surrogates had an established OEL (e.g. TLV®), the screening value was set at 10% of this number, but often decreased by one or two and, on occasion, by three safety factors of 10.

For the following analysis, four tables in the appendix in the document *Screening Values for Non-Carcinogenic Hanford Waste Tank Vapor Chemicals that Lack Established Occupational Exposure Limits* (Pacific Northwest National Laboratory, 2006) were arbitrarily selected: Table A3, Aldehydes and Phenols; Table 8A, Esters, Table A14, Silicone Containing Compound and Table A15, Cyanates, Isocyanates and Peroxides.

Table 3

OEL of the surrogate compound used for screening was established by:	**Table A3**	**Table A8**	**Table A14**	**Table A15**	**Total**
TLV®, WEEL (US)	59	36	2	5	**102**
OELs developed by other countries (UK, Germany, Sweden, Norway, Denmark)	5	12			**17**
Not Applicable	37	1	6	3	**47**

The table shows that 119 agents (71%) used as surrogate compounds had an OEL listed by bodies that routinely develop TLV®s or their equivalents. For the other 47 compounds (29%), which had no OEL values assigned to them by other bodies, screening values were developed based on existing data and/or data from surrogates. Given the large universe of chemicals found in tank headspace atmospheres without toxicity information, the use of surrogates appears to have been reasonable.

The question may be asked to what extent surrogates have been used in standard setting in general and how acceptable the practice is. As far as the ACGIH TLV® Committee is concerned, a TLV® for an agent with no toxicity data was never set by data derived from a surrogate compound. However if there was some (minimal) data, consistent with the surrogate toxicity data, a TLV® might have been set by using both the minimal data and the surrogate data (John Doull, personal communication). MAK values were set in several cases for substances where there were data only for metabolites which are anticipated to be formed in the organism. Examples are methylformiate, ethoxy ethyl acetate or butoxy ethyl acetate.

Thus, there have generally been no situations where surrogates have been used to assess inhalation hazards. The large majority of TLV®s or similar standards have generally been set for individual compounds with sufficient toxicity data. This is understandable since industry most often deals with a few, well characterized inhalation hazards, not necessarily comparable to the Hanford Tank Farm situation. However, there is a field where the surrogate approach has been extensively used: the risk assessment for food additives and other ingredients, which are present in low quantities and, as in the case of natural added ingredients such as oils and flavoring agents, have usually very little, if any, evident toxicity. It has been called the “threshold of concern” approach and has been used by the FDA, FEMA (Flavors and Extract Manufacturers Association), Health Canada and the European Union to evaluate food additives, cosmetics and other agents.

Initially, all of the available toxicity data on the adverse effects of exposure to chemicals are collected, followed by sorting these chemicals by structure and biology into categories (using structure – activity considerations), estimating potential exposures and then determining a threshold or safe dose for each of these categories. New chemicals can then be evaluated by placing them in the corresponding categories. If exposure conditions above the threshold are anticipated, testing is needed; if not, these agents can be given low priority for testing. Recent papers dealing with the subject have been published

(Kroes et al., 2005). Surrogates are thus heavily used in this process. It also might be applicable with regard to the large number of volatile headspace agents.

While surrogates are generally not used to set occupational exposure standards for inhalants, the approach has been used nationally and international for food additives and cosmetics. In view of the relatively unique conditions at Hanford, the use of surrogates is an acceptable default option.

A follow-on question might be to what extent can the estimates derived from surrogates be considered conservative? A look at the safety factors applied in setting the screening values from existing OELs might answer the question. The results are summarized in Table 4 below.

Table 4

Safety factors applied to established OELs	**Table A3**	**Table A8**	**Table A14**	**Table A15**	**Total**
10	4	2			6
100	59	34	2	5	100
1000	4	12			16
n.a.	34	1	6	3	44

The large majority (70%) of safety factors selected was 100 or more, the product of having taken 10% of an established OEL for the surrogate agent plus an additional uncertainty factor of 10. As far as safety factors classified in the n.a. (not applicable column) are concerned, the reason for their selection is spelled out in the “Comments” section of the 4 tables. By and large, safety factors for screening values have been applied throughout to existing or surmised evaluation of potential toxicity in order to use a conservative approach.

A special case for the use of surrogates is outlined in *Proposed Approach to Establishing Acceptable Limits of Exposure to Hydrocarbon Vapor Emitted from Underground Waste Storage Tanks at the Hanford Site* (United States Department of Energy, 2006), dealing with hydrocarbon mixtures. Several hundred hydrocarbons have been identified in tank headspaces. Very little, if any, toxicological data are available for the compounds (all of which have been assigned CAS numbers). The mixtures were compared to fuel streams encountered in petroleum refining operations, and the toxicities assumed to be, in general, solvent toxicity, i.e. anesthesia, sedation or asphyxiation on short term exposure and hepato- and nephrotoxicity, cardiovascular and/or central nervous system damage upon chronic exposure.

These assumptions are logical and reasonable. TLV® values for fuel stream gases have been set by ACGIH; among the TLV®s for three gases (aliphatic gases, gasoline and kerosene), kerosene has the lowest TLV® (29 ppm as opposed to 600 or 300 ppm) and was thus selected as the most conservative number. It can be surmised that, should screening levels for hydrocarbon mixtures be developed; they would follow the standard practice documented above, i.e. application of a safety factor of 100. It must also be emphasized that the approach suggested in the document might be revised in light of the new rules for the evaluation of hydrocarbon mixtures currently under development by ACGIH (ACGIH 2008).

- *Is there a realistic possibility that various chemicals in the mixture might interact and create potentiation of toxic effects or even synergisms?*

This question needs to be addressed at two levels: 1) is it conceivable that various chemicals in a mixture might interact to form more toxic compounds 2) are exposures to several chemicals concomitantly, as in complex mixtures, or sequentially, as in two stage carcinogenesis, likely to produce more harm that can be predicted from the toxicity of the individual chemicals? The first notion is supported by the fact that it is technically possible to produce binary mixtures of two chemicals which, each one by itself is comparatively harmless but, when the two are combined, they might form a highly toxic chemical. This forms the basis of “binary weapons” designed to provide highly lethal war gases only once the ammunition has been used, but not during storage. This possibility can be studied by suitable analysis of tank headspace constituents over time, but as yet, has not been considered in the documentation provided by CH2M HILL. The question of mixtures apparently remains, at present, the issue of some (perceived or real) controversy. Though such a circumstance cannot be excluded, the committee believes that this scenario is exceedingly unlikely.

The second consideration is whether exposure to several chemicals concomitantly, as in complex mixtures, or sequentially, as in two stage carcinogenesis, produces more harm that can be predicted from the toxicity of the individual chemicals. It is generally accepted that such a scenario, involving air, food and water pollutants or drugs can indeed aggravate signs and symptoms of toxicity. A large body of literature describes experimental evidence obtained via properly designed animal toxicity studies. Known examples of human disease produced by putative interactions are the potentiation of organic-solvent induced liver damage by ethanol, substantially increased risk of lung cancer development in smokers by inhalation of asbestos fibers or additive or synergistic toxicity in exposure to mixtures of pesticides.

Two stage carcinogenesis can be considered as another example of interactions where the effects of exposure to two or more agents, even when separated in time, but given in a defined sequence has effects neither agent alone would elicit. On occasion, unexpected results are found, too. For example, exposure to chloromethylether decreases the risk of developing lung cancer from smoking, presumably because increased mucus production in the respiratory tract protects to some extent against airborne carcinogens (Weiss, 1980). Nevertheless, it is not unreasonable to assume that exposure to complex mixtures on occasion might result in the occurrence of toxicological interactions.

