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Hanford Tank Vapor FY 2017 Chemicals of Potential Concern Update

May 2018

LA Mahoney
EW Hoppe

U.S. DEPARTMENT OF
ENERGY

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Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

The identification of Chemicals of Potential Concern (COPCs) in tank headspace vapors and the development of specific Occupational Exposure Limits (OEL) recommendations for these COPCs were completed over 10 years ago, in 2005-2006. The results were documented in a number of Pacific Northwest National Laboratory (PNNL) and Tank Operations Contractor reports, and a set of COPCs with corresponding Hanford Tank Farm OELs ($_{HTF}$OELs) were accepted for use. The selection of COPCs was based on measured headspace concentrations, relative to the available OELs for target vapor constituents. The $_{HTF}$OELs were set based on the toxicological information and standards at the time.

In FY 2016, two parallel efforts were undertaken to revisit the COPC list and examine the basis for assigned $_{HTF}$OELs so the most current tank vapor data and health effects information are considered in updating the COPC list. The updating process has continued in FY 2017 under Task 4 of the FY17 Health Process Plan Statement of Work[1].

This report documents the 2017 analyses and recommendations on tank vapor COPCs, which used an updated set of tank vapor concentrations and improved estimates for $_{HTF}$OELs for some of the chemicals that had been identified in FY 2016 (Hoppe et al. 2016). Several companion reports for furans[2], nitrosamines[3], and other vapor chemicals (Weber et al. 2018) were produced under Task 5 of the Statement of Work and serve to document the health effects and recommend toxicological limit information for current COPCs and COPC candidates.

As before, sample analysis results for tank headspace vapors and airborne emissions, including a range of operating conditions (i.e., quiescent, sluicing, tank transfers, etc.) were used to assess whether post-FY 2016 $_{HTF}$OELs or vapor concentration measurements changed the COPC status of any chemicals. The assessment was made using screening ratios, which are the ratios of the maximum concentrations to the toxicological screening values of the chemicals. Ratios greater than unity indicated chemicals that were of interest. From over 1400 compounds evaluated, 33 were found to have different screening ratios than had been calculated in the 2016 work. Of the 33 chemicals, 10 showed increases in the screening ratio, 22 showed decreases in the ratio, and one chemical maintained the same ratio (that one chemical is mentioned here because its screening value remained the same in 2017 as in 2016 but now has a different type of toxicological basis). There are two new COPC-related recommendations based on the work done in FY 2017.

One new COPC candidate, nitrosodipropylamine (N-nitroso-N-propyl-1-propanamine) was identified. Its new status was the result of a new screening value based on the inhalation risk-specific dose for a cancer risk level of 10^{-4}.

Two alkyl-substituted furans, 2-propylfuran and 2-heptylfuran, that were considered to have been misidentified based on pre-2006 data have been detected in measurements made during tests of air-purifying respirator cartridges. This observation supports retaining these furans and, by extension, other alkyl-substituted furans as COPCs.

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[1] Requisition #292439, Rev. 1, March 30, 2017, FY17 Contract #36437-219.

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

[3] Smith, JN, JG Teeguarden, TJ Weber, C Timchalk. 2017. Proposed Risk-Based Approach for Nitrosamine Chemical of Potential Concern. PNNL-26787 Rev. A, Pacific Northwest National Laboratory, Richland, Washington. Unpublished.

This latest study identified an ambiguity in the database concentrations whose impact was not recognized in the 2016 COPC report. Much of the concentration data in the Site-Wide Industrial Hygiene Database headspace (SWIHD HS) database and some of the data in the Tank Waste Information Network System Industrial-Hygiene (TWINS IH) database represents measurements from individual sorbent tubes or other analyte collectors that were arranged in series on the same air flow stream. The original air concentration in the stream is the sum of concentration measurements on individual tubes in each series. However, there is inadequate information in either of these databases to explicitly identify which samples were taken or in what order on the same air stream (upstream or downstream). Sampling reports and sample-head configuration drawings provide much of the needed information.

For this FY 2017 study, we employed a plausible but approximate method for using existing information in the SWIHD HS database to identify samples taken in series, so that concentrations could be appropriately summed. Because the TWINS IH database contained fewer clues for identifying samples taken on the same air flow stream, no combination of data for tubes was carried out on TWINS IH data. The extent of the need for concentration combination was not understood in 2016, so some maximum concentrations documented in that report may be underestimated. This study makes recommendations pertaining to the need for more database information about analyte collectors in series.

Objective of the Health Process Plan

The objective of the Health Process Plan Project is to define the strategy and plan for regularly and rigorously reviewing and updating Chemicals of Potential Concern (COPC) in Hanford tank vapors and corresponding Occupational Exposure Limits where established, and/or proposing exposure action levels for those COPCs or mixtures of COPCs where no acceptable limits exist. The approach is to build from the strategy and processes that form the foundation of the current industrial-hygiene technical basis (Meacham et al. 2006),[1] and extend the assessments to include evolving issues and understanding of chronic exposure limits, acute transient exposure concentrations, and COPC mixtures.

The FY 2016 priority for this effort included revisiting the COPC list using the most current tank vapor data. Specifically, this effort included the following actions:

- Reviewing historical and current data on headspace and source sampling and analyses available using the Tank Waste Information Network System databases and the Site-Wide Industrial Hygiene Database, limited to headspace data only

- Reviewing the historical basis for COPC selection decisions made more than a decade ago

- Updating the COPC list, and identifying any additional tank vapor chemicals that should undergo further review and consideration as potential COPCs based on evolving tank vapor characterization and understanding

- Making recommendations on future sampling and analyses to improve COPC identification.

The FY 2017 priorities, under Task 4 of the Health Process Plan Statement of Work, are listed below:

- Updating the review of historical and current data from the same databases

- Updating the COPC list and identifying any additional tank vapor chemicals that might be potential COPCs

- Making recommendations on sampling and vapor database changes to improve the bases for COPC identification.

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[1] Meacham JE, JO Honeyman, TJ Anderson, ML Zabel, and JL Huckaby. 2006. *Industrial Hygiene Chemical Vapor Technical Basis*. RPP-22491, Rev. 1, CH2M Hill Hanford Group, Inc., Richland, Washington.

Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
CAS	Chemical Abstracts Service
COPC	Chemicals Of Potential Concern
EPA	U.S. Environmental Protection Agency
$_{HTF}$OEL	Hanford Tank Farm Occupational Exposure Limit
IH	Industrial Hygiene
NDPA	nitrosodipropylamine (N-nitroso-N-propyl-1-propanamine)
NIOSH	National Institute of Occupational Safety and Health
OEL	Occupational Exposure Limit
OSHA	Occupational Safety and Health Administration
ppm	parts per million
PNNL	Pacific Northwest National Laboratory
QA	Quality Assurance
SWIHD	Site-Wide Industrial-Hygiene Database
TWINS	Tank Waste Information Network System

Contents

Tables

1.0   Introduction and Background

1.1   Defining a Process for Updating the COPCs

The process of defining possible new Chemicals of Potential Concern (COPCs) was based on comparing the maximum measured concentration (inside or outside the headspace) to the screening value, which is the vapor concentration above which potential adverse effects of exposures to the workers should be evaluated. A very similar approach was used by Poet et al. (2006). As noted in that study, screening values are intended to be 10% or less of an 8-hour time-weighted average Occupational Exposure Limit (OEL). Such a guideline is expected to be conservative to the extent that the maximum is an extreme value, rather than a typical value, and that the chemical is found in a relatively small number of tanks (or ventilation systems).

