PNNL-26777 Rev. 0

Pacific Northwest
NATIONAL LABORATORY

Proposed HTFOELs for Chronic Exposures – COPCs with Regulatory Guidelines

May 2018

TJ Weber
JN Smith,
JG Teeguarden

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Richland, Washington 99352

Executive Summary

Updated regulatory information for Chemicals of Potential Concern (COPC) related to Hanford Tank Farm operations is documented in this report. There are 61 current COPCs, and regulatory guidelines for 34 of the 61 current COPCs were identified in databases developed by government or private agencies. Four of the 34 COPCs with established regulatory guidelines had new updated information that was applied to propose updates for occupational exposure limits. Two COPCs were new additions to the COPC list, and both had available regulatory guidelines. No changes for the remaining 30 COPCs with regulatory information were identified, and it is proposed that current occupational exposure limits remain unchanged. An additional 27 COPCs (4 nitrosamines, 14 furans, 8 nitriles, and 2,4-dimethylpyridine) that are undergoing further review of their toxic potential are not represented in this document. The results of those reviews will be documented in separate reports.

Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
CAS	Chemical Abstracts Service
COPC	Chemical of Potential Concern
HTF	Hanford Tank Farm
$_{HTF}$OEL	Hanford Tank Farm Occupational Exposure Limit
NIOSH	National Institute for Occupational Safety and Health
OSHA	U.S. Occupational Safety and Health Administration
OEL	Occupational Exposure Limit
PCB	polychlorinated biphenyls
PEL	Permissible Exposure Limit
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
REL	Recommended Exposure Limit
TLV	Threshold Limit Value
TWA	Time-Weighted Average

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1.0 Introduction

In 2016, current Chemicals of Potential Concern (COPC) related to Hanford Tank Farm (HTF) operations were evaluated for new regulatory information that would warrant updating Occupational Exposure Limits (OEL). OELs used to guide safe HTF operations are termed $_{HTF}$OELs and were originally defined in an earlier Pacific Northwest National Laboratory (PNNL) technical report (PNNL-15736, Poet and Timchalk 2006). In this current report, we identify the subset of COPCs with established chronic regulatory guidelines, defined by government or private agencies engaged in OEL development. The information obtained from this effort can be used to update existing chronic $_{HTF}$OELs. Priority in identifying chronic OEL sources for application to HTF operations is given to values reported by the American Conference of Governmental Industrial Hygienists (ACGIH) and the Occupational Safety and Health Administration (OSHA) due to contractual obligations with the U.S. Department of Energy (ACGIH) and legal authority (OSHA). In some cases, the chronic $_{HTF}$OEL for a specified COPC was based on the use of a surrogate chemical because no regulatory information on the specified COPC could be identified. In the case of $_{HTF}$OELs based on surrogates, if regulatory information on the surrogate chemical has not changed from the values reported in PNNL-15736, continued use of the surrogate-based $_{HTF}$OEL for HTF operations is proposed. In cases in which regulatory information on surrogates had changed relative to values reported in PNNL-15736, uncertainty factors used in PNNL-15736 were reviewed and either modified (with justification) or directly applied to the new surrogate regulatory guidelines to update the $_{HTF}$OEL. Additional COPCs not represented in this document are undergoing a more in-depth review of their toxic potential (nitrosamines, furans, and nitriles) and will be summarized in separate reports at a later date.

It is noted that different agencies have elected to report chronic OEL information in relation to work shift lengths. Specifically, ACGIH OELs are based on an 8-hour work shift/40-hour work week, while National Institute for Occupational Safety and Health (NIOSH) OELs are based on a 10 hour work shift/40-hour work week to address trending changes in the workplace. OSHA has developed permissible exposure limits (PELs) that are the maximum amount or concentration of a chemical that a worker may be exposed to under OSHA regulations. OSHA PELs are based on an 8-hour time period. To guide implementation of $_{HTF}$OELs, a brief definition of regulatory values is provided.

1.1 Definitions of Key Threshold Values Used in Chronic $_{HTF}$OEL Evaluations

1.1.1 Occupational Exposure Limit

An OEL is an upper limit on the acceptable concentration of airborne hazardous substances in the workplace for a particular material or class of materials. OELs are generally set by competent national authorities and enforced by legislation to protect occupational safety and health.

