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Pacific Northwest NATIONAL LABORATORY

Chronic Hanford Tank Farm Occupational Exposure Limits: 2018 Update

September 2018

TJ Weber
JN Smith
JG Teeguarden

U.S. DEPARTMENT OF ENERGY

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Executive Summary

Chemicals of Potential Concern (COPC) related to Hanford Tank Farm (HTF) operations undergo periodic review to identify changes in regulatory guidelines that would impact occupational exposure limits (OEL; termed $_{HTF}$OELs). Data and technical information for the last COPC review was collected in 2016 and has been subsequently summarized in a series of Pacific Northwest National Laboratory technical reports. In this report, the 61 COPCs underwent periodic review for new regulatory information that has become available since the 2016 update. Of the 61 COPCs, 43 COPCs have regulatory information available in databases developed by authoritative government or private agencies. The remaining 18 COPCs undergo risk assessment as carcinogens and, therefore, do not have regulatory OELs. Rather, COPCs with carcinogenic potential are regulated as low as reasonably achievable using a risk-based approach to establish risk-specific doses for occupational exposures. Only two chemicals from the COPC list—formaldehyde and 2,4-dimethylpyridine—have been identified with new regulatory guidelines since the 2016 update. The technical basis for the change in OELs for formaldehyde and 2,4-dimethylpyridine are discussed and the most current $_{HTF}$OEL assessment for the remaining 59 COPCs is summarized for reference.

Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
CAS	Chemical Abstracts Service
COPC	Chemical of Potential Concern
DOE	U.S. Department of Energy
EBR	exposition-risiko-beziehung in German; exposure risk relationships in English
HTF	Hanford Tank Farm
$_{HTF}$OEL	Hanford Tank Farm Occupational Exposure Limit
MAK	Maximum Arbeitsplatz Konzentration values
NDMA	N-Nitrosodimethylamine
NIOSH	National Institute for Occupational Safety and Health
OSHA	U.S. Occupational Safety and Health Administration
OEL	Occupational Exposure Limit
PEL	Permissible Exposure Limit
PNNL	Pacific Northwest National Laboratory
ppm	Parts Per Million
ppb	Parts Per Billion
REL	Recommended Exposure Limit
TLV	Threshold Limit Value
TLV-Ceiling	Threshold Limit Value-Ceiling
TLV-TWA	Threshold Limit Value-Time-Weighted Average
TRGS	Technical Rules for Hazardous Substances
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 (OELs). OELs used to guide safe HTF operations are termed $_{HTF}$OELs and were originally defined in Pacific Northwest National Laboratory (PNNL) technical report PNNL-15736 (Poet and Timchalk 2006). 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. COPCs undergo periodic review, and new regulatory information is used to update $_{HTF}$OELs. The last COPC update conducted in 2016 separately evaluated 1) COPCs with known regulatory guidelines (Weber et al. 2018a), 2) nitrile class COPCs (PNNL-26819; Weber et al. 2018b), and 3) cancer risk estimates for nitrosamine and furan class COPCs.[1,2] Because these reports are based on technical information that was collected in 2016, we broadly refer to this collection of reports as the "2016 update" to avoid confusion with the public release dates of these reports occurring in subsequent years. The results of a periodic review of the 61 COPCs conducted in 2018 are detailed in this current document. In summary, two chemicals—formaldehyde and 2.4-dimethylpyridine—have new regulatory information that is different from the 2016 update. The remaining 59 COPCs do not have new regulatory information and are summarized, but not considered further here.

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

1.1.1 Occupational Exposure Limit (OEL)

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 (TLV)

Technical information on TLVs 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., the 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

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[1] Smith JN, JG Teeguarden, and TJ Weber. September 2017. *Proposed Risk-Based Approach for Nitrosamine Chemicals of Potential Concern*. PNNL-26787 Rev A, Pacific Northwest National Laboratory, Richland, Washington. Unpublished.

[2] Smith JN, JG Teeguarden, and TJ Weber. September 2017. *Proposed Occupational Exposure Limits for Furans.* PNNL-26775 Rev A, Pacific Northwest National Laboratory, Richland, Washington. Unpublished.