This section provides general descriptions of the procedures used to develop the list of headspace chemicals, specify their maximum headspace concentrations, and apply screening values for an initial review of both historical data (headspace data before 2005) and later data. The objective was to identify chemicals that might need to be added to the list of COPCs.

1.2   Concentration Data

Headspace-characterization data and industrial-hygiene (IH) data—hereafter referred to as "TWINS HS" and "TWINS IH"—were obtained from the Tank Characterization Database via the Tank Waste Information Network System (TWINS). All headspace vapor analysis results for all single-shell and double-shell tanks, as well as "stack," "ventilation," "vent system," and the small tanks 241-ER-311 and 241-Z-361 were obtained via a TWINS query on March 8, 2017. More recent headspace data also were obtained from the Site-Wide Industrial-Hygiene Database (SWIHD) via a query on March 8, 2017; this data set is referred to as "SWIHD HS." The three data sets are discussed in the following subsections.

1.2.1   Tank Waste Information Network System

The TWINS HS data set is the same one used in a FY 2016 COPC study (Hoppe et al. 2016). That study is referred to as the 2016 study throughout this document It is believed that all the data used in the 2006 IH technical basis work (Evans and Huckaby 2006, Huckaby 2006, Meacham et al. 2006, Poet et al. 2006) was considered in the 2016 study. The final sampling date shown is March 6, 2005. The TWINS HS data were checked in 2017 to confirm that no new data had been added.[1]

Some of the TWINS HS data were for blanks, laboratory control sample (LCS) standards, upwind measurements, matrix spikes, and Quality Control results. These were removed from the analysis data set and not used to find the maximum concentrations.

Some of the Chemical Abstracts Service (CAS) Registry Numbers in the TWINS HS database were interpreted by Excel as dates. Those numbers were edited to reflect the true CAS number.

The concentrations provided by TWINS HS data were uniformly converted into units of ppm. TWINS HS contained two sources of concentration data: the concentration in ppm and the concentration in

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[1] Downloaded from
https://twins.labworks.org/twinsdata/Forms/BuildQuery.aspx?SourceName=vapor.dbo.sp_WEB_TVD_analysis_results&whatsnew=Vapor.

mg/m^3 at 25°C. These two sources were not always both present for a given row of data, so different sources were used as available. The data source that was first in preference was the concentration in ppm, which could be used directly. However, in some cases, the value had to be stripped from a text string, while in other cases, a number was provided. The second-preferred source was the concentration in mg/m^3 at 25°C, which was converted to ppm by applying the ideal gas law and using the molecular weight. Here too, the concentration value sometimes had to be stripped from a text string.

As in the previous studies, TWINS HS results associated with chemicals that were ambiguously identified (e.g., "alkane," "unknown," "C6 ketone, " etc.) were removed from further analysis unless the molecular weight of one of the chemicals could be unambiguously specified (e.g., "octanenitrile and others" was kept). These data had Chemical IDs that started with "M" or "U", followed by a CAS number or other code. These were mixtures in which no single chemical was implied to be dominant, or classes of chemicals, or unknowns.

In one subset of mixture cases, where the Chemical ID consisted of a CAS number followed by M, the entire concentration was assumed to come from the identified chemical ("octanenitrile", in the example). In these mixture cases, TWINS HS provided only the concentration in mg/m^3 at 25°C, so conversion to ppm was necessary. The concentration was assigned to the CAS number of the identified chemical, and the molecular weight of the identified chemical was used for units conversion. In some cases, a molecular weight value was not found in TWINS and had to be acquired from the National Institutes of Health, National Institute of Standards and Testing, or the U.S. Environmental Protection Agency (EPA).[1] Data for total mercury, for which the CAS number is 7439-97-6T, were also kept.

The exclusion rule for unknowns and mixtures was applied more stringently in the 2016 study and in the present study than in Poet et al. (2006), in that many unknown chemicals (Chemical IDs beginning with a letter, usually "U" or "M") were deleted from the analysis data set used in this study. Poet et al. had in some cases retained these. They say, "Mixtures of two or more chemicals (e.g., "acetaldehyde and methanol") were entered separately for each analyte, and each analyte was assumed to be at the reported concentration of the mixture."

As in the 2016 study, TWINS HS concentration data were excluded from consideration as maxima if they met any of the following criteria:

- Quality Assurance samples (blanks, laboratory control samples, or spikes)

- Marked as suspect (Data Qualifier flag S)

- Associated with a contaminant in a blank, trip blank, or field blank (Data Qualifier flags B, T, or F)

- A laboratory control sample that was out of range (Data Qualifier flag a)

- An excessive relative percent difference (Data Qualifier flag c)

- Less than the Vapor Program Required Quantitation Limits (Data Qualifier flag Q)

- Marked with a laboratory-defined flag whose meaning was not generically defined and might indicate a serious data-quality issue (Data Qualifier flags L or Y).

In addition, data with concentrations that exceeded 1,000,000 ppm were eliminated as physically impracticable. This step affected one row of N$_2$O data, one row of H$_2$ data, and one row of CO$_2$ data in the TWINS HS data set, and thus did not affect organic vapor data. The five rows of data (phenol,

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[1] https://chem.nlm.nih.gov, https://pubchem.ncbi.nlm.nih.gov, http://webbook.nist.gov, https://comptox.epa.gov/dashboard.

nitrogen oxides, and nonanal) in which there were no concentration values (blanks) were also eliminated, because they could not be used.

All the sources that were included in the TWINS HS database were kept for analysis. The non-farm sources—241-C-301, 241-ER-311, and 241-Z-361—were not removed.

Finally, concentration data were tested to find out whether they were below the reporting limit. Several possible indications are listed below:

- A tentatively identified chemical not detected in the sample (Data Qualifier flag M)

- Below the analytical reporting limit (Data Qualifier flag U)

- Blanks provided for the concentration in ppm and for the concentration in mg/m^3 at 25°C

- Concentration in mg/m^3 at 25°C provided as a text string beginning with "<".

These below-report concentration data were not considered as possible maxima.