1.1.2 Threshold Limit Values

Technical information on Threshold Limit Values (TLV) was derived from ACGIH documents that provide information on TLVs and Basic Exposure Indices (ACGIH 2016). TLVs refer to airborne concentrations of chemical substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day-after-day, over a working lifetime, without experiencing adverse health effects. Because the information available for a specified chemical substance varies over time, TLVs should be regularly updated. Chemical substances with equivalent TLVs (i.e., same numerical

values) cannot be assumed to have similar toxicological effects or similar biologic potency. TLVs 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. TLVs are developed for the protection of "nearly all workers," and therefore may not adequately protect all workers. 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. There are numerous possible reasons for increased susceptibility to a chemical substance, including age, gender, ethnicity, genetic factors (predisposition), lifestyle choices (e.g., diet, smoking, abuse of alcohol and other drugs, etc.), medications, and pre-existing medical conditions (e.g., aggravation of asthma or cardiovascular disease). Some individuals may become more responsive to one or more chemical substances following previous exposures (e.g., sensitized workers). Susceptibility to the effects of chemical substances may be altered during different periods of fetal development and throughout an individual's reproductive lifetime. Some changes in susceptibility also may occur at different work levels (e.g., light versus heavy work) or during exercise periods when increased cardiopulmonary demand is experienced. In addition, variations in temperature (e.g., extreme heat or cold) and relative humidity may alter an individual's response to a toxicant. The documentation for any given TLV should be periodically reviewed and updated, keeping in mind that other factors may modify biological responses.

1.1.3 Threshold Limit Value–Time-Weighted Average

The Threshold Limit Value–Time-Weighted Average (TLV–TWA) typically represents the TWA concentration for a conventional 8-hour workday and a 40-hour workweek, during which it is believed nearly all workers may be repeatedly exposed, day-after-day, for a working lifetime without adverse effects. However, as discussed above, different regulatory agencies may report TLV–TWA information based on different work shift schedules. There are established guidelines for calculating adjustments that account for differences in exposure due to changes in work shift times. For cases in which NIOSH OELs were identified as regulatory guidelines, the documented 10-hour TLV–TWA is applied directly to the 8-hour time period reported for implementation as a chronic $_{HTF}$OEL. It is noted that the typical "in-farm" time for HTF workers is less than 8 hours; therefore, the TLV values listed for chronic exposures are conservative. It is possible that future efforts could examine the merit of exposure standard adjustments proposed by the Australian Institute of Occupational Hygienists (AIOH 2016). These suggested standard adjustments consider differences between ceiling standards, mild irritants, standards set by technological feasibility or good hygiene practices, acute toxicants, cumulative toxicants, and both acute plus cumulative toxicants.

1.1.4 Threshold Limit Value–Ceiling

TLV–Ceiling represents the concentration of a chemical substance that should not be exceeded during any part of the working exposure. If instantaneous measurements are not available, sampling should be conducted for the minimum period of time sufficient to detect exposures at or above the ceiling value. Regulatory agencies such as ACGIH believe that TLVs based on physical irritation should be considered no less binding than those based on physical impairment. There is increasing evidence that physical irritation may initiate, promote, or accelerate adverse health effects through interaction with other chemical or biologic agents or through other mechanisms.

1.1.5 Permissible Exposure Limit

A PEL is a legally enforceable OEL reported by OSHA. OSHA recognizes that many of its PELs are outdated and inadequate for ensuring protection of worker health. Most of OSHA's PELs were issued shortly after adoption of the Occupational Safety and Health Act in 1970, and have not been updated since that time. Section 6(a) of the Occupational Safety and Health Act granted OSHA the authority to adopt existing federal standards or national consensus standards as enforceable OSHA standards. Most of the OSHA PELs contained in the Z-Tables of Title 29 of the Code of Federal Regulations Parts 1910.1000 were adopted from the Walsh-Healy Public Contracts Act as existing federal standards for general industry. These in turn had been adopted from the 1968 TLVs of the ACGIH.

1.1.6 Recommended Exposure Limit

A recommended exposure limit (REL) is an OEL that has been recommended to OSHA by NIOSH for adoption as a PEL. An REL is a level that NIOSH believes would be protective of worker safety and health over a working lifetime if used in combination with engineering and work practice controls, exposure and medical monitoring, posting and labeling of hazards, worker training and personal protective equipment. No REL has ever been adopted by OSHA, but they have been used as guides by some industry and advocacy organizations. RELs for chemical exposures are usually expressed in parts per million (ppm), or sometimes in milligrams per cubic metre (mg/m^3). Although not legally enforceable, NIOSH RELs are considered by OSHA during the promulgation of legally enforceable PELs.

1.1.7 Time-Weighted Average

A TWA is the average concentration of a chemical in air for a specified time period, typically 8 hours.

1.2 Assessment Descriptions and Organizations

In this report, we provide relevant background on historical efforts to establish $_{HTF}$OELs and current efforts to update $_{HTF}$OELs based on new regulatory information where applicable. Chapter 2 provides the summary of the initial recommended chronic $_{HTF}$OELs to Washington River Protection Solutions. The recommended chronic $_{HTF}$OEL (TLV–TWA or ceiling values) for the initial set of COPCs are presented in Chapter 2 in Table 1. The COPC data set consists of 59 chemicals. Three additional chemicals that are being considered for addition to the COPC list also were reviewed. These three chemicals were grouped in the proper chemical groups and noted. The rationale and justification for the recommended $_{HTF}$OELs follow Table 1 and are listed in the same order.