The present documentation from C2HM HILL does not attempt to deal in depth with the problem of interactions. This is understandable in view of the complexity of mixtures present in tank headspaces. The Agency for Toxic Substances and Disease Registry

(ATSDR) is in the process of developing "Interaction Profiles" for a rather limited number of chemicals (at least for now). These profiles all use existing data, including information on dose response, pharmacokinetics, metabolism and mechanisms of several compounds and then arrive at some conclusions and recommendations. For example, "exposure to relatively high concentrations of a mixture of benzene, toluene, ethylbenzene and xylene (**above approximately 20 ppm for each chemical;** emphasis added) is expected to increase the potential for neurotoxicity and decrease the potential for hematotoxicity/carcinogenicity due to competitive metabolic interactions among the mixture components."

When the ATSDR web site was accessed (January 2008) it listed 11 finished Interaction Profiles and 2 draft profiles. Each profile analyzes between 4 and 5 compounds; not more. Interestingly, among the compounds analyzed only two were listed in the table "Chemicals of Potential Concern": benzene and formaldehyde, none of them assigned an OEL approaching 20 ppm (0.5 for benzene, 0.3 for formaldehyde).

Toxicological interactions are a reality, but are difficult to predict. There are several current approaches to dealing with the problem in the context of assessing risk for exposure to complex mixtures (de-Rosa et al., 2004; Mason et al., 2007; Teuschler, 2007). However, before it can be postulated that toxicological interactions occur during exposure to complex mixtures, a scientifically plausible and experimentally testable hypothesis and/or data that strongly support such a contention should be available. Given the absence of such data at the present time, the approach outlined in the documentation from C2HM HILL is reasonable.

- *Are carcinogen risk assessments appropriate relative to the OEL's that have been established or proposed?*

An "acceptable" cancer risk for the general population, as used by the US EPA and other agencies, such as CalEPA in their risk assessments, is considered to be 10^{-6}. This number presupposes daily exposures (24 hours a day) over lifetime. This is a very low risk which not only takes into account a prolonged duration of exposure, but also the existence of more sensitive subpopulations, such as children and particularly sensitive people. This approach can be contrasted with conditions met under industrial exposure conditions, where exposure to a putative carcinogen is more likely to occur only intermittently during 8 working hours per day, for 250 days per year and for a working life of 40 years.

Also, "acceptable" risks for a given exposure may be higher, in the range of 10^{-3} to 10^{-4}. The US EPA has developed a formula (quoted in the *Technical Basis*, Appendix G) to assess human risk for these conditions. According to the *Technical Basis* document, calculating OELs with a risk of 10^{-3} yields values that are close to or similar to many OSHA PELs (permissible exposure levels). To use this formula, as CH2M HILL has in the *Technical Basis* document, to calculate risk at the 10^{-4} level is thus a conservative approach, particularly in view of the fact that tank farm workers might not be exposed for all of 250 days per year, given vacation time and training sessions, and the intermittent nature of specific work tasks that may incur opportunity for exposures.

The list of COPCs contains several known or suspected human carcinogens. For 3 of them (1,3-butadiene, benzene and formaldehyde), OELs developed by OSHA or ACGIH have been used. The list also contains 3 nitrosamines. OELs for these compounds have been based on standards set by the German MAK Commission and by the Netherlands MAC (values for NMEA and NDMA). Both of these bodies are comparable to the ACGIH TLV® committee. For the third nitrosamine, N-nitrosomorpholine, an AOEL has been developed by taking into account the relative potency of this agent compared to NMEA, an agent for which an OEL has been developed. NMEA was assigned a "potency" of 1 and OELs for the other nitrosamines were calculated according to the available information on their relative potencies.

It can be concluded that the OELs for carcinogens have been calculated in a manner consistent with the use of conservative OELs (Intertox, 2006). There seems to be, however, one discrepancy in *Recommendations for Acceptable Occupational Exposure Levels (AOELs) for Selected Nitrosamine Compounds* (Intertox, 2006), which describes how the German MAK commission developed an AOEL for NMEA of 0.3 ppb. An internal document (Ch2M HILL Hanford Group, 2005), using the EPA model for establishing carcinogen exposure limits, calculated an AOEL of 0.02 ppb, an order of magnitude lower than the MAK value. This discrepancy needs to be clarified, particularly since the less conservative value of 0.3 ppb is listed in the OELs for COPC.

- *In the development of screening values, have uncertainty factors been consistently and appropriately applied?*

As mentioned previously, in the setting of screening values for some 600+ non-carcinogenic agents the most often applied safety factor was 100: 10% of an available OEL with an added safety factor of 10. However, this rule seems not to have been followed in the CH2M HILL Document "Recommendation for Management of Carcinogens…" (CH2M HILL Hanford Group, 2006c). A list of 7 compounds is provided, each classified by ACGIH as an A2 or A3 carcinogen. A table shows both the ACGIH TLV® and what is called "screening concentrations". If the criterion of a screening value being 10% of an OEL is applied, then 2 out of the 7 agents do not follow this rule; the "screening values" for carbon tetrachloride is 65% of the TLV® and of methylene chloride 39% of the TLV®. This does not seem to warrant removal of these chemicals from the COPC list. However, as noted previously, the committee recommends including all known or suspected human carcinogens on the COPC list.

Finally one note: through all the documents, OELs have been used that, with few exceptions, represent time averaged exposure limits. This is a time honored approach but it does not take into consideration an element that might be important in waste disturbing activities, where it is conceivable that "spikes" in exposure might occur. In standard setting, Haber's Law is often implied, which suggests that low-level exposures may, over a given time period, be equivalent to brief, high-level exposures, provided that the concentration times duration of exposure products are the same (C x T = constant). This may not be the case for some compounds, for example ozone or, as has been shown for certain irritants, where concentration seems the driving factor for toxicity (Shusterman, Matovinovic, & Salmon, 2006). On the other hand, for other agents, particularly carcinogens, total dose seems to be more important than peak exposure levels (discussed and referenced in Witschi, 1999).

To discuss all aspects of time-weighted average vs. peak exposures, the application of Haber's rule and its flaws would go beyond the scope of this review. But it needs to be kept in mind given the potential situations that might occur during waste disturbing activities.

In conclusion, safety factors have been consistently applied in the development of screening values. However, what might remain to be considered is whether the originally adopted cut-off point, 10% of an existing or projected OEL, is the best conservative procedure, since a sensitivity analysis seems to suggest otherwise.

- *Have all available sources that deal with permissible exposure levels been considered (even if they do not* a priori *apply to industrial conditions, they might provide additional insights and documentation)?*

In setting acceptable OELs, multiple relevant documents dealing with occupational exposures were considered, either from the U.S. (e.g. ACGIH, OSHA, and NIOSH) or internationally (e.g. German MAK, Norway, and Sweden). In the U.S., several bodies (e.g. US EPA, CalEPA, and NRC Committee on Toxicology) have developed exposure guidance levels for the public at large. Of particular interest in this context is the work, over the years, of the Committee on Toxicology, National Research Council which has developed and published SMACs (Spacecraft Maximum Allowable Concentrations for Airborne Contaminants, Acute Exposure Guidelines for Airborne Chemicals (AEGLEs) and guidelines for the confined space in submarines under different scenarios.

Reports on a total of 131 compounds that were reviewed individually are available (Susan Martel, Project Officer CoT, NRC: personal communication 10/16/2007). Out of this list, only 8 chemicals (6%) can be found listed as COPC. It is doubtful that consideration of the NRC databases would be of much use for the problem at hand, with perhaps one exception (see below). In the setting of OELs for carcinogenic nitrosamine compounds, two outside sources have been used (e.g. slope factors etc. developed by either the US EPA or Cal EPA).