During the 2016 study, it was found that for unknown reasons four chemicals that were listed in Table A-16 of Poet et al. (2006) did not appear in the TWINS HS database, or had concentrations that were more than a few percent higher than those in TWINS HS. The four chemicals were 1-methylaziridine (1072-44-2), 2-nitro-1-propanol (2902-96-7), 1,2,3,6-tetrahydropyridine (694-05-3), and nitrosomethane (865-40-7). The first three of these chemicals, on examination, were considered to be dubious data, as was discussed in Table 7 of the FY 2016 COPC study (Hoppe et al. 2016). The maximum concentration for the fourth chemical, when taken from Table A-16 of Poet et al. (2006) as a cross-check, was less than the screening value. In the current study and the FY 2016 COPC study, none of the maxima for COPCs or potential COPCs came from Poet et al. (2006); all came from databases.

1.2.2 Site-Wide Industrial-Hygiene Database, Headspace Data

The SWIHD HS data downloaded on March 8, 2017, were an update from the set used in the 2016 study for which the download date was July 12, 2016. The files were a standard "full detail" download from the SWIHD database application for headspace samples from all tank farms, including samples whose Quality Assurance (QA) reviews were not fully completed (these instances are identified with an asterisk in the Sample ID).

The following changes were made to address apparent data set errors or data handling issues:

- Changed the location of two rows of data from AX-101 to AX-103 because all other data in the survey (#15-00186) were from AX-103, and the Field Sample IDs in the survey were more consistent if all were from the same tank. The sample head drawing for the survey shows only AX-103, not AX-101.

- Replaced the CAS number for sulfur dioxide with a text string in two rows because Excel misinterpreted the original identification number format as a date.

- Removed 26 rows of data where the Air Concentration was blank because these could not be used.

Some of the SWIHD HS data were for samples whose QA review had not been completed. These data, which are denoted by survey numbers with asterisks, were retained in the analysis data set. In two cases, asterisked data appear among the maxima, as will be indicated.

The concentrations provided by SWIHD HS data were converted into units of ppm from the units provided by SWIHD. As necessary, units of mass/volume (such as mg/m^3) were converted to ppm by

applying the ideal gas law, assuming a temperature of 25°C, and using the chemical's molecular weight. The SWIHD HS data as downloaded did not include the molecular weights, so values were supplied from those found in TWINS databases or, when needed, from the National Institutes of Health, National Institute of Standards and Testing, or EPA.

Further processing[1] was required to address the need to combine data points to find the total concentration in each air stream sampled. Each row of data in the set represents a measurement made on the contents of a single sorbent tube (or other collector). It was frequently the case that a single sample air stream passed through a series of two or more collectors, which meant that the actual sample concentration was the sum of the contributions from all the collectors in the series. The intent of this sample collection method is that most or all of the vapor should be deposited in the first collector, with a relatively small amount of breakthrough into the second collector.

The 2016 study did not account for the use of collectors in series because the extent to which series collection was employed was not recognized. As a result, some SWIHD HS concentrations were underestimated in that study.

The SWIHD currently does not contain explicit information to denote which data came from collectors in series or to identify which collectors belong in a set. Therefore, in this study, an approach was devised to make a plausible approximation that accounted for combining concentrations and thus would avoid some of the underestimation in the previous study. First, because samples taken with SUMMA canisters were never taken in series, these results were removed from consideration for combination. Next, it was assumed that, for any given combination of IH survey, sampling location, analysis method, and chemical, any data rows that had field sample identification numbers in sequence (or nearly so) and also had exactly the same sample volume—for which SWIHD consistently provided 3, 4, or more significant figures—was part of a series set of collectors. It is physically reasonable to expect samples collected on the same line to have the same sample volume, calculated to the same number of significant figures. On the other hand, replicate samples or other types of samples taken on a different line would probably have visibly different (though perhaps nearly equal) sample volumes. The groupings suggested by equal sample volume was reviewed to find out whether their field sample identification numbers fell in sequence, as was generally the practice for collectors in series. If these criteria were met, all of the rows of data in the group were considered to have been part of a series.[2]

All of the 1,3-butadiene data in SWIHD HS that were not taken using SUMMA canisters fell into groups of four rows. Most of the other non-SUMMA data fell into pairs, and no three-row groups were found.

Out of more than 20,000 rows of data in the initial SWIHD HS, there were fewer than 500 rows that did not appear to fall into a group. These were reviewed in detail. For 10 of these cases in which samples initially appeared to be unmatched, it was found that there were five sets of two samples each where the two samples had sequential sample identification numbers but slight differences in sample volumes.[3] In other words, the 10 cases appeared to be five pairs where a volume error of some kind made them appear

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[1] This type of data combination was not needed for the TWINS HS data, according to JE Meacham, Washington River Projection Solutions Inc., who was involved in the 2006 IH Technical Basis effort.

[2] These criteria were discussed in conversations and e-mails with J Frye (222-S Laboratory, WRPS) and P. Jones (Industrial Hygiene, WRPS), who concurred with the general approach, but did not review its detailed application or results.

[3] The samples that appeared to be unmatched because of slightly different sample volumes were 241-T-111 pyridines (15-03477-1-010A/B); A-101 volatile organic compounds (16-03725-1-006A/B); A-105 pyridines (15-09667-1-010A/B); A-106 NH$_3$ (16-02216-1-009A/B); and A-106 semi-volatile organic compounds (16-01353-1-004A/B). The surveys' sample head drawings provided evidence that the apparently unmatched samples were in fact in series and required combination.

to be unmatched. These cases were all checked against IH air sampling survey reports. For each of these five near-pairs, every other sample in the survey fell into identical-volume pairs, and the difference in sample volume for the affected pair came from a difference in start time, end time, initial flow rate, or post-use flow rate that might be explainable as a typo. Accordingly, they were treated as pairs and their concentrations were combined.

The remaining unmatched rows could be identified with a fair degree of certainty to be either from the first collector in a pair in series – the upstream collector – or from the second collector – the downstream collector that would capture only the amount of vapor that broke through from the first collector. The Field Sample ID was used to decide which position the single remaining collector had been on, taking the sample ID conventions for the rest of the survey as guidance. The data that appeared to come from first collectors was kept, flagged with an additional data-quality code, and not combined with any other data. The data that appeared to come from second collectors, that had no available data from the first collector to supplement them, was removed from further analysis as giving misleading information; this amounted to 190 rows of data. The rows of data for which there was no matching sample, and that could not be identified as either the first or second collector, were kept and not combined with any other data.

This approach to identifying which samples to combine decreases the extent of underestimation of concentrations, compared to the 2016 study approach in which concentration combination was not performed. The approach is considered an approximation because the choices of combinations have not been compared to the survey reports and sample head configurations for all the SWIHD HS surveys, but only for a small subset of surveys. If there are cases where samples are inaccurately identified as a group to combine, these cases would produce overestimated concentrations. If there are cases where samples are inaccurately identified as singletons, then these cases would produce underestimated concentrations.