2.0 Recommended Chronic HTFOELs

2.1 Summary of Proposed Changes in Chronic HTFOELs

There are 61 current COPCs, and regulatory guidelines were identified for 34 of these 61 COPCs in databases developed by government or private agencies. Four chemicals have proposed changes in their HTFOELs. Of the four chemicals with proposed changes, one chemical (tributyl phosphate) has a direct change in regulatory values reported by government/private agencies. For the remaining three chemicals (3-methyl-3-buten-2-one, 6-methyl-2-heptanone, dibutyl butylphosphonate), proposed changes in the HTFOEL are based on changes in regulatory guidelines for a surrogate chemical on which the HTFOEL is based. In the latter case, uncertainty factors applied to surrogate chemicals in PNNL-15736 were either modified (with justification) or applied directly to the new surrogate regulatory value to update the proposed HTFOEL. Uncertainty factors used in PNNL-15736 followed established Environmental Protection Agency (EPA 2002) guidelines for chemical risk assessment. No changes in regulatory information for the remaining 30 COPCs with regulatory information were identified, and we propose that current OELs remain unchanged. Two of these 30 COPCs are new additions to the COPC list (dimethyl mercury, 2-Propenal) with available regulatory guidelines. For a few of the COPCs, the source TLV specification or the surrogate that was used had OEL concentrations that were presented in terms of mg/m^3 rather than ppm. Therefore, some concentration values are listed as mg/m^3 to be consistent with regulatory source specifications. The technical basis for the change in regulatory values is documented for each chemical in Section 2.2.

Table 1. Proposed Chronic HTFOEL Exposure Guidelines

Chemical	Chemical Abstract Service (CAS) Number	Current HTFOEL (ppm)	Proposed Regulatory Guideline (ppm)	Proposed Regulatory Guideline (mg/m^3)	Agency/ TLV Specification
Inorganic Compounds					
1. Ammonia	7664-41-7	25	25	--	ACGIH TWA
2. Nitrous Oxide	10024-97-2	50	50	--	ACGIH TWA
3. Mercury	7439-97-6	0.003	0.003	0.025	ACGIH TWA
Hydrocarbons					
4. 1,3-Butadiene	106-99-0	1	1	--	OSHA TWA
5. Benzene	71-43-2	0.5	0.5	--	ACGIH TWA
6. Biphenyl	92-52-4	0.2	0.2	--	ACGIH TWA
Alcohols				--	
7. 1-Butanol	71-36-3	20	20	--	ACGIH TWA
8. Methanol	67-56-1	200	200	--	ACGIH TWA
Ketones					
9. 2-Hexanone	591-78-6	5	5	--	ACGIH TWA
10. 3-Methyl-3-buten-2-one	814-78-8	0.02	0.07	--	(Surrogate)[b] ACGIH Ceiling
11. 4-Methyl-2-hexanone	105-42-0	0.5	0.5	--	(Surrogate) ACGIH TWA
12. 6-Methyl-2-heptanone	928-68-7	8	3	--	(Surrogate) ACGIH TWA
13. 3-Buten-2-one	78-94-4	0.2	0.2	--	ACGIH Ceiling
Aldehydes					
14. Formaldehyde	50-00-0	0.3	0.3	--	ACGIH Ceiling
15. Acetaldehyde	75-07-0	25	25	--	ACGIH Ceiling

Chemical	Chemical Abstract Service (CAS) Number	Current HTFOEL (ppm)	Proposed Regulatory Guideline (ppm)	Proposed Regulatory Guideline (mg/m^3)	Agency/ TLV Specification
16. Butanal	123-72-8	25	25	--	AIHA WEEL TWA
17. 2-Methyl-2-butenal	1115-11-3	0.03	0.03	--	(Surrogate) ACGIH Ceiling
18. 2-Ethyl-hex-2-enal	645-62-5	0.1	0.1	--	(Surrogate) ACGIH Ceiling
Phthalates					
19. Diethyl phthalate	84-66-2	0.55	0.55	5	ACGIH TWA
Amines					
20. Ethylamine	75-04-7	5	5	--	ACGIH TWA
Organophosphates and Organophosphonates					
21. Tributylphosphate	126-73-8	0.2	0.46	5	ACGIH TWA
22. Dibutyl butylphosphonate	78-46-6	0.007	0.015	0.16	(Surrogate) ACGIH TWA
Halogenated Hydrocarbons					
23. Chlorinated biphenyls	Various	0.003	0.003-pending[c]	0.03-pending	ACGIH TWA
24. 2-Fluoropropene	1184-60-7	0.1	0.1	--	(Surrogate) ACGIH TWA
Pyridines					
25. Pyridine	110-86-1	1	1	--	ACGIH TWA
Organonitrites					
26. Methyl nitrite	624-91-9	0.1	0.1	--	(Surrogate) ACGIHCeiling
27. Butyl nitrite	544-16-1	0.1	0.1	--	(Surrogate) ACGIH Ceiling
Organonitrates					
28. Butyl nitrate	928-45-0	2.5	2.5	--	(Surrogate) ACGIH TWA
29. 1,4-Butanediol, dinitrate	3457-91-8	0.05	0.05	--	(Surrogate) ACGIH TWA
30. 2-Nitro-2-methylpropane	594-70-7	0.3	0.3	--	(Surrogate) ACGIH TWA
31. 1,2,3-Propanetriol, 1,3-dinitrate	623-87-0	0.05	0.05	--	(Surrogate) ACGIH TWA
Isocyanates					
32. Methyl Isocyanate	624-83-9	0.02	0.02	--	ACGIH TWA
New COPCs					
P1. Dimethyl Mercury, as Hg[a]	593-74-8	--	0.001	0.01	ACGIH TWA
P2. 2-Propenal[a]	107-02-8	--	0.1	--	ACGIH Ceiling