There is however one comparison between AOELs suggested for COPC and another evaluation: Spacecraft Maximum Allowable Concentrations for Airborne Contaminants (SMACs). They were developed with the premise that astronauts might be exposed up to 180 days, 24 hours a day, under conditions of weightlessness in a confined environment. A comparison between listed AOELS (CH2M HILL Hanford Group, 2006a) and SMACs is presented in Table 5.

Table 5

Chemical	**AOEL (ppm)**	**SMAC (ppm)**	**SMAC % of AOEL**
Acetaldehyde	25	2	8%
Ammonia	25	10	40%
Benzene	0.5	0.07	14%
Formaldehyde	0.3	0.04	13%
Furan	0.001	0.025	250%
Mercury (mg/m^3)	0.0250	0.01	40%
Methanol	200	7	4%

It is interesting to note that, with one exception, all SMAC values are lower than AOELs. A 24 hour exposure for 180 days would correspond to 540 8-hour working days or about something more than 2 working years (250 days/year). Given the intermittent nature of work tasks that may incur opportunity for chemical exposures among tank farm workers, the fact that the AOELs for these 7 chemicals were derived from ACGIH TLV$^{®s}$, and that the screening levels are set at 10% of AOELs, the committee does not believe that the SMACs provide a suitable or appropriate benchmark for setting AOELs.

In conclusion, most other available sources on permissible exposure levels, as developed mostly by the NRC Committee on Toxicology, are not really suitable or appropriate for the setting of AOELs in the Hanford environment. Cancer slope and potency factors, on the other hand, have been taken from other existing sources in an appropriate way.

- *Is the industrial hygiene data sufficient to determine the appropriate level of personal protective equipment for workers, including during unexpected events (or sampling results)?*

Area, source, and personal sampling have been conducted in the tank farms. Targeted source and area sampling for COPCs were conducted in the A- and S- Prefix Tank Farms, which consisted of sampling in and around these tank farms. Efforts were made to conduct sampling in these farms while the tanks were exhaling: to determine this, direct reading instruments were placed at the breather filters and certain meteorological criteria were met (CH2M HILL Hanford Group, 2006b, 2007c).

Over one thousand personal samples have been collected on workers in the tank farms. The representativeness of these data is not clear however. All of the data suggest that typical exposures are well below the Administrative Control Limits (ACLs: 10% of the OEL or AOEL) under steady state conditions and at least 5 feet from the breather filters. As discussed earlier in this report, a more systematic assessment of air concentrations in the vicinity of the breather filters would increase confidence in the “protectiveness” of this 5-feet zone and the associated personal protection requirements.

The committee recommends that personal protection decisions be reconsidered in light of new data generated based on the discussion in Assumption 1 (8-14). In particular, the size of the control zone around breather filters should be expanded until new exposure data are generated.

- *Are there regular reviews or other appropriate feedback loops outlined within the* Technical Basis *that provide assurance that the sampling plans confirm predictions and that any new information is considered, if necessary, in reevaluating the AOEL's?*

The *Technical Basis* document outlines a process in which sampling data and other worksite evaluations will lead to periodic updates of the COPC list, which will in turn affect sampling methods (CH2M HILL Hanford Group, 2006a). The A- and S- Prefix Tank Farm evaluations suggested that additional personal sampling would be conducted in the future to complement the area sampling (CH2M HILL Hanford Group, 2006b, 2007c). However, the *Technical Basis* and other supporting documents do not provide a timeline for future sample collection, or specific mechanisms that will trigger re-evaluation of a chemical's toxicity.

Feedback loops for program evaluation are essential elements of any industrial hygiene program. An explicit timeline for sampling as well as reviews of OELs and chemical toxicity literature would make the *Technical Basis* an adaptive and progressive framework for industrial hygiene programs and risk assessment at the Hanford Tank Farms.

Overall conclusion for Assumption No. 2.

It is the opinion of the committee that the methodology outlined in the *Technical Basis* for setting standards is adequate and reasonable, assuming that the universe of chemicals has been adequately characterized. However, it must be kept in mind that quite a few of the current TLV®s and PELs might be quite old (> 10 years). Additionally, there may be changes in the future regarding how to best assess the risks posed by mixtures and chemical interactions. It will be necessary to follow closely all new developments (e.g. new human and animal toxicity data as well as risk assessment guidance) and, if necessary, take appropriate action by revising the AOELs for the Hanford Tank Farm environment.

Air sampling is the best method to determine whether workers could potentially be overexposed to chemicals. While a large amount of exposure data have been collected, a, more systematic approach is needed to make statistically meaningful estimates of potential worker exposures and to increase confidence that adverse health outcomes are unlikely.

CONCLUSION

The review of the *Industrial Hygiene Chemical Vapor Technical Basis* is organized into two major parts. The first part addresses the question whether the currently available database on headspace sampling adequately reflects the universe of chemicals to which tank workers may conceivably be exposed. In order to provide a solid basis for hazard assessment, such a database should cover both qualitative data (e.g. on the presence of potentially toxic chemicals) and quantitative information (e.g., to how much of such chemicals workers may become exposed).

A large amount of data from headspace sampling over the last 20 years is available. For the samples that were collected, the analytical methodology used to identify and quantify chemicals is generally state-of-the-art. However, it is unclear how great temporal and spatial variability within and between tanks may be, particularly as occurs during waste disturbing activities. Similar considerations apply to airborne concentrations of potentially toxic chemicals that may be found in the breathing zones around the tanks. Accordingly, it is recommended that a statistically representative tank headspace and breathing zone sampling strategy be developed. This will help to further reduce uncertainties in hazard assessment for exposed tank farm workers. In addition, to provide a more conservative approach, the use of 10% of an OEL as a threshold for inclusion of a chemical on the COPC list should be lowered to 1%.

The second part of the review deals with the development of AOELs. The majority (60%) of AOELs for 48 COPCs was set by adopting TLV's developed by nationally and internationally recognized expert committees. The remaining AOELs were derived by taking into account existing TLV's of surrogate compounds and analysis of available toxicity data; safety factors were often applied to existing data in order to err on the conservative side. Accepted risk assessment procedures were used for carcinogens. In general, the process that was followed reflects best practice in industry. However, it should be noted that that existing TLVs have often been developed some time ago. This necessitates that new toxicological information should be closely followed. It also must be kept in mind that compliance with TLVs does not guarantee under all circumstances or for all individuals a healthy work environment.

A vexing problem for hazard assessment of tank headspace atmospheres is that invariably they represent a very complex mixture of chemicals. The toxicology of complex mixtures is notoriously difficult to evaluate. The currently predominant view is that the toxic effects of a mixture are additive, not synergistic. For mixtures of chemicals with similar toxicities, the OSHA "mixture rule" has generally been accepted, i.e. meaning that the fractions (%) of OELs for individual chemicals in a mixture, when added, should not exceed unity (i.e. > 100%). For the special case of the hydrocarbon mixture found in headspaces, an overall conservative OEL – the one existing for kerosene – has been adopted.

By and large, the mixture problem has been addressed in a conservative manner. The same can be said for the development of OELs through using surrogates of compounds where no TLVs are available. While surrogates are usually not used in setting occupational exposure standards, it is an acceptable default option for the unique conditions found at Hanford, particularly since safety factors have throughout been applied in a conservative manner. It is also conceivable that exposure to complex mixtures results in one chemical or group of chemicals enhancing (or mitigating) the toxic effects of others. While such interactions are known to occur (e.g. enhanced cancer risk from smoking by inhalation of asbestos fibers), they are difficult to predict and should only be considered if there is a plausible hypothesis or strong data available.