The species for which the combined concentration in a single sample exceeded the highest uncombined measurement in the sample by 60% or more included the COPCs 1,3-butadiene, acetonitrile, formaldehyde, 2,3-dihydrofuran, 2,5-dihydrofuran, and mercury. The proposed COPC acrolein (2-propanal) also met this criterion. The non-COPC chemicals with concentration increases of 60% or more in individual samples because of combination were tetrahydrofuran, acetone, ethanol, decane, dodecane, 2,6,10-trimethyldodecane, n-hexane, n-tridecane, n-hexadecane, n-heptadecane, methylene chloride, and trichlorofluoromethane. For most of the listed chemicals these large increases were rare, appearing in 7% or less of the non-SUMMA samples in the SWIHD HS dataset; however, they were more common for the COPC acetonitrile (9%) and for the non-COPCs tetrahydrofuran, acetone, and dodecane (35%, 14%, and 22%, respectively). In some of these surveys, there might have been breakthrough from the second collector and a third collector might have been needed to ensure collecting all of these chemicals.

The combination procedure included summing the concentrations in a group, assigning a range code to the combined result, and concatenating the data-quality flags so that this information would not be lost. The criteria for combining data are briefly described below:

- All of the concentrations in the group that were above the reporting limit were added together to give the combined measured concentration. The concentrations that were below the reporting limit were not included; effectively, they were treated as zeros.

- The range for the combined measurement was set to "<", indicating a value below the reporting limit, only if all the single-collector measurements in the group were below the reporting limit.

- Data-quality flags for all the collectors that were above the reporting limit and that had concentrations greater than 10% of the total concentration were concatenated into a combined data-quality flag. The

flags for below-reports and low-contributing collectors were omitted because they did not relate to the major part of the concentration and so might be misleading.

The sample names were concatenated into a combined-sample name. Other metadata were carried through without change, if it pertained to all samples in the group rather than being specific only to individual collectors.

The final step performed on the combined SWIHD HS data was to check data quality. Data-quality flags that were taken as reasons to exclude concentration data from consideration as maxima are listed below:

- Flag a − Having a laboratory control sample that was out of range

- Flags b or B − Associated with a contaminant in a blank

- Flags c or d − Having an excessive relative percent difference or relative standard deviation

- Flag e − Having an excessive difference between the sample result and its serial dilution

- Flag f − Having a failed mass spectrometer reading on the sample but not on its serial dilution

- Flag L − a laboratory control standard had an out-of-range percent recovery

- Flag Y − Marked with a laboratory-defined flag whose meaning was not generically defined and might indicate a serious data-quality issue.

Flags d, e, and f were not present in the data set downloaded on March 8, 2017, so they did not have any effect. The full set of data-quality flags used by SWIHD is defined in *Data Qualifiers for Vapor Samples* (ATS-GD-1048, Rev. A-7, November 16, 2016). Flags excluded in the current study are not the same set used in the 2016 study for which a different document—*Data Qualifiers for Vapor Samples* (ATS-GD-1028, Rev. D-2, April 9, 2015)—provided data flag information for the 2016 analyses. These documents provide internal guidance for assigning data qualifiers for vapor sample analyses conducted at the 222-S analytical laboratories operated by Wastren Advantage, Inc and Washington River Protection Solutions.

The data qualifiers document also listed flags D, E, J, N, H, Q, T, and p. Of these, H (sample holding time exceeded) and p (compound identification based on an instrument not specifically calibrated for the compound) did not appear in the SWIHD data used in this study. Data with flags D (sample diluted before analysis) and E (exceeded the calibration range) were kept because they were likely to represent high concentrations. Flags J, N, Q, and T all refer to qualitative or estimated concentration or compound identification. These flags tend to occur with low concentrations. The data with these flags are retained. Of the concentration maxima that came from SWIHD HS or TWINS IH (which uses the same flags), none that exceeded their screening value had flags E, N, Q, or T.

The flag "U", for a concentration less than the minimum detection limit, and the range indicator, "<", were used to identify concentrations that were less than reportable limits. Such data were examined as part of the analysis, but were not considered as possible concentration maxima.

1.2.3   TWINS IH

The TWINS IH data downloaded on March 8, 2017, for this study were an update from the set downloaded for the 2016 study (June 20, 2016).

The following changes were made in the analysis data set to address data handling issues:

- Replaced the CAS number for sulfur dioxide with a text string, because Excel misinterpreted the original identification number format as a date.

- In Hexavalent Chromium rows, replaced blanks for the molecular weight with 51.996 (units g/mol).

Some of the TWINS IH data were for QA samples. These were removed from the analysis data set and not used to find the maximum concentrations. All the sources that were included in the TWINS IH database were kept for analysis. The non-farm sources—the 222-S laboratory, the AR-204 waste unloading facility, and other sources listed as "non-farm"—were not removed. Source data for the 242-A evaporator also were kept.

TWINS IH contained four sources of concentration data: 1) the concentration in ppm, 2) the concentration in mg/m^3 at 25°C, 3) the standard concentration, and 4) the reported value. All sources were not always present for a given row of data, so different sources were used as available. The data source that was first in preference was the concentration in ppm, which could be used directly and, if present, was always provided as a number. The second-preferred source was the concentration in mg/m^3 at 25°C, which was converted to ppm by applying the ideal gas law and using the molecular weight. Concentrations provided by TWINS IH data were converted into units of ppm from the units that were provided. As necessary, units of mass/volume (such as mg/m^3) were converted to ppm by applying the ideal gas law, assuming a temperature of 25°C, and using the chemical's molecular weight. The full set of all concentration units appearing in TWINS IH was checked to make sure the units-conversion logic would handle them properly. One row of data for airborne fibers was not handled properly; but these were not organic vapors and did not affect the determination of organic vapor maxima.

A number of chemicals in the TWINS IH data set—primarily nitrosamines and furans—often had "needs conversion" text notes rather than numeric values in the two preferred concentration columns (concentration in ppm and concentration in mg/m^3 at 25°C). In these cases, or others where the first- and second-preferred concentration data sources were not usable, the standard concentration was almost always available as the third choice. It was necessary to resort to the fourth choice in fewer than 20 out of the more than 29,000 rows of data. The calculations made use of the Reported Value and its units. Logic was provided, but turned out not to be needed, to use the molecular weight and the ideal gas law at the Reference Temperature and 1 atm to convert mass/volume Reported Value units to ppm. Logic also was provided, and also was not needed, to convert Reported Value units of mass (as NG, NGS, etc.) to mass/volume by dividing the reported mass by the database entry for the Sample Volume and its units (which were always liters).

Like the SWIHD, the TWINS IH database currently does not contain explicit information to denote which data came from sample collectors in series or to identify which collectors belong in a set. The same general approach to combining concentrations that was used on SWIHD HS data was tested on TWINS IH data as for SWIHD data, with modifications related to the types of data present in TWINS IH. First, because samples taken with SUMMA canisters, vacuum bottles, badges, or filters were never taken in series, these results were removed from consideration for combination. Next, it was assumed that, for any given combination of farm, location, chemical identification number, sample device, and sampling method, any rows of data that had sequential (or nearly sequential) field sample identification numbers and that also had exactly the same sample volume was part of a series set of collectors.