[a] Dimethyl mercury and 2-Propenal are new additions to the COPC list as of September, 2017. We used P1 and P2, respectively, to identify these new COPCs as they were proposed additions when this study began.
[b] HTFOEL is based on the use of a surrogate chemical and the applicable regulatory guidelines are referenced.
[c] An internal review is being conducted to determine the basis for different values listed in Washington River Protection Solutions documentation versus the current HTFOEL established in PNNL-15736.

2.2 Justification for Proposed Chronic $_{HTF}$OELs

2.2.1 Inorganic Compounds

Ammonia Recommendation: 25 ppm TLV–TWA 8 hours
Source/Justification: ACGIH 2016 handbook.

Nitrous Oxide Recommendation: 50 ppm TLV–TWA 8 hours
Source/Justification: ACGIH 2016 handbook.

Mercury Recommendation: 0.003 ppm TLV–TWA 8 hours
Source/Justification: ACGIH 2016 handbook. The ACGIH handbook lists an 8-hour TWA of 0. 025 mg/m^3 for elemental and inorganic forms of mercury. To convert units from mg/m^3 to ppm, the ACGIH uses the formula:

TLV in ppm = (24.45 × TLV in mg/m^3) ÷ (gram molecular weight of substance)

Therefore, $TLV_{mercury}$ in ppm = (24.45 × 0.025) ÷ 200.59 = 0.003 ppm

Dimethyl Mercury Recommendation: 0.001 ppm TLV–TWA 8 hours
Source/Justification: ACGIH 2016 handbook. The ACGIH handbook lists an 8-hour TWA of 0.01 mg/m^3 for alkyl compounds of mercury, as mercury. In practical terms, the conversion to ppm results in a 0.001 ppm final number, whether the molecular weight of mercury or dimethyl mercury is used in the equation. To convert units from mg/m^3 to ppm, the following formula is used with the molecular weight of mercury:

TLV in ppm (24.45 × TLV in mg/m^3) ÷ (gram molecular weight of substance)

Therefore, $TLV_{dimethyl\ mercury}$ in ppm = (24.45 × 0.01) ÷ 200.59 = 0.001 ppm

2.2.2 Hydrocarbons

1,3-Butadiene Recommendation: 1 ppm TLV–TWA 8 hours
Source/Justification: OSHA PEL. OSHA recognizes that many of its PEL values are outdated, being established shortly after adoption of the Occupational Safety and Health Act in 1970. The current ACGIH 2016 handbook lists a TWA 8-hour value of 2 ppm, which may be more accurate. However, due to uncertainties with complex mixtures associated with HTF operations and the carcinogenic potential of 1,3-butadiene, we suggest continued application of the more conservative OSHA PEL. Many butadiene metabolites are mutagenic in vivo and in vitro, and it is believed that the carcinogenic effects of 1,3-butadiene observed in animal models are mediated by genotoxic metabolites (ACGIH, 2006). Several epidemiological studies of workers in styrene-butadiene rubber factories have shown increased incidence of respiratory, bladder, stomach, and lymphopoietic cancers. However, these studies are not sufficient to determine a causal association between 1,3-butadiene exposure and cancer. The International Agency for Research on Cancer has classified 1,3-butadiene as a probable human carcinogen (group 2A). It is unclear why ACGIH recommends a higher TLV at this time as compared with the OSHA PEL.

