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Maximum Concentration Values Review for Use in NUCON Vapor Abatement Unit Testing

March 2018

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

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Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

Testing of the NUCON Vapor Abatement Unit will use “high inlet spike” concentrations to represent the maximum measured headspace concentrations for Single Shell Tanks (SST) at Hanford. In the initial analysis (Rev. A Test Plan), WRPS utilized the Site-Wide Industrial Hygiene Database (SWIHD) going back to 2005, which contained information that has been verified since WRPS became the Tank Farms Operations Contractor. This current report verified the “high inlet spike” values for accuracy against the data for single-shell tanks in all the historical databases, not only SWIHD. Measurements made prior to interim waste stabilization or waste retrieval were not considered in the verification of maximum measured concentrations as they are not representative of current tank farm conditions. Data for surrogate Chemicals of Potential Concern (COPCs) were also considered in determining the “high inlet spike” concentrations. Table S.1 shows the newly evaluated concentrations (COPC and surrogate). The original and revised test conditions are also shown with changes indicated by red text. Section 2 discusses how the targeted groups of COPCs were selected for the NUCON Testing. Section 3 gives details of the maximum concentrations and the tanks and sampling dates that provided them.

Table S.1. COPC Concentrations for 2x Occupational Exposure Level (OEL) and High Concentration Tests (original and revised test concentrations based on reevaluation of SWIHD and Tank Waste Information Network System [TWINS] data)

CAS	Name	2x OEL Test Original	High Conc. Test Original	Maximum Conc. SWIHD/TWINS (COPC or Surrogate)	2x OEL Test Revised (Preliminary)	High Test Revised (Preliminary)
75-07-0	Acetaldehyde	50 ppm	None	39 ppm	50 ppm	None
75-05-8	Acetonitrile	40 ppm	None	18.8 ppm	40 ppm	None
106-99-0	1,3-Butadiene	2 ppm	2.6 ppm	3.38 ppm	None[a]	3.4 ppm
107-12-0	Propanenitrile	12 ppm	12 ppm	0.78 ppm	None[a]	12 ppm
71-43-2	Benzene	1 ppm	1.26 ppm	0.189 ppm	1 ppm	None[b]
50-00-0	Formaldehyde	0.6 ppm	0.6 ppm	0.157 ppm	0.6 ppm	None[b]
108-47-4	2,4-Dimethyl pyridine	1 ppm	3.6 ppm	0.147 ppm	1 ppm	None[b]
62-75-9	N-Nitroso-dimethylamine	0.0006 ppm	0.0096 ppm	0.0621 ppm	0.0006 ppm	0.062 ppm
110-00-9	Furan	0.002 ppm	0.017 ppm	0.721 ppm[c]	0.002 ppm[c]	0.017 ppm[c]
7664-41-7	Ammonia	50 ppm	630 ppm	2,502 ppm[d]	50 ppm[d]	630 ppm[d]
10024-97-2	Nitrous Oxide	100 ppm	630 ppm	831 ppm	100 ppm	831 ppm

(a) Due to the similarities of the test conditions and in the interest of cost efficiency, the 2x OEL Test and High Concentration Test for 1,3-butadiene and propanenitrile are combined.

(b) Since the 2x OEL concentrations are higher than the maximums identified in the single-shell tanks, the High Concentration Tests for benzene, formaldehyde, and 2,4-dimethylpyridine are combined into the 2x OEL testing.

(c) The furan maximum concentration of 0.721 ppm is associated with tank BY-107, which is in the same cascade as BY-108, the tank selected for the vapor abatement unit (VAU) field demonstration (i.e., their headspaces are connected by an overflow line). For comparison, the highest concentration of a furanic compound in BY-108 was 0.547 ppm of furan on 10/27/1994. Destruction efficiencies of this high furan concentration will be evaluated during the field demonstration.

(d) The new ammonia maximum concentration of 2,502 ppm is associated with a U Farm tank, which will not be retrieved for more than 10 years. If the NUCON VAU is needed to mitigate vapors in U Farm at that time, additional tank vapor sampling would be likely and the VAU would be evaluated at the sampled maximum ammonia concentrations at that time.