For the setting of OELs for carcinogens, risk assessments have been used in a conservative manner but it is recommended that all known or suspected human carcinogens (IARC Group 1 and 2) be included in the COPC list. For non-carcinogenic agents, screening values have been developed by a consistent and conservative application of safety factors. Outside the sources that were used for setting AOELs, no other databases have been identified that should have been considered.

The data and conclusions within the *Technical Basis* document should be re-evaluated on an annual basis. In addition, it is important to remember that the goals of the risk assessment process described in the *Technical Basis* document are to minimize the potential for adverse health effects. As noted by the ACGIH, "TLV®s do not represent a fine line between a healthy versus an unhealthy work environment or the point at which material impairment of health will occur. Some individuals may experience discomfort or even more serious adverse health effects when exposed to a chemical substance at the TLV® or even at concentrations below the TLV®" (ACGIH, 2007). It is also important to note that it is not possible to protect workers without integrated exposure and medical surveillance programs. The periodic reevaluation of the *Technical Basis* document must include input from the medical surveillance activities to provide additional assurance that adverse health effects are not occurring.

In conclusion, the committee can answer the two questions it was asked by HCC as follows. In response to the first question the committee concluded that, where toxicological data are available, the methodology for developing acceptable occupational exposure limits outlined in the *Technical Basis* document is consistent with industry best practices. Although the use of surrogates, as described by the *Technical Basis* document, is not a standard practice for setting occupational exposure limits (by NIOSH, ACGIH, or OSHA), it constitutes an acceptable default option. This approach has been used in other types of chemical risk assessments for agents where there is little toxicological data such as additives and contaminants found in consumer products.

With respect to the second question, the committee concludes that while the risk assessment process described in the *Technical Basis* Document is generally sound, its implementation is limited by inadequately representative source and exposure data. As a result, the committee is unable to conclude that the protective measures are sufficiently conservative to safeguard worker health under all circumstances. There are several areas in the *Technical Basis* where there is significant uncertainty in sampling data. One area in particular deals with the impact of waste disturbing activities on the emission characteristics of a tank over time. The committee has identified several opportunities where the approach outlined in the *Technical Basis* document could be made more conservative, i.e., more protective of workers, by reducing uncertainty. These include:

- Lowering threshold for inclusion of chemicals on the COPC list;
- Revaluating the tank head space chemical inventory using a systematic sampling strategy; and
- Revaluating the source, area, and personal exposures using a systematic sampling strategy.

Signed,

Patrick N Breysse

Patrick N. Breysse, PhD, Board Certified Industrial Hygienist

K. Clark

Katherine Clark, MHS, DrPH Candidate, Johns Hopkins University

July 8, 2008

Al Franzblau, MD, Board Certified Internal Medicine and Preventive and Occupational Medicine

Hanspeter Witschi, MD, Diplomate, American Board of Toxicology; Fellow, Academy of Toxicological Sciences

June 30, 2008

REFERENCES

ACGIH. (2007). *TLVs and BEIs; Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices*. Cincinnati, Ohio.

ACGIH. (2008). *NIC Documentation, Appendix H: Reciprocal Calculation Method for Certain Refined Hydrocarbon Solvent Vapors*. Draft open for comments.

Boekelheide, K. (2007). Toxicological Highlight - Mixed Messages. *Toxicol.Sci, 99,* 1-2.

Ch2M HILL Hanford Group. (2005). Development of Acceptable Occupational Exposure Limits (AOEL's) for N-nitrosodimethylamine, N-nitrosomethylethylamine, and A-napthylamine. In 7B600-MLZ-05-013 (Ed.). Richland, WA: Environmental Health.

CH2M HILL Hanford Group. (2006a). *Industrial Hygiene Chemical Vapor Technical Basis, Rev 1* (No. RPP-22491 Revision 1). Richland, Washington.

CH2M HILL Hanford Group. (2006b). *A-Prefix Tank Farms Vapor Characterization, Rev. 0* (No. RPP-RPT-29262). Richland, WA.

CH2M HILL Hanford Group. (2006c). Recommendation for Management of Carcinogens with ACGIH Threshold Limit Values (TLV's) on the COPC List. In 7M500-MLZ-06-008 (Ed.). Richland, WA: Environmental Health.

CH2M HILL Hanford Group. (2006d). *Statistical Analysis of Tank Headspace Vapor Data*.

CH2M HILL Hanford Group. (2007a). *IH Data.xls*.

CH2M HILL Hanford Group. (2007b). *Industrial Hygiene Exposure Assessment Strategy* (No. TFC-PLN-34, Rev C-1).

CH2M HILL Hanford Group. (2007c). *S-Prefix Tank Farm Vapor Hazard Characterization*. Richland, WA.

CH2M HILL Hanford Group. (2007d). Tank Headspace Raw Data.xls.

de-Rosa, C. T., Masri, H. A. E., Pohl, H., Cibulas, W., & Mumtaz, M. M. (2004). Implications of chemical mixtures in public health practice. *J.Toxicol.Environ.Health B Crit Rev, 7,* 339-350.

Feron, V. J., Groten, J. P., Jonker, D., Cassee, F. R., & Bladeren, P. J. (1995). Toxicology of chemical mixtures: challenges for today and the future. *Toxicology, 105,* 415-427.

Groten, J. P., Schoen, E. D., Bladeren, P. J. v., Kuper, C. F., Zorge, J. A. v., & Feron, V. J. (1997). Subacute toxicity of a mixture of nine chemicals in rats: detecting interactive effects with a fractionated two-level factorial design. *Fundam.Appl.Toxicol, 36,* 15-29.

Hattis, D., Baird, S., & Goble, R. (2002). A straw man proposal for a quantitative definition of the RfD. *Drug and Chemical Toxicology, 25*(4), 403-436.

Intertox. (2006). *Recommendations for Acceptable Occupational Exposure Levels (AOELs) for Selected Nitrosamine Compounds*. Seattle, WA: Intertox.

Kroes, R., Kleiner, J., & Renwick, A. (2005). The threshold of toxicological concern concept in risk assessment. *Toxicol.Sci, 86*, 226-230.

Mason, A. M., Borgert, C. J., Bus, J. S., Moiz, M. M., Simmons, J. E., & Sipes, I. G. (2007). Improving the scientific foundation for mixtures joint toxicity and risk assessment: contributions from the SOT mixtures project--introduction. *Toxicol.Appl.Pharmacol, 223*, 99-103.

McKee, R. H., Medeiros, A. M., & Daughtrey, W. C. (2005). A proposeed methodology for setting occupational exposure limits for hydrocarbon solvents. *J. Occup. Env. Hygiene, 2*(524-542).

NASA Toxicology Group. (1999). *Spacecraft Maximum Allowable Concentrations for Airborne Contaminants*. Houston, TX: NASA.

National Research Council. (1983). *Risk Assessment in the Federal Government: Managing the Process*. Washington D.C.

National Research Council. (1997). *Framework for Environmental Health Risk Management*. http://www.riskworld.com/Nreports/1997/risk-rpt/pdf/EPAJAN.PDF: Presidential/Congressional Commission on Risk Assessment and Risk Management

National Research Council. (1988). *Complex mixtures - methods for in vivo toxicity testing*. Washington D.C. .