Benzene Recommendation: 0.5 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. The current ACGIH 2016 handbook lists a TWA 8-hour value of 0.5 ppm for benzene. The NIOSH REL is 0.1 ppm with a TWA of 10 hours, and the OSHA PEL is 1 ppm with a TWA of 8 hours. The lower NIOSH REL is derived from information published in 1988 (CDC 1988a). The NIOSH REL is based on analytical detection limits, not health effects. The current ACGIH assessment provides a more comprehensive review of the available literature on health effects and includes evaluation of the information from the Centers for Disease Control and Prevention document in their risk assessment. This proposed value is unchanged from PNNL-15736.

Biphenyl Recommendation: 0.2 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. This proposed value is unchanged from PNNL-15736.

2.2.3 Alcohols

1-Butanol Recommendation: 20 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. This proposed value is unchanged from PNNL-15736.

Methanol Recommendation: 200 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. This proposed value is unchanged from PNNL-15736.

2.2.4 Ketones

2-Hexanone Recommendation: 5 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. The ACGIH value (5 ppm) is the lower of the two prioritized regulatory sources (ACGIH, OSHA) and was selected for conservatism. The OSHA PEL for 2-hexanone is 100 ppm, and NIOSH recommends a 1 ppm OEL. The lower value from NIOSH is based on an epidemiologic study describing an outbreak of neurologic disease among workers in a plant that manufactured printed fabrics. This study reported that a screening of 1157 exposed workers revealed 86 verified cases of distal neuropathy. 2-Hexanone was suspected of being the neurotoxicant because it had only recently been introduced into the process. When recommending its limit, NIOSH relied on an industrial hygiene survey of the plant in 1974, which showed that 2-hexanone concentrations near the textile printing machines ranged from 1 to 156 ppm (from analyses of 10-minute area samples). After reviewing this evidence, NIOSH concluded that 1 ppm could not be considered a no-effect level for 2-hexanone-induced neuropathy. The ACGIH TLV–TWA value was considered to be more valid than the NIOSH REL due to increased weight-of-evidence in the ACGIH risk assessment. The proposed ACGIH value of 5 ppm is unchanged from the original assessment in PNNL-15736.

3-Methyl-3-buten-2-one Recommendation: 0.07 ppm TLV-ceiling

Source/Justification: ACGIH 2016 handbook using 3-buten-2-one (CAS 78-94-4) as surrogate. Current ACGIH guidelines for 3-buten-2-one (also termed methyl vinyl ketone) indicate a TLV-ceiling of 0.2 ppm. Based on the uncertainty associated with chemical and toxicological differences between 3-methyl-3-buten-2-one and 3-buten-2-one, a 3× uncertainty factor was applied, and an additional 3× uncertainty factor was applied for extrapolation from the TLV-ceiling to a TWA. Regulatory guidelines apply two 3× uncertainty factors as a 10×; hence, a net 10× uncertainty factor was applied to the 3-buten-2-one $_{HTF}$OEL established in PNNL-15736. However, it is unnecessary to convert a ceiling value to a TWA, and in the current re-evaluation, the ceiling value is proposed with application of a single 3× uncertainty factor, resulting in a proposed $_{HTF}$OEL of 0.07 ppm TLV-ceiling. This proposed value is changed from PNNL-15736.

4-Methyl-2-hexanone Recommendation: 0.5 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook using 2-hexanone as surrogate. Based on uncertainty associated with chemical and toxicological differences between 2-hexanone and 4-methyl-2-hexanone, an additional 10× uncertainty factor was applied to the 2-hexanone OEL to establish an $_{HTF}$OEL of 0.5 ppm for 4-methyl-2-hexanone. This proposed value is not changed from PNNL-15736.

6-Methyl-2-heptanone Recommendation: 3 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook using 5-methyl-3-heptanone (also termed ethyl amyl ketone; CAS 541-85-5) as a surrogate. Current ACGIH guidelines for 5-methyl-3-heptanone indicate a TLV–TWA 8 hours of 10 ppm, which is changed from the prior OEL of 25 ppm as reported in PNNL-15736. This change in the OEL for 5-methyl-3-heptanone is based on emerging evidence of neurotoxicity. Based on minimal uncertainty associated with chemical differences between 5-methyl-3-heptanone and 6-methyl-2-heptanone, a 3× uncertainty factor was applied to 5-methyl-3-heptanone in PNNL-15736. Applying this same 3× uncertainty factor to the new surrogate OEL establishes 3 ppm as a proposed $_{HTF}$OEL for 6-methyl-2-heptanone. This proposed value is a change from PNNL-15736.

3-Buten-2-one Recommendation: 0.2 ppm TLV-ceiling

Source/Justification: ACGIH 2016 handbook. The ACGIH TLV-ceiling value for 3-buten-2-one (also termed methyl vinyl ketone) has not changed from PNNL-15736.