Acronyms and Abbreviations

2x OEL	two times the Hanford tank farm occupational exposure limit
CAS	Chemical Abstract Service Registry Number
COPC	chemical of potential concern
DEP	diethylphthalate
HDI	How Do I…?
$_{HTF}$OEL	Hanford tank farm occupational exposure limit
NUCON	NUCON International, Inc.
OEL	occupational exposure limit
ppm	parts per million
PNNL	Pacific Northwest National Laboratory
SST	single-shell tank (located in the Hanford tank farms)
SWIHD HS	Site-Wide Industrial Hygiene Database for Headspace
TWINS IH	Tank Waste Information Network System Industrial Hygiene database
TWINS HS	Tank Waste Information Network System Headspace database
VAU	vapor abatement unit
VOC	volatile organic compound

Contents

Tables

1.0 Introduction

The objective of the NUCON International, Inc. (NUCON) testing is to assess the performance of the NUCON vapor abatement unit (VAU) prototype. The *PNNL Assessment of NUCON Vapor Abatement Unit for Single-Shell Tank (SST) Farm Off-Gas Chemicals of Potential Concern (COPCs)* test plan[1] covers the methodology and approach towards determining the abatement of 11 specific chemicals of potential concern (COPCs) when processed through the VAU.

NUCON has developed a novel toxic vapor thermal oxidation technology, known as the NUCON VAU. Pacific Northwest National Laboratory (PNNL) is to conduct an engineering-scale evaluation of the fate of COPCs in a VAU prototype. The purpose of the test is to evaluate the VAU vapor destruction efficiency for a selection of 11 COPCs that have been measured in Hanford high-level waste single-shell tank (SST) passive breather tank vapor emissions.

During the review cycle of the PNNL test plan, Exponent recommended that the "high inlet spike" concentrations be verified for accuracy regarding their representation of the maximum measured headspace concentrations for tanks at Hanford. Exponent further recommended that "high inlet spike" COPC concentrations be inclusive of the COPCs for which the subset of tested COPCs are surrogates.

The remainder of this report discusses the basis for choosing the subset of COPCs to be tested and the results of the determination of maximum concentrations.

This report was developed under the *NUCON Vapor Abatement Unit Testing Quality Assurance Plan*, 71248-QA-001, Rev. 0 (Meier 2018). The PNNL Quality Assurance (QA) Program is based upon the requirements as defined in DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830, *Energy/Nuclear Safety Management*, Subpart A, "Quality Assurance Requirements" (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part I, "Requirements for Quality Assurance Programs for Nuclear Facilities."
- ASME NQA-1-2000, Part II, Subpart 2.7, "Quality Assurance Requirements for Computer Software for Nuclear Facility Applications," including problem reporting and corrective action.
- ASME NQA-1-2000, Part IV, Subpart 4.2, "Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development."

The PNNL Quality Assurance Program Description / Quality Management M&O Program Description describes the Laboratory-level QA program that applies to all work performed by PNNL. Laboratory-level procedures for implementing the QA requirements described in the standards identified above are deployed through PNNL's web-based "How Do I…?" (HDI) system, a standards-based system for managing and deploying requirements and procedures to PNNL staff. The HDI procedures (called Workflows and Work Controls) provide detailed guidance for performing some types of tasks, such as protecting classified information and procuring items and services, as well as general guidelines for

[1] Rappe KG. 2017. *PNNL Assessment of NUCON Vapor Abatement Unit for Single-Shell Tank (SST) Farm Off-Gas Chemicals of Potential Concern (COPCs).* Test Plan TP-71248-01, Rev. 0, Draft, November 2017, Pacific Northwest National Laboratory, Richland, Washington.

performing research-related tasks, such as preparing and reviewing calculations and calibrating and controlling measuring and test equipment.

The technology maturity of the work is considered scoping in nature, and the NUCON project used PNNL HDI to meet the Basic Research requirements of the *NUCON Vapor Abatement Unit Testing Quality Assurance Plan*. This determination is based on the revised WRPS Quality Assurance Requirements (QAR) form, revision 1a, signed 2/5/2018 by WRPS Quality Engineer.