National Institute for Occupational Safety and Health. (2004). *NIOSH Health Hazard Evaluation Report: CH2M Hill Hanford Group, Inc. and United States Department of Energy, Office of River Protection, Richland, WA*: Centers for Disease Control.

Pacific Northwest National Laboratory. (2004). *A Survey of Vapors in the Headspaces of Single-Shell Waste Tanks*. Richland, WA.

Pacific Northwest National Laboratory. (2005). *Effects of Globally Waste-Disturbing Activities on Gas Generation, Retention, and Release in Hanford Waste Tanks*.

Pacific Northwest National Laboratory. (2006). *Screening Values for Non-Carcinogenic Hanford Waste Tank Vapor Chemicals that Lack Established Occupational Exposure Limits*.

Rappaport, S., & Kupper, L. (2008). *Quantitative Exposure Assessment*. El Centro, CA: Stephen Rappaport http://www.lulu.com/content/1341905.

Rappaport, S. M. (1993). Threshold limit values, permissible exposure limits, and feasibility: the bases for exposure limits in the United States. *Am.J.Ind.Med, 23*, 683-694.

Roach, S., & Rappaport, S. (1990). But they are not thresholds: a critical analysis of the documentation of Threshold Limit Values. *Am.J.Ind.Med, 17*, 727-753.

Shusterman, D., Matovinovic, E., & Salmon, A. (2006). Does Haber's law apply to human sensory irritation? *Inhal.Toxicol, 18*, 457-471.

Smith, R. L., Cohen, S. M., Doull, J., Feron, V. J., Goodman, J. I., Marnett, L. J., et al. (2005). A procedure for the safety evaluation of natural flavor complexes used as ingredients in food: essential oils. *Food Chem.Toxicol, 43,* 345-363.

Teuschler, L. K. (2007). Deciding which chemical mixtures risk assessment methods work best for what mixtures. *Toxicol.Appl.Pharmacol, 223*, 139-147.

United States Department of Energy. (2006). *Proposed Approach to Establishing Acceptable Limits of Exposure to Hydrocarbon Vapor Emitted from Underground Waste Storage Tanks at the Hanford Site*.

Weiss, W. (1980). The cigarette factor in lung cancer due to chloromethyl ethers. *J.Occup.Med, 22*, 527-529.

Witschi, H. (1999). Some notes on the history of Haber's law. *Toxicol.Sci, 50*, 164-168.

LIST OF **ACRONYMS**

ACGIH	American Conference of Governmental Industrial Hygienists
ACL	Administrative Control Limit
AIHA	American Industrial Hygiene Association
AOEL	Acceptable Occupational Exposure Limit
ATSDR	Agency for Toxic Substances and Disease Registry
CalEPA	California Environmental Protection Agency
CNFE	Chemicals Needing Further Evaluation
COPC	Chemical of Potential Concern
DOE	Department of Energy
EPA	Environmental Protection Agency
FDA	Food and Drug Administration
GAP	Government Accountability Project
HCC	Hanford Concerns Council
MAK	Maximale Arbeitsplatz Konzentration (Maximum Workplace Concentration)
NASA	National Aeronautics and Space Administration
NDMA	N-Nitrosodimethylamine
NIOSH	National Institute for Occupational Safety and Health
NMEA	N-Nitrosomethylethylamine
NOAEL	No Observable Adverse Effect Level
NRC	National Research Council
NTP	National Toxicology Program
OEL	Occupational Exposure Limit
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
SMACS	Spacecraft Maximum Allowable Concentrations of Airborne Contaminants
SST	Single Shell Tank
TLV	Threshold Limit Value
VOC	Volatile Organic Compound
WEEL	Workplace Environmental Exposure Limit

APPENDIX A

CH2M HILL Hanford Group IH Data.xls (provided in 2007).

CH2M HILL Hanford Group "Tank Headspace Raw Data.xls" (provided in 2007).

CH2M HILL Hanford Group "Tank Headspace Vapor Averaged Data.xls" (provided in 2007)

CH2M HILL Hanford Group (2005). Development of Acceptable Occupational Exposure Limits (AOEL's) for N-nitrosodimethylamine, N-nitrosomethylethylamine, and A-napthylamine. 7B600-MLZ-05-013. Richland, WA, Environmental Health.

CH2M HILL Hanford Group (2006). Health Effects Panel Evaluation of Pulmonary Function and Liver Enzyme Levels Among Hanford Tank Farm Workers. S. Eberlein. RPP-30560 Rev 0.

CH2M HILL Hanford Group (2006). Industrial Hygiene Chemical Vapor Technical Basis, Rev 1. J. Meacham, J. Honeyman, T. Anderson, M. Zabel and J. Huckaby. Richland, Washington. RPP-22491, 2006.

CH2M HILL Hanford Group (2006). A-Prefix Tank Farms Vapor Characterization, Rev. 0. T. Anderson, M. Zabel and N. Butler. Richland, WA. RPP-RPT-29262.

CH2M HILL Hanford Group (2006). Recommendation for Management of Carcinogens with ACGIH Threshold Limit Values (TLV's) on the COPC List. 7M500-MLZ-06-008. Richland, WA, Environmental Health.

CH2M HILL Hanford Group (2006). Statistical Analysis of Tank Headspace Vapor Data. J. Meacham, C. Anderson and J. Huckaby. RPP-21972 Rev 1.

CH2M HILL Hanford Group (2007). Industrial Hygiene Exposure Assessment Strategy. TFC-PLN-34, Rev D.

CH2M HILL Hanford Group (2007). S-Prefix Tank Farm Vapor Hazard Characterization. M. Hughey, B. Van Morris and D. Farler. Richland, WA.

Government Accountability Project (2003). Knowing Endangerment: Worker Exposure to Toxic Vapors at the Hanford Tank Farms.

Intertox (2005). Review of Acceptable Risk Levels Applied in the Establishment of Published Occupational Exposure Levels- REVISED. G. Bruce and G. Pascoe. Seattle, WA. Subcontract No. 25645.

Intertox (2006). Recommendation for an Acceptable Occupational Exposure Level (AOEL) for 1-Napthylamine. G. Bruce and G. Pascoe. Seattle, WA, Intertox. Subcontract No. 28222.

Intertox (2006). Recommendations for Acceptable Occupational Exposure Levels (AOELs) for Selected Nitrosamine Compounds. G. Bruce and G. Pascoe. Seattle, WA, Intertox. Subcontract No. 28222.

National Institute for Occupational Safety and Health (2004). NIOSH Health Hazard Evaluation Report: CH2M Hill Hanford Group, Inc. and United States Department of Energy, Office of River Protection, Richland, WA, Centers for Disease Control. HETA #2004-0145-2941

Pacific Northwest National Laboratory (1999). Gas Release During Saltwell Pumping: Interpretation of Operational Data. J. Huckaby, L. Peurrund and P. Ganglitz. PNNL-13029.

Pacific Northwest National Laboratory (2004). A Survey of Vapors in the Headspaces of Single-Shell Waste Tanks. L. Stock and J. Huckaby. Richland, WA. PNNL-13366, Rev. 1.

Pacific Northwest National Laboratory (2005). Effects of Globally Waste-Disturbing Activities on Gas Generation, Retention, and Release in Hanford Waste Tanks. C. Stewart, M. Fountain, J. Huckaby et al. PNNL-13781 Rev. 3.

Pacific Northwest National Laboratory (2006). Proposed Occupational Exposure Limits for Non-carcinogenic Hanford Waste Tank Vapor Chemicals. T. Poet and C. Timchalk. PNNL-15736.