2.2.5 Aldehydes

Formaldehyde Recommendation: 0.3 ppm TLV-ceiling

Source/Justification: ACGIH 2016 handbook. Guidance from multiple values for formaldehyde were identified. Values included ACGIH (0.3 ppm), NIOSH (0.016 ppm), and OSHA sources (0.75 ppm). The lowest value reported by NIOSH is based on analytical detection limits, not documented adverse health effects (CDC 1988b). The 0.3 ppm ACGIH standard is selected as a conservatism of the lower of the two prioritized regulatory agencies (ACGIH/OSHA). OSHA indicates emerging evidence that may impact their standard in a fact sheet, which suggests that 0.1 ppm formaldehyde may cause respiratory irritation. HTF operations employ an administrative control for all COPCs, which is one-half of the OEL. Therefore, the administrative control for formaldehyde provides an additional safety margin that is nearly consistent with emerging concerns identified by OSHA. The OSHA standard should be monitored for consideration in future $_{HTF}$OEL assessements. This proposed value is unchanged from PNNL-15736.

Acetaldehyde Recommendation: 25 ppm TLV-Ceiling

Source/Justification: ACGIH 2016 handbook. This proposed value is unchanged from PNNL-15736.

Butanal Recommendation: 25 ppm TLV–TWA 8 hours

Source/Justification: American Industrial Hygiene Association Workplace Environmental Exposure Level 2013. This proposed value is unchanged from PNNL-15736.

2-Methyl-2-butenal Recommendation: 0.03 ppm TLV-ceiling

Source/Justification: ACGIH 2016 handbook. No regulatory information is available for 2-methyl-2-butenal, and crotonaldehyde is used as a surrogate. In reviewing the available toxicity databases on 2-Propenal derivatives with similar structures to 2-methyl-2-butenal, the most robust data were found for crotonaldehyde and 2-Propenal, which differ in that they lack branching and have smaller carbon chains. Crotonaldehyde has the closest structural similarity to 2-methyl-2-butenal with differences in the branching carbon chains notes. The ACGIH-recommended TLV-ceilings for crotonaldehyde and 2-Propenal are 0.3 and 0.1 ppm, respectively, which are not different from the values used previously in PNNL-15736. A 3× uncertainty factor was applied to extrapolate a recommended $_{HTF}$OEL for 2-methyl-2-butenal from crotonaldehyde due to the structural differences inherent with branching of the side-chain, which may result in metabolic or toxicological differences. An additional 3× uncertainty factor is recommended due to the limited toxicological data for 2-methyl-2-butenal. Thus, a 9× uncertainty factor was applied to 2-methyl-2-butenal in PNNL-15736. The crotonaldehyde TLV-ceiling has not changed since the previous assessment, therefore, a 0.03 ppm TLV-ceiling is proposed for continued application. This proposed value is unchanged from PNNL-15736.

2-Ethyl-2-hexenal Recommendation: 0.1 ppm TLV-ceiling

Source/Justification: ACGIH 2016 handbook. No regulatory information is available for 2-ethyl-2-hexenal, and crotonaldehyde is used as a surrogate. In reviewing the available toxicity databases on 2-Propenal derivatives with similar structures to 2-ethyl-2-hexenal, the most robust data were found for crotonaldehyde and 2-Propenal, which differ in that they lack branching and have smaller carbon chains. Crotonaldehyde has the closest structural similarity to 2-ethyl-2-hexenal with differences in the branching carbon chains notes. The ACGIH-recommended TLV-ceilings for crotonaldehyde and 2-Propenal are 0.3 and 0.1 ppm, respectively, which are not different from the values used in PNNL-15736. A 3× uncertainty factor was applied to extrapolate a recommended $_{HTF}$OEL for 2-ethyl-2-hexenal from crotonaldehyde due to the structural differences inherent with branching of the side-chain, which may result in metabolic or toxicological differences. The crotonaldehyde TLV-ceiling has not changed since publication of PNNL-15736; therefore, a 0.1 ppm TLV-ceiling is proposed for continued application.

2-Propenal Recommendation: 0.1 ppm TLV-ceiling

Source/Justification: ACGIH 2016 handbook.

2.2.6 Phthalates

Diethyl phthalate Recommendation: 0.55 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. The ACGIH handbook lists an 8-hour TWA of 5 mg/m^3 for diethyl phthalate. To convert units from mg/m^3 to ppm, ACGIH uses the following formula:

TLV in ppm = (24.45 × TLV in mg/m^3) ÷ (gram molecular weight of substance)

Therefore, $TLV_{diethyl\ phthalate}$ in ppm = (24.45 × 5) ÷ 222.24 = 0.55 ppm

2.2.7 Amines

Ethylamine Recommendation: 5 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. This proposed value is unchanged from PNNL-15736.