2.0 Selected Chemicals of Potential Concern

The 11 COPCs to be employed in the NUCON VAU testing were chosen to adequately represent the worst-case scenario of destruction removal efficiency for the different classes of compounds in the Hanford tank farm COPC list. The list of Hanford tank farm COPCs includes 61 compounds consisting of inorganic compounds, hydrocarbons (primary olefinic species), alcohols, ketones, aldehydes, furans and substituted furans, phthalates, nitriles, amines, nitrosamines, organophosphates and organophosphonates, halogenated hydrocarbons, pyridines, organonitrites, organonitrates, and isocyanates. The basis for selection of these 11 COPCs was as follows:

- Both ammonia and nitrous oxide were selected as part of the test due to their unique and somewhat unpredictable chemical behavior in combustion and catalytic systems.
- 1,3-butadiene and benzene were chosen to represent two comparatively recalcitrant hydrocarbon species and aromatic species.
- Formaldehyde and acetaldehyde were both selected to represent the most recalcitrant carbonyl groups, and thus adequately represent ketones as well. Additionally, aldehydes will conservatively predict alcohols as an aldehyde represents a more recalcitrant analog of an alcohol.
- Furan was chosen as the most recalcitrant furanic component.
- Phthalates are comparatively much less stable than benzene. The aromatic ring is the most recalcitrant portion of the phthalate molecule, and thus is adequately represented by benzene.
- Acetonitrile and propanenitrile were both chosen to represent the very unique and recalcitrant nitrile-functionality. The nitrile-functionality adequately represents the amine functionality as it is a comparatively more recalcitrant analog.
- N-nitrosodimethylamine (NDMA) was chosen to represent the nitrosamine functionality. A nitrosamine was chosen because there is not adequate information available to predict how a nitrosamine will decompose in combustion chemistry. With two methyl-groups, NDMA is comparatively more recalcitrant than one or two ethyl groups or a cyclic species, which are represented by the other nitrosamines on the COPC list.
- Regarding halogenated hydrocarbons, the presence of a halogen within a hydrocarbon molecule almost always destabilizes that structure within combustion chemistry. For this reason, halogenated hydrocarbons were not considered for inclusion in this study.
- A pyridine was chosen to represent the unique pyridine aromatic functionality. Since pyridine itself is expected to behave very similar yet slightly less recalcitrant than benzene, 2,4-dimethyl pyridine was chosen for comparison.
- Organophosphates and -phosphonates, organonitrites and -nitrates, and organoisocyanates are all molecules containing hydrocarbon cation complexes and inorganic anions. The very strongly dominating electronic nature of the anionic portion of these molecules dominates their behavior in combustion chemistry and renders them highly reactive and very non-recalcitrant. This knowledge base has been built upon a large amount of vehicle-based combustion chemistry dealing with, for example, phosphate derivatives such as lube oil components and organic sulfates as fuel-derived lubricants.

- Mercury compounds were excluded from the NUCON VAU testing since the understanding of the Mersorb© filter media has already been established in industrial applications.

Table 1 provides a list of the 11 COPCs selected for testing. Note that the Chemical Abstract Service (CAS) numbers referenced in this test plan are considered definitive. Common chemical names are provided only for convenience and readability.

Table 1. COPCs Selected for NUCON VAU Testing

COPC #	Name	CAS #	Formula	$_{HTF}$OEL (ppm)
20	Ammonia	7664-41-7	NH_3	25
51	Nitrous Oxide	10024-97-2	N_2O	50
2	1,3-Butadiene	106-99-0	C_4H_6	1
21	Benzene	71-43-2	C_6H_6	0.5
30	Formaldehyde	50-00-0	CH_2O	0.3
18	Acetaldehyde	75-07-0	C_2H_4O	25
31	Furan	110-00-9	C_4H_4O	0.001
19	Acetonitrile	75-05-8	C_2H_3N	20
57	Propanenitrile	107-12-0	C_3H_5N	6
6	2,4-Dimethylpyridine	108-47-4	C_7H_9N	0.5
53	N-Nitrosodimethylamine (NDMA)	62-75-9	$C_2H_6N_2O$	0.0003

$_{HTF}$OEL = Hanford tank farm occupational exposure limit

3.0 Review of the Maximum Concentrations

The 2018 tests of the NUCON VAU are intended to ensure that the feed gas for the system test includes concentrations of certain selected Hanford tank COPC vapors that are bounding both for those vapors themselves and for other COPC vapors, those for which the test feed vapors are surrogates. To determine the bounding feed concentrations applicable to planned NUCON VAU operations, several vapor databases were examined to determine the currently relevant maxima for the types of tanks on which the system will be used.