Pacific Northwest National Laboratory (2006). Screening Values for Non-Carcinogenic Hanford Waste Tank Vapor Chemicals that Lack Established Occupational Exposure Limits. T. Poet, T. Mast and J. Huckaby. PNNL-15640.

United States Department of Energy (2005). Independent Oversight Follow-up Review of Worker Vapor Exposure and Occupational Medicine Program at the Hanford Site, DOE Office of Independent Oversight and Performance Assurance, Office of Security and Safety Performance Assurance, Office of the Secretary of Energy.

United States Department of Energy (2004). Investigation of Worker Vapor Exposure and Occupational Medicine Program Allegations at the Hanford Site, US DOE Office of Independent Oversight and Performance Assurance, Office of Security and Safety Performance Assurance.

United Stated Department of Energy (2006). Proposed Approach to Establishing Acceptable Limits of Exposure to Hydrocarbon Vapor Emitted from Underground Waste Storage Tanks at the Hanford Site. C. Mackerer. RPP-RPT-29404 Rev.0.

United States Department of Energy (2007). Type A Accident Investigation Report: The July 27, 2007 Tank 241-S-102 Waste Spill at the Hanford Tank Farms, US DOE Office of Health, Safety and Security: Office of Corporate Safety Programs.

APPENDIX B

Hanspeter Witschi, MD

Professor Emeritus of Toxicology, UC Davis
Diplomate, American Board of Toxicology
Fellow, Academy of Toxicological Sciences

June 22, 2008

Dr. Max Power
Hanford Concerns Council
3311 W. Clearwater Ave.
Kennewick WA 99336

Dear Dr. Power:

Thank you for transmitting the reports on the fact checks of our Technical Review Report, prepared on behalf of CH2MHill and Hanford Challenge. Our committee (Pat Breysse, Katie Clark, Al Franzblau and I) have examined the material. We are pleased to hereby submit our response.

In several places the reviewers pointed out some errors or made suggestions that would improve the accuracy of our report (e.g. CH2MHill comments No. 4, 5, 6 and Hanford Challenge responses 3, 4). Accordingly, we have modified the final text of our report (Technical Review June 16, 2008). In other places, the committee felt it could not address the comments within the Technical Review, be it because they addressed information that was not available in the primary review document (The “Industrial Hygiene Chemical Vapor Technical Basis”) or because the issues in question were not within the scope of our review (e.g. CH2Hill Nos. 1, 7 and Hanford Challenge 6, 8, 9). Finally there were some circumstances where there could be bona fide differences in professional opinion and judgment (e.g. CH2M Hill 4, 6, 8, Hanford Challenge response 6).

I hope that our response will address the “fact checking” comments in a satisfactory way. The detailed answers to each point that was raised by the reviewers are provided in Appendix I and II.

Please do not hesitate to get in touch with the committee should you have any additional questions.

Yours sincerely,
Hanspeter Witschi, MD

COMMENTS FROM HANFORD CHALLENGE

Tom Carpenter
Executive Director
Hanford Challenge

Subject: Industrial Hygiene Based Comments to ICVTBR Draft

Dear Mr. Carpenter;

I would like to commend the committee on a highly professional, well balanced document. I reviewed it from the stand point of a government contractor and found it to be a well substantiated, objective review. I have a few general comments for your consideration, followed by comments regarding personal protection in light of the information available. My comments are based on years of field support efforts, field audits, compliance consultation, and to a lesser extent; litigation support.

- Page 4, paragraph 4, statement 3, believe you want to add "which" prior to the word were.

  Response 1: At the time of review, several documents were in circulation and the exact location could not be identified, but will probably being taken care of in final copy editing of the report.

- Page 14, last paragraph; please note that the TLV for butadiene is 2 ppm, while the PEL is 1 ppm. I believe from my DOE experience, that contra

  Response 2: This comment cannot be addressed since the above sentence/paragraph seems to be incomplete (probably lost in transit).

- There are several justifiable references made to the undocumented nature of much of the sampling relative to environmental conditions and the questionable effects of wind, pressure and buoyancy forces. It may be noteworthy to add the temperature extremes of lows in the 20's to a recorded high of 113 F which has an obvious significant effect on volatility rates.

  Response 3: Agree - We added the following sentence to Page 10 last paragraph to address this point: "In addition, ambient temperature extremes may also impact volatility."

- You may want to make mention of the variable of the waste constituents':
    - Vapor pressure
    - Specific gravity &
    - Water solubility

Case in point: per comments on Page 23; carbon tetrachloride has low water solubility, VP of 91 and a SG of 1.59, meaning it is largely capped by the water layer, as is methylene chloride with an SG of 1.33, low water solubility, yet a vapor pressure of 350 mm Hg. Bottom line, of course, is as water levels drop off or as the water layer is disturbed, these other products are allowed to release vapor at a less impeded rate. In my experience, this is a very significant factor, and one that HAZMAT crews are very cognizant of in anticipating changes in risk over time.

Response 4: Agree - We added the following to bottom of page 10 continuing to the top of page 11to address this point: "Volatility can be greatly affected by the amount of water in each tank. For example, substances with low water solubility and specific gravity greater than 1.0 (like carbon tetrachloride and methylene chloride) will be largely capped by the water layer. As the water levels drops or if the water layer is disturbed, these and similar substance will be released at a greater rate."

- Page 13; it may be of value to tie in the concern of synergy particularly with regard to carcinogens with the argument of utilizing the 1% of OEL in view of the 40 chemicals greater then cutoff.* The document makes a point of this in the latter section, of course.

  Response 5: We feel this i
  the report (as of June, 200

* The unknowns of the "stew" effect have a long history of serving as ample justification for a level B PPE regime. For Example, Basin F of the Rocky Mountain Arsenal All RI/FS and remedial activities were conducted in Level B, a highly conservative move by DOD, deemed necessary due to unknowns.

- Regarding Follow up sampling, please note that 29 CFR 1910.120 ***Monitoring:*** The following monitoring shall be conducted during initial site entry when the site evaluation produces information which shows the potential for ionizing radiation or IDLH conditions, or when the site information is not sufficient reasonably to eliminate these possible conditions:

1910.120(c)(6)(i)
Monitoring with direct reading instruments for hazardous levels of ionizing radiation.
1910.120(c)(6)(ii)
Monitoring the air with appropriate direct reading test equipment for (i.e., combustible gas meters, detector tubes) for IDLH and other conditions that may cause death or serious harm (combustible or explosive atmospheres, oxygen deficiency, toxic substances.)
1910.120(c)(6)(iii)
Visually observing for signs of actual or potential IDLH or other dangerous conditions.
1910.120(c)(6)(iv)
An ongoing air monitoring program in accordance with paragraph (h) of this section shall be implemented after site characterization has determined the site is safe for the start-up of operations.

Response 6: It is the understanding of the committee that monitoring, as described above, is conducted prior to initial site entry to the tank farms. Since no IDLH conditions have been documented we are not sure this section of 29 1919.120 applies.

- In support of the argument against use of SMACs, Page 24/25; please note qualifiers used on page one of that document:

SPACECRAFT MAXIMUM ALLOWABLE CONCENTRATIONS FOR AIRBORNE CONTAMINANTS

“The enclosed table lists official spacecraft maximum allowable concentrations (SMACs), which are guideline values set by the NASA/JSC Toxicology Group in cooperation with the National Research Council Committee on Toxicology (NRCCOT). These values should not be used for situations other than human space flight without careful consideration of the criteria used to set each value. The SMACs take into account a number of unique factors such as the effect of space-flight stress on human physiology, the uniform good health of astronauts, and the absence of pregnant or very young individuals.” (highlight added)

Response 7: We agree with this comment and, indeed, mention explicitly in the discussion of SMACs that “the committee does not believe that the SMACs provide a suitable or appropriate benchmark for setting AOELs”.