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 (TLV-TWA)

The 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 National Institutes of Occupational Safety and Health (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-C)

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 (PEL)

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 Part 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 (REL)

An 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 usually are expressed in parts per million (ppm), or sometimes in milligrams per cubic meter (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 (TWA)

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

2.0 Chronic $_{HTF}$OELs

2.1 Summary of Chronic $_{HTF}$OELs Proposed in the 2016 update

Current $_{HTF}$OELs and changes to current $_{HTF}$OELs proposed in the 2016 update are listed in Tables 1, 2, and 3. Table 1 lists 43 COPCs with available regulatory guidelines. The 2016 update proposed changes in the $_{HTF}$OELs for four chemicals with existing regulatory guidelines. Of the four chemicals with proposed changes, one chemical (tributyl phosphate) had a direct change in regulatory values reported by government/private agencies. The remaining three chemicals (3-methyl-3-buten-2-one, 6-methyl-2-heptanone, dibutyl butylphosphonate) had changes in regulatory guidelines for surrogate chemicals on which the $_{HTF}$OEL was based. Uncertainty factors originally applied to surrogate chemicals in PNNL-15736 (Poet and Timchalk 2006) were either modified (with justification) or applied directly to the new surrogate regulatory value in the 2016 update. Uncertainty factors used to develop $_{HTF}$OELs follow established Environmental Protection Agency (EPA 2002) guidelines for chemical risk assessment. Regulatory values published in 2018 for tributyl phosphate and surrogates used for 3-methyl-3-buten-2-one, 6-methyl-2-heptanone and dibutyl butylphosphonate are the same as those reported in the 2016 update. Therefore, the proposed $_{HTF}$OELs for these chemicals presented in Weber et al. (2018a) are based on the most current science, and these COPCs do not require further consideration here. Adoption or rejection of proposed changes to $_{HTF}$OELs is under review and will be applied as appropriate pending final decisions. The technical basis of $_{HTF}$OELs listed in Table 1 can be found in Weber et al. (2018a). 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.

Table 2 lists four N-nitrosamine class COPCs for which a risk-based approach is used to recommend $_{HTF}$OELs due to their carcinogenic potential. N-nitrosamines are genotoxic, and exposure has been historically regulated based on cancer as the endpoint of concern. Currently, $_{HTF}$OELs are based on German Maximum Arbeitsplatz Konzentration (MAK) values, which are no longer used. NIOSH recently released new policy applying a risk-based approach to develop OELs for occupational carcinogens and plans to release guidance on specific chemicals in the future. Consistent with this new NIOSH policy, PNNL proposed a risk-based approach to establish risk-specific doses for occupational exposures to N-nitrosamine COPCs in the 2016 update.[1] This approach establishes a range of N-nitrosamine inhalation exposures that are associated with risk levels that can be used as a tool for protecting HTF workers.

In 2015, the German Committee on Hazardous Substances (AGS)[3] published exposure risk relationships (exposition-risiko-beziehung [EBR] in German) for N-Nitrosodimethylamine (NDMA) (AGS 2015). Similar to the risk-based approach proposed by PNNL,[1] the Committee on Hazardous Substances document establishes NDMA exposures associated with risk of adverse effects. To make risk-based calculations, the EBR used an inhalation unit risk of 0.0053 (µg/m^3) to calculate risk specific doses of 0.75, 0.075, and 0.0075 µg/m^3 for risk levels of 4:1000; 4:10,000; and 4:100,000; respectively (AGS 2015). The inhalation unit risk was derived from a study that exposed rats to NDMA by inhalation four times per week, 4 to 5 hr/day, 207 days (Klein et al. 1991). A 10% benchmark dose level (18.66 µg/m^3) was calculated from tumor incidence measured in this study, which was used as the point

[3] The AGS is a consultative body of the Federal Ministry of Labour and Social Affairs on issues of the Ordinance on Hazardous Substances. Experts from all areas of occupational health and safety work together to create a framework of rules. The committee meets twice a year to advise and decide on work results, in particular Technical Rules for Hazardous Substances (TRGS). The rule applicable to the content of this report is TRGS 910, “Risk-Related Concept of Measures for Activities Involving Carcinogenic Hazardous Substances.”

of departure without species extrapolation (AGS 2015). The inhalation unit risk used for ERB calculations was identical to the unit risked used by PNNL prior to adjustment for an Occupational Work Life (Table 2). Therefore, no changes to $_{HTF}$OELs for N-nitrosamine class COPCs are proposed, and this class of chemicals does not require further review in this report. A detailed description of the risk-based approach used to recommend proposed $_{HTF}$OELs for nitrosamines was in a PNNL report submitted to Washington River Protection Solutions in September 2017. That report has not been made publically available yet.