The process produced 27 sets of three rows (triplets) of dimethylmercury data that had sample identification numbers of the form Survey-1-001A/B/C, Survey-2-001A/B/C, Survey-1-001A/002A/003A, or Survey-1-004B/005B/006B. In every case, the volumes within any triplet were equal to all the significant figures provided, which was considered to be a true distinguishing feature

because the volumes were given to four or more significant figures. These sampling results, which were obtained during 2014 and 2015, were considered to be valid sets of three tubes in series.

Only a few hundred sets of two rows were found that met the criteria given above to define them as pairs. It was noted that the decisions about whether sets of two rows were true pairs in series, or replicates, or true singletons were often judgment calls. There were too many ambiguous cases to allow survey reports and sampling head information to be consulted. Also, data initially classified as singlets were too numerous to allow them to be reviewed line-by-line to check for possible pairs with sample volumes that might incorrectly be slightly unequal, as had been done for some cases in the SWIHD HS. In addition, it was not generally possible to be sure if a singleton that appeared (based on nomenclature) to be part of a pair, but whose mate was missing, was from a first collector or a second collector. Finally, compared to the SWIHD HS, the TWINS IH database had a greater variety of field sample nomenclature and more frequent appearance of sample volumes with a small number of significant figures, so there was less information on which to base decisions that apparent singletons were actually pairs.

For the reasons listed above, it was determined that combining tube data for TWINS IH could not be practically implemented. The decisions about which TWINS IH data could be combined would involve a greater degree of guesswork and approximation, more effort, and less impact on maxima than the SWIHD HS data. Therefore, no combination was carried out for the TWINS IH data set.

The lack of combination would produce underestimated concentrations for whichever TWINS IH samples actually belonged to pairs or triplets. The set of dimethylmercury samples already mentioned would be affected.

The final step performed on the combined TWINS IH data was to check data quality. The data-quality flags that were taken as reasons to exclude concentration data from consideration as maxima were the same as for SWIHD HS and were employed for data selection in the same way for the same reasons.

1.2.4   Concentration Maxima

As the last step, the present study repeated the approach used in the 2016 study. The maximum concentration was determined over all the individual measurements made for each chemical that were above the reporting limit and not flagged with the data-quality codes used to exclude data from consideration. The evaluation included every unique CAS number found in any of the three databases, a total of 1415 chemicals.

The approach used—selecting the maximum individual measurement—gave higher (and more conservative) maxima for TWINS HS data than did the approach used by Poet et al. (2006). Their method included an averaging step before finding the maxima. According to Poet et al., "The resulting data were averaged by sample device and laboratory for each day of sampling from a given source (tank, vent system, etc.). This process resulted in averaged individual sample results. The maximum averaged concentrations were then determined for each tank and ventilation system."

The most significant concentration maxima—those that were highest with respect to the toxicological screening value—were reviewed to find out how many other data, from the same tank and from all tanks, were also high compared to the screening value. Maxima that were uniquely high, or that were not seen again in later measurements made on the same tank, might be questionable or at least outliers.

A large majority of the maxima came from TWINS HS, the same database used for the 2006 technical basis development. These maxima were checked against several reviews conducted at that time (Meacham et al. 2006, Evans and Huckaby 2006, Huckaby 2006, Sklarew and Mitroshkov 2006) to make

sure maxima were being assessed for validity using logic similar to that of the original basis, including possible misidentification or contamination by laboratory equipment or handling.

As in the 2016 study, no attempt has been made to sum all the contributions of individual contributing chemicals in a sample to obtain a maximum for any "family" of chemicals (e.g., furans, alkanes, chlorinated biphenyls, etc.). Only the maxima of individual chemicals have been considered.

This review of concentration maxima does not include any chemicals that have been tentatively identified in vapors as a result of 2016 respirator cartridge testing, and that were not included in the TWINS or SWIHD databases. A number of such chemicals have been observed—the listing of newly observed chemicals is in progress, but incomplete—and some may need to be compared to toxicological limits.

1.3   Screening Values

This study is a further step, following up on 2016 work, toward identifying chemicals that may need identification or development of OELs that are accepted for Hanford Tank Farm use ($_{HTF}$OEL). Most of the toxicological criterion information used in the study came from the 2016 study. Screening values were set equal to 10% of the existing toxicological criteria: OEL, Threshold Limit Value-Time Weighted Average, Occupational Safety and Health Administration Permissible Exposure Limit, or National Institute of Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL).

In this study, toxicological information that was newly developed or located since 2016 was used for furans[1], nitrosamines[2], and some other vapor chemicals (Weber et al. 2018), including a few of the COPCs and the chemicals identified in the 2016 study as strong candidates for COPC status. The toxicological basis for $_{HTF}$OELs was reviewed and updated under Task 5 of the Health Process Plan Statement of Work for most of the COPCs and for the three COPC candidates from 2016: 2-propenal (acrolein), dimethylmercury, and N-butyl-N-nitroso-1-butanamine.

For background, it should be noted that the new screening values for the nitrosamines have a different type of toxicological basis than those for other chemicals. The existing OEL used in 2016 study was based on a European toxicological limit that was in use in 2006, but since then has been put aside in favor of keeping exposures as low as reasonably achievable for this group of carcinogens. The American Conference of Governmental Industrial Hygienists (ACGIH) and the Occupational Safety and Health Administration also recommend as low as reasonably achievable exposure levels. The new screening values for nitrosamines that have been proposed, but not at this time accepted, are based on an EPA risk-based approach modified for occupational exposure. These screening values are calculated using cancer slope factors for each individual chemical, reasonable assumptions for inhalation rate, body weight, bioavailability, and factors related to lifetime occupational exposures. Risk levels from 10^{-6} to 10^{-3} were considered in calculating the concentration that produces the inhalation risk-specific dose for each risk level. The screening values for nitrosamines that are used in this study are based on the 10^{-4} risk level.

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

[2] Smith, JN, JG Teeguarden, TJ Weber, C Timchalk. 2017. Proposed Risk-Based Approach for Nitrosamine Chemical of Potential Concern. PNNL-26787 Rev. A, Pacific Northwest National Laboratory, Richland, Washington. Unpublished.

2.0   Data Review and Assessment of Vapor Chemicals

The ratio of maximum concentration-to-screening value (over all available data, not just headspace data) was calculated for all chemicals with unique CAS numbers. The intent was to identify chemicals for which this screening ratio had increased or decreased since the FY 2016 study, whether because of a new maximum concentration or a new screening value had become available. Table 1 provides 1) a list of the 33 chemicals with ratios that had changed and 2) reasons for the changes.

One chemical, a nitrosamine, was found to have a screening ratio that increased to such an extent that the ratio was greater than unity in 2017 but had been less than unity in 2016. The increase in screening ratio was caused solely by a decrease in the screening value; the concentration maximum did not change. As is further discussed below, this nitrosamine is a new candidate for COPC status.