Regarding Decision Making and PPE

- Employers are res
administration of
administrative co
some accountabil
nitrogen blankets .

1910.120(c)(5)(iii)
If the preliminary site evaluation does not produce sufficient information to identify the hazards or suspected hazards of the site an ensemble providing equivalent to Level B PPE shall be provided as minimum protection, and direct reading instruments shall be used as appropriate for identifying IDLH conditions. (See Appendix B for guidelines on Level B protective equipment.)

Response 8: This issue was outside the scope of our review.

- If such controls are not feasible/cost effective and verified as effective; then PPE is warranted, due to the unknowns of the products, the emission rates (a function of weather, time, mixtures and disturbance), proximity of personnel beyond the 5 foot delineation, and the movement of fugitive emissions from the existing filters.
    - There are no air purifying respirators approved for unknowns or carcinogens – Level B ie SCBA or supplied air respirators are required by both NIOSH and AIHA respirator decision logic, as well as OSHA, 29 CFR 1910.120 (see text box).

Response 9: The review of PPE decisions and worker protection programs in general were outside the scope of this review. The main focus of this review was on the Technical Basis document, which outlines a process for identifying chemicals that may be present at hazardous levels in the workplace.

I would be happy to expand on any of these issues, please provide some guidance on what type of documentation, etc is appropriate. I did not see anything in the document that I disagreed with.

I wait your comments,

Best Regards,

Rich Urie, MS, CIH, CSP

COMMENTS FROM CH2M HILL

Comment 1:

p. 9, Ln 10-19. [*"Furthermore, although mixing and sharing of tank constituents and headspaces has occurred between tanks, many chemicals have only been identified (or tentatively identified) in one or a few tank headspaces (Pacific Northwest National Laboratory, 2004). Waste-disturbing activities have been shown to greatly impact headspace concentrations found in the tank (CH2M HILL Hanford Group, 2006d; Pacific Northwest National Laboratory, 2005). If the tanks are assumed to have similar chemistries, then the current headspace inventory may be adequate. However, sampling data suggests that they have differing chemistries, and the sampling that has been conducted may not capture all of the headspace constituents or the upper concentration range of headspace constituents."*]

As summarized in the tank waste history in the chemistry section of the Industrial Hygiene (IH) Technical Basis, tanks have been used for a variety of purposes over time. They group into chemistry types depending on the chemistry of the specific purpose they performed. The historical headspace sampling data was planned to cover the range of historical waste types that were known to exist to understand flammable gas safety risks. Any given farm may have tanks containing several differing waste types, so wastes are not consistent between tanks in a farm.

The way the *Technical Basis* used the information from the historical samples is to add any detected or tentatively identified compounds in any given tank to the list of chemicals that might be present anywhere in tank farms. The subsequent IH source and workplace sampling makes no assumptions about what may be in any given tank or farm. Source and workplace characterizations are conducted with broad spectrum methods that include the COPC chemicals; but also will detect any other chemicals that might be present in the workplace. Regardless of whether a tank was characterized or not characterized prior to the issuance of the *Technical Basis*, workers remain on supplied air until that farm's workspace is characterized under actual workplace conditions. For waste-disturbing activities, that means characterization with robust methods during waste-disturbing activities. If additional chemicals are being generated in significant quantities by tanks uncharacterized prior to the *Technical Basis*, they would be detected and the technical basis updated. The field implementation IH team focus is on what may actually be present in sources and the workplace, regardless of what headspace characterization has been done. The PPE decisions are made based on what data are available in a specific workplace under similar conditions. Workers are provided with supplied air until data is collected and evaluated that support any adjustments.

We think the passage above needs to be reflected in the above stated passage.

Response 1:

> ***The committee was asked to review the Technical Basis document. The information provided above was not included in the Technical Basis document or in the supporting material provided and is outside the scope of this review. However, additional sampling in the tank farms will increase understanding of the tank chemistry, which was a shortcoming identified in the committee's review. Based on the discussion above it appears that there have been significant changes to the procedures described in the Technical Basis Document. The committee recommends that the Technical Basis be updated to reflect, in detail, the additional monitoring procedures summarized above. In conclusion, the above comments do not alter the committee's review of the Technical Basis Document.***

Comment 2:

p. 10, Ln 29-32. [*"samples were stored for weeks or months prior to analysis"*]

> We think the passage above needs to be changed to reflect that the storage issues were prior to 2004 and have been remedied.
>
> This is a historical issue that was resolved in the very earliest stages of the vapor resolution process and is not relevant to subsequent or current workplace characterization sampling. Samples taken since 2004 have formal sampling plans, with strict chain of custody and timing requirements, along with field, trip, and lab blanks taken and evaluated. IH samples without adequate QA characteristics are not used for IH purposes and must be retaken.

Response 2:

> ***The committee did assume that the storage issues were remedied. However, such remedies are not retroactive: the Technical Basis document reports that data dating back to the early 1990s informs the headspace inventory characterization. The committee has not been made aware of any efforts to determine what effects the poor sampling handling methods in the past may have had on data quality. Further, it is unclear how much of the headspace data comes from the potentially flawed data or whether these data are weighted differently. Since the toxicological evaluation paradigm outlined in the Technical Basis document is based on headspace data, it is important to recognize the strengths and weaknesses of this dataset.***
>
> ***The panel recommends addressing the sampling handling issues within the Technical Basis document by including an analysis of how poor storage may affect results. We have added the following to the our review report on page 13: "Although these issues have been resolved since 2004, it is not clear how much***

of an effect sample storage issues may have on data quality and subsequent interpretation of samples collected prior to 2004, with respect to COPCs and other tank waste chemistry analyses."

Comment 3:

P 10, Ln 36-38. [*"we are not confident that the current sampling data capture the right universe of chemicals"*]

We agree that the *Technical Basis* may not capture the entire universe of chemicals that might be present during unspecified operations in the future. However, as we discussed earlier, the *Technical Basis* alone does not establish any requirements for PPE. No adjustments from supplied air are possible until source and workplace are completed under actual workplace conditions. We think this sentence should be modified to reflect that the COPC list was intended to provide an estimate of which chemicals might be present. Subsequent source and workplace sampling uses robust methodologies not limited to those chemicals. All chemicals detectable by those robust methods are analyzed, and any significant findings are quantitated. This expanded sampling strategy is used when tank conditions change (e.g., start of retrieval or other waste disturbing activity) consistent with the activity risk (i.e., not during routine operations). Once characterization sampling has been completed for a given work activity (e.g., C-109 retrieval)in a tank farm, subsequent sampling concentrates on those chemicals actually detected in that tank farm during that source and workplace sampling. The process is repeated when a new activity is begun (e.g., C-104 retrieval)

Response 3:

The panel did not address worker protection programs (including PPE) in their review and did not review the Technical Basis document in that context. As noted in the review, the headspace data are a key input to the risk assessment process at the Tank Farms, as described by the Technical Basis document. If this is not the case and other inputs are used, the document should be updated to outline the processes actually used by the Industrial Hygiene team. This comment does not change the final conclusions of the committee.