The data sets from which relevant subsets of vapor concentration data were extracted were TWINS Headspace (TWINS HS), TWINS Industrial Hygiene (TWINS IH), and SWIHD Headspace (SWIHD HS), as follows:

- TWINS HS concentrations measured in tank headspaces between 1994 and 2005
- TWINS IH concentrations measured between 2005 and July 2017 in stacks, exhausters, breather filters, inlet filters, and a variety of other sources
- SWIHD HS concentrations measured in tank headspaces between 2014 and July 2017

Some of the data were not considered for maxima because they had analytical data quality flags that made them suspect (Hoppe et al. 2016). In cases where there were data for two or more (e.g.,) sorbent tubes in series on the same sampled stream of gas, the concentrations for the individual tubes were summed to give the total concentration for the sample.

Two constraints were applied to reduce these data sets by removing measurements that were not applicable to the NUCON VAU system operations.

First, all data that were not from SSTs were removed from consideration because the NUCON VAU system is intended for use only on SST gas/vapor streams from headspaces. SST data were also removed in this step if they were not clearly headspace data – for example, if they were drillstring gas or measured at “sources around” a tank or farm.

Second, SST data were removed from consideration if they had been measured before the tank’s waste was last modified by remediation or retrieval operations. Pre-stabilization and pre-retrieval data were considered to be out of date and unrepresentative of possible headspace conditions under which the NUCON VAU system would be used. In two cases, C-105 and C-106, the Best Basis Inventory tank activity databases[1] were used to supply latest-activity dates where other sources did not give retrieval end dates. Table 2 shows the cutoff dates that were used and the online sources of information[2] on which they were based; however, the stabilization report (Swaney 2005) was the preferred basis.

[1] These databases can be found at
https://twins.labworks.org/twinsdata/Forms/BuildQuery.aspx?SourceName=txfr.dbo.p_TWINS_Get_Transfer_Events&whatsnew=Tank|Transfers
https://twins.labworks.org/twinsdata/Forms/BuildQuery.aspx?SourceName=tcd.dbo.transfers_denorm&whatsnew=Tank|Transfers

[2] Phoenix Tank Farms Dashboard: https://phoenix.pnnl.gov/apps/tankfarm/index.html
Phoenix Waste Tank Summary Report: https://phoenix.pnnl.gov/apps/tanksummary/summary.html

The above-reporting-limit measurements in the reduced data sets were searched for the maximum concentration of each of the COPCs that were within the scope of NUCON VAU testing.[1] As a cross-check, these maxima were compared to the ones that had been reported in PNNL-13366, Rev. 1 (Stock and Huckaby 2004). In many cases the maxima reported in that July 2004 report were no longer applicable because of remediation or retrieval, or had been superseded by later, higher maxima. Table 3 shows the test-applicable maximum concentrations of the COPCs that are within the scope of NUCON VAU testing.

The subset of COPCs that are to be used in NUCON VAU test feeds are listed below, together with comments on their maximum concentrations:

- Ammonia: The maximum of 2502 ppm may have been the result of post-stabilization evaporation from liquid left behind in exposed pores of the waste, although stabilization had been completed 4 years before. There are no later measurements from the same tank to confirm this, though. Headspace ammonia concentrations for other SSTs in SWIHD HS, covering 2014-2017, are less than 500 ppm.
- Nitrous oxide: The maximum was 831 ppm.
- 1,3-butadiene: The maximum was 3.38 ppm.
- Benzene, for itself and as a surrogate for the other aromatic COPCs, which are biphenyl and diethylphthalate (DEP): The maximum benzene was 0.189 ppm, considerably higher than the maximum biphenyl concentration of 0.00142 ppm and also higher than the maximum DEP concentration of 0.064 ppm.
- Formaldehyde and acetaldehyde, for themselves and as surrogates for other oxygenated aliphatic COPCs including alcohols, aldehydes, and ketones: The maxima for these two aldehydes were 0.157 and 2.82 ppm, respectively. While the maxima for other aldehydes and for ketones are in this same range, the alcohols had much higher maxima, 63.5 ppm for 1-butanol (measured in 1994) and 39 ppm for methanol (measured in 2004, 4 years after stabilization). For comparison, the $_{HTF}$OELs of formaldehyde and acetaldehyde are 0.3 and 25 ppm, respectively. The 1994 maximum of 1-butanol was not used, as it appears to have decreased substantially, based on several later data points in the same tank. In addition, the methanol maximum may have decreased as the time since stabilization has increased, but data to corroborate this assumption are not available.
- Furan, for itself and as a surrogate for other COPCs with furan rings: Two of the furan compounds have higher maxima than any of the others. These higher maxima are 0.547 ppm for furan and 0.721 ppm for 2,5-dihydrofuran.
- Acetonitrile and propanenitrile, for themselves and as surrogates for other nitrile COPCs and for ethylamine: The maxima for these two nitriles were 18.8 and 0.517 ppm, respectively. The propanenitrile maximum is higher than that for any of the longer-chain nitriles, though lower than the ethylamine (ethanamine) maximum of 0.78 ppm. The acetonitrile maximum is much higher. For comparison, the $_{HTF}$OELs of acetonitrile and propanenitrile are 20 and 6 ppm, respectively.