Table 1. Proposed Chronic $_{HTF}$OEL Updates for COPCs with Available Regulatory Guidelines from the 2016 Update

Chemical	Chemical Abstract Service (CAS) Number	Current $_{HTF}$OEL (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
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
19. 2-Propenal[a]	107-02-8	--	0.1	--	ACGIH Ceiling
Phthalates					
20. Diethyl phthalate	84-66-2	0.55	0.55	5	ACGIH TWA
Amines					
21. Ethylamine	75-04-7	5	5	--	ACGIH TWA
Organophosphates and Organophosphonates					
22. Tributylphosphate	126-73-8	0.2	0.46	5	ACGIH TWA
23. Dibutyl butylphosphonate	78-46-6	0.007	0.015	0.16	(Surrogate) ACGIH TWA
Halogenated Hydrocarbons					
24. Chlorinated biphenyls	Various	0.003	0.003	0.03	ACGIH TWA

Chemical	Chemical Abstract Service (CAS) Number	Current HTFOEL (ppm)	Proposed Regulatory Guideline (ppm)	Proposed Regulatory Guideline (mg/m^3)	Agency/ TLV Specification
25. 2-Fluoropropene	1184-60-7	0.1	0.1	--	(Surrogate) ACGIH TWA
Pyridines					
26. Pyridine	110-86-1	1	1	--	ACGIH TWA
27. 2,4-Dimethylpyridine	108-47-4	0.5	0.5	--	U.S. Department of Energy (DOE) TEEL-1
Organonitrites					
28. Methyl nitrite	624-91-9	0.1	0.1	--	(Surrogate) ACGIH Ceiling
29. Butyl nitrite	544-16-1	0.1	0.1	--	(Surrogate) ACGIH Ceiling
Organonitrates					
30. Butyl nitrate	928-45-0	2.5	2.5	--	(Surrogate) ACGIH TWA
31. 1,4-Butanediol, dinitrate	3457-91-8	0.05	0.05	--	(Surrogate) ACGIH TWA
32. 2-Nitro-2-methylpropane	594-70-7	0.3	0.3	--	(Surrogate) ACGIH TWA
33. 1,2,3-Propanetriol, 1,3-dinitrate	623-87-0	0.05	0.05	--	(Surrogate) ACGIH TWA
Isocyanates					
34. Methyl Isocyanate	624-83-9	0.02	0.02	--	ACGIH TWA
Organometallics					
35. Dimethyl Mercury, as Hg[a]	593-74-8	--	0.001	0.01	ACGIH TWA
Nitriles					
36. Acetonitrile	75-05-8	20	20	--	ACGIH TWA
37. Propanenitrile	107-12-0	6	6		NIOSH TTWA
38. Butanenitrile	109-74-0	8	8		NIOSH TWA
39. Pentanenitrile	110-59-8	6	6		(Surrogate) NIOSH TWA
40. Hexanenitrile	628-73-9	6	6		(Surrogate) NIOSH TWA
41. Heptanenitrile	629-08-3	6	6		(Surrogate) NIOSH TWA
42. 2-Methylene butanenitrile	1647-11-6	0.3	0.3		(Surrogate) NIOSH TWA
43. 2,4-Pentadienenitrile	1615-70-9	0.3	0.3		(Surrogate) NIOSH TWA

[a] 2-Propenal and Dimethyl mercury are new additions to the COPC list as of September, 2017. Therefore, current HTFOELs were not in practice when the 2016 update was conducted and available regulatory guidelines were identified and used to propose HTFOELs for these chemicals in the 2016 update.
[b] The term surrogate refers to HTFOELs that are based on the use of a surrogate chemical with the regulatory source for the surrogate value referenced.

Table 2. Proposed Chronic $_{HTF}$OELs for Nitrosamine Class COPCs Derived Using a Risk-Based Approach Reported in the 2016 COPC Update

Chemical	Chemical Abstract Service (CAS) Number	MAK-Based OEL (ppb)	Inhalation Risk Specific Dose (ppb)			
			1:1,000	1:10,000	1:100,000	1:1,000,000
1. N-Nitrosodimethylamine (NDMA)	62-75-9	0.3	0.15	1.5E-02	1.5E-03	1.5E-04
2. N-Nitrosodiethylamine	55-18-5	0.1	0.04	3.8E-03	3.8E-04	3.8E-05
3. N-Nitrosomethylethylamine	10595-95-6	0.3	0.30	3.0E-02	3.0E-03	3.0E-04
4. N-Nitrosomorpholine	59-89-2	0.6	1.24	1.2E-01	1.2E-02	1.2E-03