In one case, a change in the screening ratio resulted from the use of combined data for tubes in series. Combination doubled the maximum concentration for 2-propenal (acrolein), which was already a COPC candidate.

Of the seven nitrosamines for which new risk-based screening values were proposed in 2017, one kept the same screening ratio,[1] two had decreased ratios, and four had increased ratios. In one case, the ratio remained below unity; in one case (nitrosodipropylamine), the ratio increased to above unity; and in five cases, the ratio remained above unity. Nitrosodipropylamine (N-nitroso-N-propyl-1-propanamine [NDPA]) is recommended as a new COPC candidate at the 10^{-4} risk level. There are a number of measurements of NDPA from different tank, source, and stack data. Those in the TWINS IH database are all from stack or source locations and are at or below 0.026 ppb, or about 40% of the observed maximum of 0.084 ppb, which was from headspace data. No other headspace data are close to the maximum, but it should be noted that the reporting limit in SWIHD HS data is often about 0.06 ppb, which is high enough to make it hard to capture measurements that might have been near the new screening value of 0.063 ppb.

The chemicals in the furan group had their screening ratios decreased by the newly proposed $_{HTF}$OELs. However, all furan ratios remained above unity.

Based on work by Sklarew and Mitroshkov (2006), five substituted furan compounds were noted in the 2016 study as possibly being misidentifications in the pre-2006 data and, therefore, as being potentially removable from the COPC list. However, two of these compounds—2-propylfuran and 2-heptylfuran—have been detected (although below reportable levels) in vapors from more than one tank or exhaust system during recent respirator cartridge testing.[2] The pre-2006 misidentification of these chemicals may therefore be superseded by later data. In addition, the detection of two alkyl-substituted furans suggests that others of the family could be present, even if not detected in the particular sources used in cartridge testing. Further examination of the cartridge testing data might indicate other chemicals, not all furans, that were misidentifications in pre-2006 data but that have better-identified status now.

Since 2016, three chemicals—1-hexene, 1-butene, and 2-methyl-pentane—had screening ratios that decreased by enough to bring the ratios below unity. The ratios of these hydrocarbons changed because 2016 ACGIH TLVs were found to support new chemical-specific screening values, rather than using a generic-hydrocarbon value of 10% of the NIOSH REL for kerosene (100 mg/m³) as was done in the 2016 study. Based on the new screening values, these three chemicals are no longer hypothetical candidates for

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[1] This nitrosamine, nitrosomethylethylamine, is included in Table 1 for completeness. Although its screening ratio and screening value remained the same as in 2016, a new basis was used to obtain the screening value.

[2] First stage of analyses draft reports PNNL-25860 (AP Tank Exhauster); PNNL-26041 (SY-102); PNNL-26131 (A-101); PNNL-26180 (BY-108); PNNL-26243 (AY/AZ Exhauster); PNNL-26254 (AX-101); PNNL-26337 (AW Exhauster); PNNL-26317 Rev. A (AN Exhauster). These reports are unpublished.

COPC status. It is possible that a number of the other hydrocarbons that gave screening ratios greater than unity in the 2016 study, based on the generic-hydrocarbon screening value, would also have their ratios decrease to less than unity if chemical-specific toxicological limits were available.

Table 1. Chemicals with Screening Ratios that Changed since the 2016 Study

Chemical Abstracts Service (CAS) Registry Number	2017 Study Screening Value (ppm)	2016 Study Screening Value (ppm)	2017 Study Maximum (ppm)	2016 Study Maximum (ppm)	2017 Screening Ratio	Notes	Effect on Screening Ratio
2-Heptanone, 6-methyl- (928-68-7)	0.3	0.8	2.27	2.27	7.6	The maximum concentration of this COPC has not changed since FY 2016; it came from TWINS HS data, (5/17/1994, C-103). A new screening value of 0.3 ppm is used, based on 10% of 3 ppm, a new HTFOEL proposed in FY 2017 (PNNL-26777 Rev. A).	Increase; ratio is >1, as in FY 2016
1,3-Dichloropropene (542-75-6)	0.1	0.1	0.013	0.005	0.13	A new maximum concentration of this non-COPC was found in the SWIHD HS database for A-103 on April 28, 2016. The measurement was not present in the database used in FY 2016. There is no change in the screening value.	Increase; ratio is <1, as in FY 2016
2-Propenal 107-02-8	0.01	0.01	0.162	0.084	16	The new maximum of this COPC candidate is from the same SWIHD HS sample as before (December 18, 2014, AX Farm, AX-104, no data-quality code). A higher concentration was obtained in the present analysis because the measurements of samples 14-07750-1-007 and -008, tubes in series, were added together to give the total concentration in the air sample. There is no change in the screening value.	Increase; ratio is >1, as in FY 2016
Acetonitrile 75-05-8	2	2	18.8	14	9.4	A new maximum concentration for this COPC was found in the SWIHD HS database for BY-108 on October 18, 2016. The measurement was not present in the database used in FY 2016. There is no change in the screening value. The new measurement was from a survey (16-09168) that had not completed quality review (asterisked). Its results do not appear unreasonably high compared to those in fully-reviewed surveys in other tanks.	Increase; ratio is >1, as in FY 2016

Chemical Abstracts Service (CAS) Registry Number	2017 Study Screening Value (ppm)	2016 Study Screening Value (ppm)	2017 Study Maximum (ppm)	2016 Study Maximum (ppm)	2017 Screening Ratio	Notes	Effect on Screening Ratio
Mercury (total) 7439-97-6T	0.0001	0.00012	0.0145	0.0145	145	The maximum concentration of this COPC has not changed since FY 2016; it came from TWINS HS data (9/21/04, C-104). A new screening value of 0.0001 ppm is used, based on 10% of 0.001 ppm, a new HTFOEL proposed for dimethylmercury in FY 2017 (PNNL-26777 Rev. A). As in FY 2016, total mercury is conservatively assumed to have the same screening value as dimethylmercury, rather than mercury. If the screening value of elemental mercury (0.0003 ppm) were used instead, the screening ratio would be 48, still considerably higher than unity.	Increase; ratio is >1, as in FY 2016
Mercury, dimethyl- 593-74-8	0.0001	0.00012	0.000173	0.000173	1.7	The maximum concentration of this COPC candidate has not changed since FY 2016; it came from TWINS IH data (02/09/16, 702-AZ, Stack, DMM Sampling for AP102 to AZ102 Transfer, no data quality code). A new screening value of 0.0001 ppm is used, based on 10% of 0.001 ppm, a new HTFOEL proposed in FY 2017 (PNNL-26777 Rev. A).	Increase; ratio is >1, as in FY 2016
1-Hexene 592-41-6	5	2.91	4.61	4.61	0.92	The maximum concentration of this non-COPC has not changed since FY 2016; it came from TWINS HS (5/17/94, C-103). The screening value of this non-COPC was set to 10% of the 2016 ACGIH TLV for 1-hexene (50 ppm), rather than using a generic-hydrocarbon value of 10% of the NIOSH REL for kerosene (100 mg/m^3) as was done in FY 2016.	Decrease; ratio is now <1; was >1 in FY 2016