2.2.8 Organophosphates and Organophosphonates

Tributyl phosphate Recommendation: 0.46 ppm TWA 8 hours

Source/Justification: ACGIH 2016 handbook. The ACGIH handbook lists an 8-hour TWA of 5 mg/m^3 for tributyl phosphate. To convert units from mg/m^3 to ppm, the ACGIH uses the formula:

TLV in ppm = (24.45 × TLV in mg/m^3) ÷ (gram molecular weight of substance)

Therefore, $TLV_{\text{tributyl phosphate}}$ in ppm = (24.45 × 5) ÷ 266.318 = 0.46 ppm

An increase in ACGIH exposure guidelines from 2005 (0.2 ppm) to 2016 (0.46 ppm) was noted. The adverse effect of concern is irritation of the bladder epithelium resulting in necrosis and hyperplasia and subsequent neoplasia. The bladder effect was not replicated in mice. The mechanism for cancer effect is well understood, resulting in classification of tributylphosphate as an A3 carcinogen. Therefore, the new guidelines are based on protection of irritation to bladder epithelium occurring at high dose that could lead to cancer in some animal models due to cytotoxic mode-of-action.

Dibutyl butylphosphonate Recommendation: 0.015 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook using tributyl phosphate as a surrogate. The ACGIH TLV–TWA for tributyl phosphate used in PNNL-15736 (2.29 mg/m^3; 0.2 ppm) has been updated in the ACGIH 2016 handbook (5 mg/m^3; 0.46 ppm). The original TWA value was established primarily by analogy with triphenyl phosphate and reports of worker complaints at 1.4 ppm exposure. Based on uncertainty associated with chemical and toxicological differences between dibutyl butylphosphonate and tributyl phosphate, a 30× uncertainty factor was applied to the tributyl phosphate TLV–TWA in PNNL-15736 to establish an $_{\text{HTF}}$OEL of 0.007 ppm for dibutyl butylphosphonate. The 30× uncertainty factor was derived from a tenfold factor used to account for the lack of a robust toxicity data set, and an additional threefold factor used to account for structural differences between dibutyl butylphosphonate and tributyl phosphate. Applying the 30× uncertainty factor to the updated surrogate TLV (ppm) yields a new regulatory value of 0.015 ppm. This is a change in the $_{\text{HTF}}$OEL from the previous assessment reported in PNNL-15736. The change is due to new regulatory information on tributyl phosphate associated with carcinogenesis in animal models described in the justification section for tributyl phosphate.

2.2.9 Halogenated Hydrocarbons

Chlorinated Biphenyls Recommendation: 0.003 ppm – pending TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. An $_{\text{HTF}}$OEL was proposed for a family of polychlorinated biphenyls (PCB). There are 209 different congeners of PCBs, and their toxic potential is dependent on the extent and location of chlorine substituents on the aromatic rings. The PCB congeners found in the HTF waste tank headspaces are much more similar to the PCBs with lower percentages of chlorine, and the proposed $_{\text{HTF}}$OEL for these PCBs is 0.03 mg/m^3 (~0.003 ppm) based on the ACGIH TLV for 42% chlorinated PCBs (Chlorodiphenyl – 42% chlorine; CAS 53469-21-9; ACGIH TWA: 1 mg/m^3) with an additional 3× uncertainty factor based on the uncertainty associated with the exact mixture of PCBs in the tank and the potential for chloracne. This proposed value has not changed from PNNL-15736.

2-Fluoropropene Recommendation: 0.1 ppm TLV–TWA 8 h

Source/Justification: Current regulatory values found in 2016 ACGIH handbook indicate that the surrogates vinyl fluoride (CAS 75-02-5; 1 ppm TWA ACGIH), vinyl chloride (CAS 75-01-4; 1 ppm TWA ACGIH), and vinyl bromide (CAS 593-60-2; 0.5 ppm TWA ACGIH), upon which the $_{HTF}$OEL is based, have not changed since the 2005 handbook edition. Therefore, the current chronic $_{HTF}$OEL of 0.1 ppm TWA 8 hours, which includes the application of a 10× uncertainty factor based on the uncertainty associated with chemical differences between 2-fluoropropene and vinyl fluoride, is proposed for continued application to HTF operations. This proposed value is unchanged from PNNL-15736.

2.2.10 Pyridines

Pyridine Recommendation: 1 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. This proposed value is unchanged from PNNL-15736.

2.2.11 Organonitrites

Methyl nitrite Recommendation: 0.1 ppm TLV-ceiling

Source/Justification: ACGIH 2016 handbook using isobutyl nitrite as a surrogate. The ACGIH maintains a 1 ppm TLV-ceiling for isobutyl nitrite as a surrogate. Based on uncertainties associated with chemical differences between methyl nitrite and isobutyl nitrite and clear evidence of a cancer risk for isobutyl nitrite in animal studies, a 10× uncertainty factor was applied in PNNL-15736, resulting in an $_{HTF}$OEL of 0.1 ppm TLV-ceiling. This proposed value is unchanged from PNNL-15736.