Table 3 lists the current $_{HTF}$OEL and proposed updates to the current $_{HTF}$OEL for 14 furan class COPCs, comprised of furan and 13 substitited furans presented in the 2016 update, which was submitted to Washington River Protection Solutions in September 2017 but has not been made publically available.[2] Furan causes liver toxicity and cancer in laboratory animals. Recent toxicity studies in animal models have established a non-genotoxic mechanism-of-action, and this new data was used to re-evaluate furan class COPC $_{HTF}$OELs.[2] As such, PNNL proposed to adjust the $_{HTF}$OEL for furan class COPCs from 1 ppb to 1.9 ppb based on a no-observed-adverse-effect level in Fischer-344 rats (the most sensitive species tested) exposed to subchronic oral administration of furan as a point of departure modified by species extrapolation of dose and route, inter- and intra-species uncertainty factors, and adjustments for life-time vs. occupational exposure periods. Because of limited data and similar hypothesized mechanisms of toxicity, PNNL recommended continuation of the use of the furan $_{HTF}$OEL as a surrogate for substituted furans until further data for substituted furans becomes available. No new regulatory information for furan class COPCs was identified in the current 2018 update. Therefore, no changes to $_{HTF}$OELs for furan class COPCs described in the September 2017 PNNL report[2] are proposed, and this class of chemicals does not require further review in this report.

Table 3. Current and Proposed Chronic $_{HTF}$OELs for Furan and Substituted Furans Reported in the 2016 COPC Update

Chemical	Chemical Abstract Service (CAS) Number	Current OEL (ppb)	Proposed OEL (ppb)
1. Furan	110-00-9	1	1.9
2. 2-Heptylfuran	3777-71-7	1	1.9
3. 2-Octylfuran	4179-38-8	1	1.9
4. 2-Pentylfuran	3777-69-3	1	1.9
5. 2-Methylfuran	534-22-5	1	1.9
6. 2-Propylfuran	4229-91-8	1	1.9
7. 2-Ethyl-5-methlyfuran	1703-52-2	1	1.9
8. 2-(2-Methyl-6-oxoheptyl)furan	51591-87-0	1	1.9
9. 2-(3-Oxo-3-phenylprop-1-enyl)furan	717-21-5	1	1.9
10. 2,3-Dihydrofuran	1191-99-7	1	1.9
11. 2,5-Dihydrofuran	1708-29-8	1	1.9
12. 2,5-Dimethylfuran	625-86-5	1	1.9
13. 3-(1,1-Dimethylethyl)-2,3-dihydrofuran	34314-82-4	1	1.9
14. 4-(1-Methpropyl)-2,3-dihydrofuran	34379-54-9	1	1.9

Table 4 lists the two COPCs for which new regulatory information was identified in the current 2018 update. A description of the technical basis for the change in regulatory values for formaldehyde and 2,4-dimethylpyridine can be found in Section 2.2.

Table 4. Proposed Changes to Chronic $_{HTF}$OELs Based on Regulatory Information Identified in 2018

Compound	Chemical Abstract Service (CAS) Number	Current OEL (ppm)	Proposed Regulatory Guideline (ppm)	Agency/TLV Specification
1. Formaldehyde	50-00-0	0.3	0.1 TWA 0.3 STEL	ACGIH/TWA/STEL
2. 2,4-Dimethylpyridine	108-47-4	0.5	0.14	DOE/TEEL-1

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

2.2.1 Formaldehyde

Formaldehyde Recommendation: 0.1 ppm TLV-TWA; 0.3 ppm STEL

Source/Justification: ACGIH 2018 handbook. The previous assessment of formaldehyde used a STEL ceiling regulatory value from ACGIH, and no formal guidance on a TLV-TWA was provided by the ACGIH at that time. Guidance from multiple regulatory agencies for formaldehyde were considered in the 2016 assessment. Values included ACGIH (0.3 ppm), NIOSH (0.016 ppm), and OSHA sources (0.75 ppm). The lowest value reported by NIOSH was based on analytical detection limits, not documented adverse health effects (CDC 1988). The 0.3 ppm ACGIH standard was the lower of the two prioritized regulatory agencies (ACGIH/OSHA) and was selected to be conservative. OSHA indicated emerging evidence that may impact their standard in a fact sheet, which suggests that 0.1 ppm formaldehyde may cause respiratory irritation. In 2018, the ACGIH formalized a TLV–TWA of 0.1 ppm formaldehyde. The change in regulatory guidance is based primarily on human studies, supplemented by evidence from experimental animal studies. The value proposed is recommended to minimize the potential for sensory irritation, chiefly of the eye and upper respiratory tract. Experimental evidence raises the possibility that formaldehyde may induce squamous cell nasal cancer via a mechanisms that involves cytotoxicity, cell proliferation and/or genotoxicity. Minimizing repeated irritation to the respiratory tract is expected to be protective against upper respiratory tract cancers. Therefore, a combination of the TWA and STEL guidelines is recommended by the ACGIH. 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 consistent with emerging concerns identified by OSHA. The proposed value (0.1 ppm TWA; 0.3 ppm STEL) represents a change in $_{HTF}$OEL for formaldehyde from the prior assessment conducted in 2016 (Weber et al. 2018a).