Comment 4:

p. 13, Ln 14. [*"selection of 10 is arbitrary"*]

> This statement is not correct. The selection of 10% is not arbitrary. The use of the 10 percent screening level for selection of chemicals of potential concern (COPC) from the headspace data was derived from guidance in the DOE Implementation Guide for use with DOE Order 440.1, as well as common practice in general industry. The American Industrial Hygiene publication *A Strategy for Assessing and Managing Occupational Exposures*, also recommends using 10% of the exposure limit as a guide when conducting baseline surveys.
>
> In retrospect, looking at the source data collected to date, on 88 tanks, only 53% of the COPC identified using the 10% screening value have been detected in source samples. Of the 59 COPC sampled at source locations, only 24% were greater than 10 % of the exposure limit, and only 14% were greater than 50% of the exposure limit. Additionally, only seven COPCs have been detected greater than 10% of the exposure limit in area or personal samples, and no COPCs have been detected greater than 50% of the exposure limit to date in area or personal samples.
>
> Fundamentally, the review committee's suggestion to consider a cutoff at 1% of an exposure limit would, based on the most current data, do little in the way of additional worker protection. However, we recognize that this may be a difference in professional opinion with the Technical Expert panel – we do think it is important to include that the 10% has a foundation.

Response 4:

> ***The panel agrees that this statement regarding the selection of 10 is misleading and the text is changed by deleting the reference to "arbitrary". This statement was meant to reflect that factors of 10 are not based on a biological mechanism. However, dividing by one or more factors of 10 is generally recognized as a conservative approach when dealing with uncertainty.***
>
> ***The committee maintains that using two factors of 10 (i.e., a 1% threshold) is a more conservative approach. According to the information above, these chemicals are already being analyzed anyways. Further, based on uncertainties in the source data quality noted above, a more conservative approach is merited.***

Comment 5:

p. 14, Ln 41-44. [*"For another 13 agents, OELs have been derived by looking up existing TLVs®"*]

We think that this statement is factually inaccurate and does not accurately describe the process – it infers that the only process followed is someone looking up the existing TLVs in a book. That is not true. The statement over-simplifies the process. Beyond "looking up" surrogates, the toxicologists evaluated toxicity, data availability and adequacy, chemical and functional similarity, and other relevant factors. Safety factors were then established for each level of uncertainty. The next step involved a meeting of a board of experts (called the Exposure Assessment Strategy review team) to review the information and make a judgment on the actual OEL that would be used. This process is described in the Exposure Assessment Strategy Document.

Response 5: The reviewers are correct and the text has been amended as follows: " For another 13 agents, OELs have been derived by looking up existing TLVs® (developed by ACGIH) of compounds that might serve as reasonable surrogates for the agent in question (e.g. butyl nitrate, chlorinated biphenyls or methyl nitrite). The surrogates that were selected usually had a robust toxicological data base. In addition, all available toxicity data for the compounds that did not have an established TLV were scrutinized. Based on this analysis, the TLVs derived from the surrogate compounds were modified by additional safety factors".

Comment 6:

p. 21, Ln 15-17. [*"binary mixtures of two chemicals which, each one by itself is comparatively harmless but, when the two are combined, they might form a highly toxic chemical…This forms the basis of "binary weapons" designed to provide highly lethal war gases once the ammunition has been used, but not during storage….."*]

We have a concern that, as written, this is an inflammatory statement, which creates an inaccurate impression. While that binary mixture issue is true, although a rare occurrence, OSHA, NIOSH, and AGCIH note the state of the science is not sufficiently advanced to provide further guidance on this issue.

As described in the *Technical Basis* Document, Rev. 1, CH2M HILL has specifically addressed the potential impacts of hydrocarbon mixtures by using the extensive oil industry data for hydrocarbon mixtures and evaluating individual hydrocarbon OELs for prevalent individual compounds. This allows treating the hydrocarbons both individually and as an aggregated mixture. Hydrocarbons account for over half of the compounds evaluated in the IH *Technical Basis* effort.

We supplemented that approach by the use of the OSHA mixture rule for compounds actually detected in source or workplace samples. As noted in the

> report, this is appropriate for evaluation of hazards in the tank farms and is consistent with industry practice.

Response 6: We point out a theoretically plausible possibility and use binary weapons as an illustration. However, the panel also believes that this would be a very unlikely problem for the Hanford situation. Accordingly, the text was modified as follows: "The question of this type of interaction between chemicals apparently remains, at present, the issue of some (perceived or real) controversy. Though such a circumstance cannot be excluded, the committee believes that this scenario is exceedingly unlikely".

Comment 7:

p. 23, Ln 20-21. [*"This discrepancy needs to be clarified"*]

> As written, the DRAFT paper implies that this is a mistake or an oversight. If fact, CHM HILL was and is aware of the information referenced and made an informed choice.
>
> The EAS (Exposure Assessment Strategy) review team did consider this issue (see the EAS Review Group meeting minutes). We understood that there was a calculated value that was lower than the MAK. The conclusion was that since the MAK was an accepted national standard, it had been subjected to a business/legal vetting process very similar to the U.S. OSHA/PEL process for other carcinogens (e.g., benzene), and, therefore, the MAK value was accepted rather than the lower calculated value. As the reviewer mentions, this is a process founded in legal interpretations of OSHA standards.

Response 7: The discrepancy has been explained in the above comment (and the explanation is acceptable), but it was not obvious in the review material. It also can be observed that taking a higher (MAK) value because it has been developed by a well qualified body over a lower value, developed according to generally accepted methods (EPA) seems not to be the best or most conservative approach.

Comment 8:

p. 24, Ln 39. [“*Spacecraft Maximum Allowable Concentrations for Airborne Contaminants (SMACs)”*]

> We recognize that the inclusion of this information is a result of a search for parallel, but we think that it has little applicability to the tank farm work environment. The panel agreed as stated on page 25, “…*we do not believe that the SAMCs provide a suitable or appropriate benchmark for setting AOELs*.” We agree that the difference in exposure profile between a confined astronaut on an extended 24 hour-a-day assignment and a tank farm worker is enormous. We think there is agreement that there is no reason SMACs would or should even be considered for adoption as tank farm OELs.
>
> As a side note, our Independent Toxicology Panel included two members from the National Academy of Science Panel that developed SMACs, Dr. Snyder and Dr. Still. The Independent Toxicology Panel (ITP) discussed application of the data generated in the SMAC effort, but in general they also felt that the SMACs were not directly useful for our purposes. Therefore, they steered the development of the tank farm IH *Technical Basis* elsewhere (discussed in the ITP report; included as Appendix C of the Rev. 0 of the IH Technical Basis document).
>
> We therefore recommend this discussion be eliminated from the report or amended to acknowledge it in its proper context. That being, the spacecraft limits were evaluated and determined not to be applicable.

Response 8: The committee is in full agreement with the remark that the SMACs are of no help in setting AOELs for the Hanford situation, viz. the text:” Given the intermittent nature of work tasks that may incur opportunity for chemical exposures among tank farm workers, the fact that the AOELs for these 7 chemicals were derived from ACGIH TLV$^{®s}$, and that the screening levels are set at 10% of AOELs, the committee does not believe that the SMACs provide a suitable or appropriate benchmark for setting AOELs”. However, the reference to SMACs should be retained since it might provide some guidance and insight into the work by other panels of experts.

Comment 9:

p. 27, Ln 41-45 [“*..it is not possible to protect workers without an integrated exposure and medical surveillance programs..”*]

> We think, as written, the comment suggests that there is no medical surveillance program ongoing. That is not true, and we think the comment or section should reflect that there are medical surveillance programs being conducted. We do not expect the Technical Expert Panel to accept the scope of those programs, since

they were not reviewed, but we think they should acknowledge that CH2M HILL agrees with the committee on this point.

Response: The committee did not want to imply that there is no such program ongoing. It also was not charged with the task to review present and ongoing programs. Nevertheless, the committee wanted to emphasize the importance of the issue.