Chemical Abstracts Service (CAS) Registry Number	2017 Study Screening Value (ppm)	2016 Study Screening Value (ppm)	2017 Study Maximum (ppm)	2016 Study Maximum (ppm)	2017 Screening Ratio	Notes	Effect on Screening Ratio
Furan 110-00-9	0.00019	0.0001	3.2	3.2	16842	The maximum concentrations of these COPCs have not changed since FY 2016. The screening value for this group of chemicals was set to 10% of 1.9 ppb, a new HTFOEL proposed in FY 2017 (PNNL-26775 Rev. A). All furans have this screening value.	Decrease; all have ratios >1, as in FY 2016
Furan, 2,5-dihydro- 1708-29-8			1.82	1.82	9560		
Furan, 2-methyl- 534-22-5			1	1	5263		
Furan, 2,3-dihydro- 1191-99-7			0.025	0.025	132	The measurements all came from TWINS HS, for the following sources: Furan: 5/17/94, C-103.	
Furan, 2-ethyl-5-methyl- 1703-52-2			0.0102	0.0102	54	Furan, 2,5-dihydro- : 5/17/94, C-103. Furan, 2-methyl- : 5/17/94, C-103.	
Furan, 2,5-dimethyl- 625-86-5			0.00933	0.00933	49	Furan, 2,3-dihydro- : 7/10/01, AP-101. Furan, 2-ethyl-5-methyl- : 6/24/94, BY-104.	
Furan, 2-pentyl- 3777-69-3			0.00274	0.00274	14	Furan, 2,5-dimethyl- : 6/24/94, BY-104 Furan, 2-pentyl- : 6/15/95, AX-101.	
Furan, 2,3-dihydro-4-(1-methylpropyl)-, (S)- 34379-54-9			0.00098	0.00098	5.2	Furan, 2,3-dihydro-4-(1-methylpropyl)-, (S)- : 6/27/95, AX-102.	
2-Heptanone, 6-(2-furanyl)-6-methyl- 51595-87-0			0.000577	0.000577	3.0	2-Heptanone, 6-(2-furanyl)-6-methyl- : 2/16/94, C-105.	
Furan, 2-propyl- 4229-91-8			0.654	0.654	3443	Furan, 2-propyl- : 9/22/94, BY-109.	
Furan, 2-heptyl- 3777-71-7			0.0612	0.0612	322	Furan, 2-heptyl- : 10/27/94, BY-108.	
Furan, 2-octyl- 4179-38-8			0.00087	0.00087	4.6	Furan, 2-octyl- : 7/8/94, BY-106.	
2-Propen-1-one, 3-(2-furanyl)-1-phenyl- 717-21-5			0.00058	0.00058	3.1	2-Propen-1-one, 3-(2-furanyl)-1-phenyl- : 3/24/95, SX-106.	
Furan, 3-(1,1-dimethylethyl)-2,3-dihydro- 34314-82-4			0.000533	0.000533	2.8	Furan, 3-(1,1-dimethylethyl)-2,3-dihydro-: 7/7/94, BY-105.	
Phosphonic acid, butyl-, dibutyl ester 78-46-6	0.0015	0.0007	0.0802	0.0802	53	The maximum concentration of this COPC has not changed since FY 2016; it came from TWINS HS (5/16/94, C-103). A new screening value of 0.0015 ppm is used, based on 10% of 0.015 ppm, a new HTFOEL proposed in FY 2017 (PNNL-26777 Rev. A).	Decrease; ratio is >1, as in FY 2016

Chemical Abstracts Service (CAS) Registry Number	2017 Study Screening Value (ppm)	2016 Study Screening Value (ppm)	2017 Study Maximum (ppm)	2016 Study Maximum (ppm)	2017 Screening Ratio	Notes	Effect on Screening Ratio
Phosphoric acid tributyl ester 126-73-8	0.046	0.02	0.625	0.625	14	The maximum concentration of this COPC has not changed since FY 2016; it came from TWINS HS (5/16/94, C-103). A new screening value of 0.046 ppm is used, based on 10% of 0.46 ppm, a new $_{HTF}$OEL proposed in FY 2017 (PNNL-26777 Rev. A).	Decrease; ratio is >1, as in FY 2016
3-Buten-2-one, 3-methyl- 814-78-8	0.007	0.002	0.0213	0.0213	3.0	The maximum concentration of this COPC has not changed since FY 2016; it came from TWINS HS (6/24/94, BY-104). A new screening value of 0.007 ppm is used, based on 10% of 0.07 ppm, a new $_{HTF}$OEL proposed in FY 2017 (PNNL-26777 Rev. A).	Decrease; ratio is >1, as in FY 2016
1-Butene 106-98-9	25	4.36	14.8	14.8	0.59	The maximum concentration of this COPC has not changed since FY 2016; it came from TWINS HS (5/17/94, C-103). The screening value of this non-COPC was set to 10% of the FY 2016 ACGIH TLV for 1-butene (250 ppm), rather than using a generic-hydrocarbon value of 10% of the NIOSH REL for kerosene (100 mg/m^3) as was done in FY 2016.	Decrease; ratio is now <1; was >1 in FY 2016
Pentane, 2-methyl- 107-83-5	50	2.84	4.20	4.20	0.08	The maximum concentration of this COPC has not changed since FY 2016; it came from TWINS HS (10/27/94, BY-108). The screening value of this non-COPC was set to 10% of the FY 2016 ACGIH TLV for 2-methyl-pentane (500 ppm), rather than using a generic-hydrocarbon value of 10% of the NIOSH REL for kerosene (100 mg/m^3) as was done in FY 2016.	Decrease; ratio is now <1; was >1 in FY 2016
Ethanamine, N-ethyl-N-nitroso- 55-18-5 (NDEA)	0.0000038	0.00001	0.000328	0.000328	86	The maximum concentration of this COPC has not changed since FY 2016; it came from TWINS IH (8/16/2012, AP Exhauster). A new screening value of 0.0000038 ppm is used, based on a FY 2017 estimate of the inhalation risk-specific dose at a 10^{-4} cancer risk level (PNNL-26787 Rev. A).	Increase; Ratio is >1, as in FY 2016