2.2.2 2,4-Dimethylpyridine

2,4-Dimethylpyridine Recommendation: 0.14 ppm TLV–TWA

Source/Justification: DOE TEEL-1.

Prioritized regulatory sources (ACGIH, OSHA) have not provided guidance on the OEL for 2,4-dimethylpyridine and alternative regulatory sources were identified. DOE has established a TEEL-1 value of 0.5 ppm for 2,4-dimethylpyridine which was proposed as the $_{HTF}$OEL in PNNL-15736 (Poet and Timchalk 2006), based on the comparison of acute and subchronic effects of 5-ethyl-2-picoline, pyridine, and 2,4-dimethylpyridine in laboratory animals, and the effects from human exposures to pyridine mixtures. In the present 2018 update, a change in the DOE TEEL-1 value for 2,4-dimethylpyridine from 0.5 ppm to 0.14 ppm was reported. TEELs are developed according to procedures outlined in a DOE handbook—DOE-HDBK-1046-16, *Temporary Emergency Exposure Limits for Chemicals: Methods and Practice*.[4] The TEEL-1 value for 2,4-dimethylpyridine was changed in Rev. 27 of the DOE handbook. The following discussion provides the technical basis for this change. There were no published exposure limits for 2,4-dimethylpyridine, and as a result, in accordance with Section 3.3 of the handbook, the TEEL-3 value was derived from a rat oral LD_{50} study. Because no other toxicity data was available, in accordance with Section 3.4.1 of the DOE handbook, the TEEL-2 value was derived by dividing the TEEL-3 value by 6. The TEEL-1 value was then derived from the TEEL-2 value by dividing that value by 11.

TEEL-1 is similar to the ACGIH TLV of 1 ppm for pyridine and the AIHA TEEL of 2 ppm for 2-methylpyridine, 3-methylpyridine, and 4-methylpyridine. The definition of TEEL-1 is, "… the maximum airborne concentration below which it is believed that nearly all individuals could be exposed without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odor." The TEEL-1 value usually is based on a 1-hour TWA. In addition, the World Health Organization recognizes 2,4-dimethylpyridine as having "no safety concern" for oral exposures (WHO 2012). Therefore, the TEEL-1 value is considered to be very conservative. With the publication of Revision 29 in May 2016, a culminating point in the DOE project was reached and no further plans for development or in-depth review of existing TEELs are being considered. This revision in the TEEL derivation process resulted in a change in 2,4-dimethylpyridine guidelines from 0.5 ppm to 0.14 ppm.

[4] Available at: https://energy.gov/ehss/downloads/doe-hdbk-1046-2016.

3.0 Summary

Periodic review of the COPCs conducted in 2018 identified new regulatory information for formaldehyde and 2,4-dimethylpyridine. This new information was used to propose changes in the $_{HTF}$OELs for formaldehyde and 2,4-dimethylpyridine. No new regulatory information was identified for the remaining 59 COPCs and current or proposed changes to $_{HTF}$OELs from the 2016 update are recommended for continued application to HTF operations. In the 2016 update (Weber et al. 2018a), changes to the $_{HTF}$OELs for four COPCs (tributyl phosphate, 3-methyl-3-buten-2-one, 6-methyl-2-heptanone, dibutyl butylphosphonate) were proposed, and these changes are currently under review. Regulatory information for these four COPCs in the 2018 update is identical to the 2016 update. Therefore, recommended changes to tributyl phosphate, 3-methyl-3-buten-2-one, 6-methyl-2-heptanone, and dibutyl butylphosphonate suggested in Weber et al. (2018a) can be directly applied to the current update when a final decision on proposed changes has been reached.

4.0 References

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