[1] For reasons discussed in Section 2, the COPCs that did not need to be considered were organic nitrates and nitrites, organic nitro compounds, mercury, dimethylmercury, methyl isocyanate, tributyl phosphate), dibutyl butylphosphonate, poly-chlorinated biphenyls, and 2-fluoro-1-propene.

- NDMA, for itself and as a surrogate for other nitrosamine COPCs: The highest maximum among the nitrosamine COPCs is for NDMA, 0.0621 ppm. The next highest maximum is for N-nitrosomorpholine, 0.00495 ppm.
- 2,4-dimethylpyridine, for itself and as a surrogate for pyridine: Pyridine has the higher of the two maxima, 0.147 ppm versus 0.0338 ppm for 2,4-dimethylpyridine. The $_{HTF}$OEL for 2,4-dimethylpyridine is 0.5 ppm, higher than either of the maxima.

Table 2. Cutoff Dates for Vapor Concentration Data Relevant to NUCON VAU Testing

SST	Cutoff date (delete all data before this)	Source
A-101	6/17/2004	a
A-102	8/28/1989	a
A-103	6/29/1988	a
A-104	9/30/1978	a
A-105	7/31/1979	a
A-106	8/31/1982	a
AX-101	12/11/2003	a
AX-102	9/9/1988	a
AX-103	8/19/1987	a
AX-104	8/22/1981	a
B-101	3/31/1981	a2
B-102	8/23/1985	a
B-103	2/26/1985	a
B-104	6/28/1985	a
B-105	12/27/1984	a
B-106	3/20/1985	a
B-107	3/20/1985	a
B-108	5/22/1985	a
B-109	4/9/1985	a
B-110	12/20/1984	a
B-111	6/28/1985	a
B-112	5/31/1985	a
B-201	8/31/1981	a2
B-202	5/31/1985	a
B-203	6/29/1984	a
B-204	6/29/1984	a

SST	Cutoff date (delete all data before this)	Source
BX-101	9/30/1978	a
BX-102	11/30/1978	a
BX-103	11/29/1983	a2
BX-104	9/26/1989	a
BX-105	9/3/1986	a
BX-106	8/1/1995	a
BX-107	9/26/1990	a
BX-108	7/31/1979	a
BX-109	9/26/1990	a
BX-110	8/22/1985	a
BX-111	3/14/1995	a
BX-112	9/26/1990	a
BY-101	5/22/1984	a
BY-102	4/27/1995	a
BY-103	11/24/1997	a
BY-104	1/25/1985	a
BY-105	3/7/2003	a
BY-106	6/27/2005	a
BY-107	7/31/1979	a
BY-108	2/6/1985	a
BY-109	6/20/1997	a
BY-110	1/25/1985	a
BY-111	1/25/1985	a
BY-112	6/13/1984	a

a: Hanford Tank Stabilization Report HNF-SD-TI-178 Rev. 9
a2: same as (a), but used end of month because no day-of-month was supplied
b: Phoenix Waste Tank Summary Report, retrieval complete ("stabilization date" not applicable to tanks that were retrieved rather than stabilized)
c: BBI tank activity database indicates transfers until this date; Phoenix has no official retrieval completion date
d: Phoenix Tank Dashboard reports March 2013 stabilization date

SST	Cutoff date (delete all data before this)	Source
C-101	9/25/2013	b
C-102	11/30/2015	b
C-103	8/23/2006	b
C-104	8/17/2012	b
C-105	5/20/2017	c
C-106	1/27/2004	c
C-107	9/30/2014	b
C-108	3/22/2012	b
C-109	9/12/2012	b
C-110	10/30/2013	b
C-111	8/29/2016	b
C-112	5/29/2014	b
C-201	3/23/2006	b
C-202	8/11/2005	b
C-203	3/23/2006	b
C-204	12/11/2006	b
S-101	4/21/2004	a
S-102	3/31/2013	d
S-103	3/24/2000	a
S-104	12/20/1984	a
S-105	8/31/1978	a2
S-106	2/1/2001	a
S-107	2/4/2004	a
S-108	12/20/1996	a
S-109	6/11/2001	a
S-110	1/31/1997	a2
S-111	5/18/2005	a
S-112	3/2/2007	b