Chemical Abstracts Service (CAS) Registry Number	2017 Study Screening Value (ppm)	2016 Study Screening Value (ppm)	2017 Study Maximum (ppm)	2016 Study Maximum (ppm)	2017 Screening Ratio	Notes	Effect on Screening Ratio
Methanamine, N-methyl-N-nitroso- 62-75-9 (NDMA)	0.000015	0.00003	1.11	1.11	73895	The maximum concentration of this COPC has not changed since FY16; it came from TWINS IH (9/21/2010, C-111). A new proposed screening value of 0.000015 ppm is used, based on an FY 2017 estimate of the inhalation risk-specific dose at a 10^{-4} cancer risk level (PNNL-26787 Rev. A).	Increase; Ratio is >1, as in FY 2016
Ethanamine, N-methyl-N-nitroso- 10595-95-6 (NMEA)	0.00003	0.00003	0.0614	0.0614	2045	The maximum concentration of this COPC has not changed since FY 2016; it came from TWINS IH (9/21/2010, C-111). The screening value is also unchanged, although its proposed basis is new: an FY 2017 estimate of the inhalation risk-specific dose at a 10^{-4} cancer risk level (PNNL-26787 Rev. A).	No change; ratio is >1, as in FY 2016
Morpholine, N-nitroso- 59-89-2	0.000124	0.00006	0.0116	0.0116	93	The maximum concentration of this COPC has not changed since FY 2016; it came from TWINS HS (8/29/95, U-108). The new proposed screening value of 0.00012 ppm is used, based on an FY 2017 estimate of the inhalation risk-specific dose at a 10^{-4} cancer risk level (PNNL-26787 Rev. A).	Decrease; ratio is >1, as in FY 2016
1-Butanamine, N-butyl-N-nitroso- 924-16-3 (NDBA)	0.000068	0.00001[a]	0.00123	0.00123	18	The maximum concentration of this COPC candidate has not changed since FY 2016; it came from TWINS IH (1/25/2010, C-104). The new proposed screening value of 0.000068 ppm is used, based on an FY 2017 estimate of the inhalation risk-specific dose at a 10^{-4} cancer risk level (PNNL-26787 Rev. A). The second-highest concentration is 0.00022 ppm; there are a total of six measurements above the new proposed screening value.	Decrease; ratio is >1, as in FY 2016
1-Propanamine, N-nitroso-N-propyl, 621-64-7 (NDPA)	0.000063	0.0001	0.000084	0.000084	1.3	The maximum concentration of this COPC candidate has not changed since FY 2016. The maximum was measured in TX-114 on August 6, 2015, and was from the SWIHD headspace database. It was part of a survey (15-06300) that had not completed quality review (asterisked). All other SWIHD HS data are less than the reporting limit, with reporting limits ranging from 0.000021 to 0.000078 ppm.	Increase; ratio is now >1; was <1 in FY 2016

Chemical Abstracts Service (CAS) Registry Number	2017 Study Screening Value (ppm)	2016 Study Screening Value (ppm)	2017 Study Maximum (ppm)	2016 Study Maximum (ppm)	2017 Screening Ratio	Notes	Effect on Screening Ratio
						There are a number of measurements at 0.000026 ppm and lower in TWINS IH data, at more than 10 source or stack locations. A new proposed screening value, 0.000063 ppm, is used, based on an FY 2017 estimate of the inhalation risk-specific dose at a 10^{-4} cancer risk level (PNNL-26787 Rev. A).	
n-Nitrosopiperidine, 100-75-4	0.00017	0.0008	0.0000147	0.0000147	0.09	The maximum concentration of this COPC candidate has not changed since FY 2016; it came from TWINS IH (7/21/2005, AN Exhauster). A new proposed screening value of 0.00017 ppm is used, based on an FY 2017 estimate of the inhalation risk-specific dose at a 10^{-4} cancer risk level (PNNL-26787 Rev. A).	Increase; Ratio is <1, as in FY 2016

(a) 0.1 ppb (0.0001 ppm) was used in 2016 (Hoppe et al. 2016) as a bounding value for the NDBA OEL. It was based on NMEA, because it was thought no OEL had been set for NDBA. However, there was an established OEL of 4 ppb (0.004 ppm), per Appendix E of Meacham et al. (2006). The maximum observed NDBA concentration is the only one greater than 10% of 4 ppb.

3.0   Recommendations

This section presents recommendations based on the present study. They supplement or modify the recommendations made in the FY 2016 study.

3.1   Changes to COPCs

The following three recommendations are made regarding changes to COPCs:

- As a result of applying updated screening values using the newly proposed risk-based approach for nitrosamine COPCs, which are based on inhalation risk-specific dose at a risk level of 10^{-4}, NDPA was moved to a screening ratio that was greater than unity. This compound is recommended as a strong candidate for COPC status.

- Two alkyl-substituted furans—2-propylfuran and 2-heptylfuran—that were considered to have been misidentified based on pre-2006 data used in the 2016 study have been detected in 2016 respirator cartridge-testing measurements. This observation supports retaining these furans, and by extension other alkyl-substituted furans, as COPCs.

- Further examination of the cartridge-testing data should be carried out to clarify whether there are other chemicals, not all furans, that were misidentifications in pre-2006 data but that now have better-identified status.

3.2   Recommendations Related to OELs

As noted in Section 1.3, this study uses screening values for nitrosamines that are based on the 10^{-4} risk level. This is an approach proposed in report PNNL-26787 Rev. A; a consensus on the use of a risk basis for screening values is needed.

3.3   Sampling and Sample Databases

The following recommendations regarding sampling and sampling databases are based on the data review described in Section 1.2 and the identification of COPCs in Section 3.1:

- As noted in Section 1.2.2 and Section 1.2.3, much of the concentration data in the SWIHD headspace database and some of the data in the TWINS IH database represent measurements from individual tubes or other collectors that were arranged in series on the same air flow stream. Although the original air concentration is the sum of concentration measurements on individual tubes in each series and cannot be properly understood without this summation, there is inadequate information in either of these databases to explicitly identify which samples were taken on the same air stream, or whether samples were taken upstream or downstream. This study has employed a plausible but approximate method for using sample volumes and sample numbers to identify samples taken in series, so that concentrations could be summed in SWIHD HS. Because the information by which tubes were identified as needing combination was more sparse and more ambiguous in the TWINS IH database, no combinations were carried out with those data. It is strongly recommended that some form of series-sample identification be added to these databases, covering both past and ongoing sampling. The extent of the need for concentration combination was not understood in 2016, so some of the maximum concentrations in the 2016 study may be underestimated.

- In cases where one collector of a set in series has been broken or its concentration data have been otherwise lost, data from other collectors in the series should be marked with a data-quality flag.

- In the SWIHD HS data, some chemicals showed high concentrations on the second tube in series as well as the first, including 1,3-butadiene, acetonitrile, formaldehyde, 2,3-dihydrofuran, 2,5-dihydrofuran, mercury, 2-propenal (acrolein), tetrahydrofuran, acetone, ethanol, decane, dodecane, n-hexane, 2,6,10-trimethyldodecane, n-tridecane, n-hexadecane, n-heptadecane, methylene chloride, and trichlorofluoromethane. These data should be reviewed to determine whether more tubes in series, or some other change in sampling, is needed to avoid loss of some vapor via breakthrough from the second tube, which would underestimate the concentrations of these chemicals.

- The new COPC candidate—nitrosodipropylamine—has a new proposed screening value that is near the SWIHD HS reporting limit. It may be necessary to change the sampling or analysis procedure to lower the reporting limit.

4.0   References

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