Butyl nitrite Recommendation: 0.1 ppm TLV-ceiling

Source/Justification: ACGIH 2016 handbook using isobutyl nitrite as a surrogate. The ACGIH maintains a 1 ppm TLV-ceiling for isobutyl nitrite as a surrogate. Based on uncertainties associated with chemical differences between butyl nitrite and isobutyl nitrite and clear evidence of a cancer risk for isobutyl nitrite in animal studies, a 10× uncertainty factor was applied in PNNL-15736, resulting in an $_{HTF}$OEL of 0.1 ppm TLV-ceiling. This proposed value is unchanged from PNNL-15736.

2.2.12 Organonitrates

Butyl nitrate Recommendation: 2.5 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. The $_{HTF}$OEL for butyl nitrate is based on use of the structurally similar compound propyl nitrate as a surrogate. The ACGIH 2016 OEL for propyl nitrate is 25 ppm TLV–TWA 8-hour, which is unchanged from that reported in PNNL-15736. To address underlying uncertainties (e.g., potential pharmacokinetic differences, limited database, etc.) in the use of a chemically similar surrogate compound, a modifying factor of 10 was applied to the OEL for propyl nitrate to arrive at a 2.5 ppm TLV–TWA 8-hour $_{HTF}$OEL for butyl nitrate. This proposed value is unchanged from PNNL-15736.

1,4-Butanediol, dinitrate Recommendation: 0.05 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. The $_{HTF}$OEL for 1,4-butanediol, dinitrate is based on the use of ethylene glycol dinitrate, propylene glycol dinitrate, and nitroglycerine as surrogates. The 2016 ACGIH handbook has assigned TLVs of 0.05 ppm for these surrogates, which is unchanged from the surrogate values reported in PNNL-15736. The most robust set of toxicological data was for

propylene glycol dinitrate. The ACGIH has used this data set as the bases for OELs of other di- and tri-nitrates. Therefore, a 0.05 ppm TLV–TWA is proposed for continued application, which is unchanged from PNNL-15736. By analogy with the short-chain aliphatic mononitrates, this HTFOEL is conservative for these dinitrates.

2-Nitro-2-methylpropane Recommendation: 0.3 ppm TLV–TWA 8 hours

Source/Justification: The 2016 ACGIH handbook using 2-nitropropane as a surrogate. The surrogate value (10 ppm) has not changed from the value documented in PNNL-15736. In reviewing the available toxicity databases on nitro compounds with similar structures to 2-nitro-methylpropane, the most robust data were found for 2-nitropropane and 1-nitropropane, which differ from 2-nitro-methylpropane by the addition of an extra carbon group. 2-Nitro-2-methylpropane is a branched nitro compound with one more methyl groups than 2-nitropropane. The recommended HTFOEL for 2-nitro-2-methyl propane is based on the OEL for 2- nitropropane (10 ppm) with a 10× uncertainty factor for structural differences and a 3× uncertainty factor for limited toxicity data. The 2016 ACGIH-recommended TWA-TLVs for 2-nitropropane and 1-nitropropane are 10 and 25 ppm, respectively, which are the same used in PNNL-15736. Thus, by applying the same 10× and 3× uncertainty factors, the recommended HTFOEL for 2-nitro-methylpropane is 0.3 ppm.

1,2,3-Propanetriol, 1,3-dinitrate Recommendation: 0.05 TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. The HTFOEL for 1,2,3-Propanetriol, 1,3-dinitrate is based on the use of ethylene glycol dinitrate, propylene glycol dinitrate, and nitroglycerine as surrogates. The 2016 ACGIH handbook has assigned TLVs of 0.05 ppm for these surrogates, which is unchanged from PNNL-15736. The most robust set of toxicological data were for propylene glycol dinitrate. The ACGIH has used this data set as the bases for OELs of other di- and tri-nitrates. Therefore, a 0.05 ppm TLV–TWA is proposed for continued application, which is unchanged from PNNL-15736. By analogy with the short-chain aliphatic mononitrates, this HTFOEL of 0.05 ppm is conservative for these dinitrates.

2.2.13 Isocyanates

Methyl Isocyanate Recommendation: 0.02 ppm TLV–TWA 8 hours

Source/Justification: ACGIH 2016 handbook. This proposed value is unchanged from the 2005 ACGIH value reported in the tank vapors technical basis (Meacham et al 2006).

3.0 Summary

Available regulatory guidelines that facilitated the proposed $_{HTF}$OEL values to guide safe HTF operations were identified. Of the 61 chemicals being considered (59 COPCs [2016] plus 2 new COPCs [2017]), information on chronic regulatory guidelines for 34 chemicals was identified. Chronic regulatory values are established for the COPCs, and the chemicals not listed here are undergoing an in-depth internal review to update $_{HTF}$OEL values. The results of those reviews will be documented in separate reports.

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