SST	Cutoff date (delete all data before this)	Source
SX-101	8/18/2003	a
SX-102	7/19/2004	a
SX-103	5/30/2003	a
SX-104	4/3/2000	a
SX-105	8/6/2002	a
SX-106	5/2/2000	a
SX-107	10/19/1979	a
SX-108	8/31/1979	a
SX-109	5/31/1981	a2
SX-110	8/31/1979	a
SX-111	7/31/1979	a
SX-112	7/31/1979	a
SX-113	11/30/1978	a
SX-114	7/31/1979	a
SX-115	9/30/1978	a
T-101	4/14/1993	a
T-102	3/31/1981	a2
T-103	11/28/1983	a
T-104	11/16/1999	a
T-105	6/2/1987	a
T-106	8/10/1981	a
T-107	5/22/1996	a
T-108	11/30/1978	a
T-109	12/20/1984	a
T-110	1/5/2000	a
T-111	2/22/1995	a
T-112	3/31/1981	a2

a: Hanford Tank Stabilization Report HNF-SD-TI-178 Rev. 9

a2: same as (a), but used end of month because no day-of-month was supplied

b: Phoenix Waste Tank Summary Report, retrieval complete ("stabilization date" not applicable to tanks that were retrieved rather than stabilized)

c: BBI tank activity database indicates transfers until this date; Phoenix has no official retrieval completion date

d: Phoenix Tank Dashboard reports March 2013 stabilization date

SST	Cutoff date (delete all data before this)	Source
T-201	4/30/1981	a2
T-202	8/31/1981	a2
T-203	4/30/1981	a2
T-204	8/31/1981	a2
TX-101	2/3/1984	a
TX-102	4/5/1983	a
TX-103	8/12/1983	a
TX-104	9/19/1979	a
TX-105	9/29/1983	a
TX-106	6/8/1983	a
TX-107	10/19/1979	a
TX-108	3/24/1983	a
TX-109	4/18/1983	a
TX-110	4/5/1983	a
TX-111	4/5/1983	a
TX-112	4/5/1983	a
TX-113	4/5/1983	a
TX-114	4/5/1983	a
TX-115	9/29/1983	a
TX-116	4/5/1983	a
TX-117	3/28/1983	a
TX-118	4/5/1983	a
TY-101	4/5/1983	a
TY-102	9/18/1979	a
TY-103	3/1/1983	a
TY-104	11/1/1983	a
TY-105	3/1/1983	a
TY-106	11/30/1978	a

SST	Cutoff date (delete all data before this)	Source
U-101	9/17/1979	a
U-102	6/19/2002	a
U-103	8/16/2000	a
U-104	11/2/1978	a
U-105	3/29/2001	a
U-106	3/9/2001	a
U-107	12/16/2003	a
U-108	8/16/2004	a
U-109	4/5/2002	a
U-110	12/20/1984	a
U-111	6/25/2003	a
U-112	9/19/1979	a
U-201	8/31/1979	a
U-202	8/31/1979	a
U-203	8/31/1979	a
U-204	8/31/1979	a

a: Hanford Tank Stabilization Report HNF-SD-TI-178 Rev. 9

a2: same as (a), but used end of month because no day-of-month was supplied

b: Phoenix Waste Tank Summary Report, retrieval complete ("stabilization date" not applicable to tanks that were retrieved rather than stabilized)

c: BBI tank activity database indicates transfers until this date; Phoenix has no official retrieval completion date

d: Phoenix Tank Dashboard reports March 2013 stabilization date

Table 3. Vapor Concentration Maxima for Historical Data Relevant to NUCON VAU Testing

COPC	Maximum for Test-Applicable Concentrations over All Sources (ppm)	Date, Tank, and Database (Plus Survey Title, for TWINS IH)	Notes from Historical Databases
INORGANICS			
Ammonia, 7664-41-7	2502	12/15/2004, U-103, TWINS HS	U-103 stabilization was complete as of 8/16/2000. This U-103 maximum was measured after the PNNL-13366 R.1 report was published in July 2004 and both supersedes and exceeds the 1043 ppm given there.
Nitrous oxide (N_2O), 10024-97-2	831	9/10/1996, BY-108, TWINS HS	The U-102 maximum in the PNNL-13366 R.1 report was 1100 ppm on 10/23/1998, but this was before the U-102 stabilization date of 6/19/2002.
HYDROCARBONS			
1,3-Butadiene, 106-99-0	3.38	4/8/2008, BY-108, "BY-108 COPC Sampling", TWINS IH	This BY-108 maximum was measured after the PNNL-13366 R.1 report was published in July 2004 and both supersedes and exceeds the 0.223 ppm given there.
AROMATIC COMPOUNDS			
Benzene, 71-43-2	0.189	10/27/1994, BY-108, TWINS HS	The U-102 maximum in the PNNL-13366 R.1 report was 2.15 ppm in BY-104, but this measurement was not found in current databases for any tank or date. The highest concentration found in the current TWINS HS database was 1.26 ppm, for C-102 on 8/23/1994, before its retrieval in 2015.
1,1'-Biphenyl, 92-52-4	0.00142	10/12/2005, S-101, "S COMPLEX SAMPLING", TWINS IH	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 2.18 ppm, but this was before the C-103 retrieval that ended in 2006.
1,2-Benzenedicarboxylic acid, diethyl ester, (diethylphthalate, DEP) 84-66-2	0.064	2/28/2005, A-104, TWINS HS	The U-106 maximum in the 2004 PNNL-13366 R.1 report was 0.131 ppm, but this was measured on 8/25/1994, before the U-106 stabilization that ended in 2001.

COPC	Maximum for Test-Applicable Concentrations over All Sources (ppm)	Date, Tank, and Database (Plus Survey Title, for TWINS IH)	Notes from Historical Databases
ALCOHOLS			
1-Butanol, 71-36-3	63.5	10/27/1994, BY-108, TWINS HS	The maximum given here is the highest measurement from the same set whose average provided the 58.4 ppm value given in the PNNL-13366 R.1 report. Later measurements in BY-108 were lower. TWINS HS shows 10/27/1994, 54 - 63.5 ppm; 1/23/1996, 7.2 - 22.0 ppm, 3/28/1996, 7.0 - 17.1 ppm; 9/10/1996, 10.2 - 21.4 ppm; 11/14/1996, 9.9 - 20.7 ppm; 1/30/1997, 6.9 - 15.9 ppm. TWINS IH data for BY-108 on 9/17/2009 was 3.4 - 4.3 ppm. SWIHD HS contains the measurements 10/06/2016, 1.4 - 3.3 ppm; 10/18/2016, 2.8 ppm. For tanks other than BY-108, the highest measurement was 13.6 ppm, on 10/26/1994, in BY-107 (TWINS HS).
Methanol, 67-56-1	39	12/15/2004, U-103, TWINS HS	U-103 stabilization was complete as of 8/16/2000. This U-103 maximum was measured after the PNNL-13366 R.1 report was published in July 2004 and both supersedes and exceeds the 28 ppm given there. There are no later data for U-103 methanol, but concentrations measured later in other tanks are lower. In TWINS IH, the highest concentration is 0.867 ppm, TX-109, 6/7/2007. In SWIHD HS the highest is 0.754 ppm, A-103, 2016.
KETONES			
2-Hexanone, 591-78-6	0.175	10/26/1994, BY-107, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 0.600 ppm, but this was before the C-103 retrieval that ended in 2006. Note: the same 0.175 ppm concentration was also measured in BY-108 the next day.

COPC	Maximum for Test-Applicable Concentrations over All Sources (ppm)	Date, Tank, and Database (Plus Survey Title, for TWINS IH)	Notes from Historical Databases
3-Methyl-3-buten-2-one, 814-78-8	0.0213	6/24/1994, BY-104, TWINS HS	The maximum given here is the same one that provided the 0.021 ppm BY-104 value given in the PNNL-13366 R.1 report.
4-Methyl-2-hexanone, 105-42-0	0.0412	6/24/1994, BY-104, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 1.08 ppm, but this was before the C-103 retrieval that ended in 2006.
6-Methyl-2-heptanone, 928-68-7	0.343	10/27/1994, BY-108, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 2.098 ppm, but this was before the C-103 retrieval that ended in 2006.
3-Buten-2-one, 78-94-4	0.0576	6/24/1994, BY-104, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 1.151 ppm, but this was before the C-103 retrieval that ended in 2006.
ALDEHYDES			
Formaldehyde, 50-00-0	0.157	2/10/2016, A-102, SWIHD HS	No maximum was given in the PNNL-13366 R.1 report. The present maximum was measured after the report.
Acetaldehyde, 75-07-0	2.82	4/8/2008, BY-108, "BY-108 COPC Sampling", TWINS IH	The C-105 maximum in the 2004 PNNL-13366 R.1 report was 12 ppm, but this was before the C-105 retrieval that ended in 2017. This BY-108 maximum was measured after the PNNL-13366 R.1 report was published in July 2004 and both supersedes and exceeds the maximum given there.
Butanal, 123-72-8	1.62	10/27/1994, BY-108, TWINS HS	The C-105 maximum in the 2004 PNNL-13366 R.1 report was 6.6 ppm, but this was before the C-105 retrieval that ended in 2017.
2-Methyl-2-butenal, 1115-11-3	0.0248	10/16/1996, B-103, TWINS HS	The maximum given here is the highest measurement from the same B-103 group of measurements whose average provided the 0.014 ppm value given in the PNNL-13366 R.1 report.

COPC	Maximum for Test-Applicable Concentrations over All Sources (ppm)	Date, Tank, and Database (Plus Survey Title, for TWINS IH)	Notes from Historical Databases
2-Ethyl-2-hexenal, 645-62-5	0.00376	6/27/1995, AX-102, TWINS HS	The C-105 maximum in the 2004 PNNL-13366 R.1 report was 0.021 ppm, but this was before the C-105 retrieval that ended in 2017.
2-Propenal, 107-02-8	0.162	12/18/2014, AX-104, SWIHD HS	The maximum in the 2004 PNNL-13366 R.1 report was 0.006 ppm in B-103. The new maximum exceeds the reported one..
FURANS			
Furan, 110-00-9	0.547	10/27/1994, BY-108, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 3.194 ppm, but this was before the C-103 retrieval that ended in 2006. In TWINS HS data, the next highest measurement was 0.013 ppm in BY-102 in 1994. Maxima from more recent data are 0.040 ppm (T-111, 2015, volatile organic compound (VOC) method, SWIHD HS) and 0.0104 ppm (BY-108 breather filter, 2009, VOC method, TWINS IH)
2,3-Dihydrofuran, 1191-99-7	0.0114	10/12/1995, TX-111, TWINS HS	The C-110 maximum in the 2004 PNNL-13366 R.1 report was 0.016 ppm, but this was before the C-110 retrieval that ended in 2013.
2,5-Dihydrofuran, 1708-29-8	0.721	10/26/1994, BY-107, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 1.823 ppm, but this was before the C-103 retrieval that ended in 2006. In TWINS HS data, the next highest (and only other) measurement was 0.0016 ppm in U-112, 1996. There is only one above-report measurement in more recent data: 0.00457 ppm (BY-110, 2015, furans method, SWIHD HS).
2-Methylfuran, 534-22-5	0.0218	6/24/1994, BY-104, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 1.01 ppm, but this was before the C-103 retrieval that ended in 2006.

COPC	Maximum for Test-Applicable Concentrations over All Sources (ppm)	Date, Tank, and Database (Plus Survey Title, for TWINS IH)	Notes from Historical Databases
2,5-Dimethylfuran, 625-86-5	0.00933	6/24/1994, BY-104, TWINS HS	The maximum given here is the same one that provided the 0.0093 ppm BY-104 value given in the PNNL-13366 R.1 report.
2-Ethyl-5-methylfuran, 1703-52-2	0.0102	6/24/1994, BY-104, TWINS HS	The maximum given here is the same one that provided the 0.010 ppm value given for BY-104 in the PNNL-13366 R.1 report.
(S)-2,3-dihydro-4-(1-methylpropyl)-furan, 34379-54-9	0.000977	6/27/1995, AX-102, TWINS HS	The maximum given here is the same one that provided the 0.00098 ppm value given for AX-102 in the PNNL-13366 R.1 report.
3-(1,1-dimethylethyl)-2,3-dihydrofuran, 34314-82-4	n/a	n/a	The BY-105 maximum in the 2004 PNNL-13366 R.1 report was 0.00053 ppm, measured on 7/7/1994, but this was before the BY-105 stabilization that ended in 2003. No data found for this COPC in the current NUCON-relevant database
2-Pentylfuran, 3777-69-3	0.000493	1/13/2016, A-105, SWIHD HS	The AX-101 maximum in the 2004 PNNL-13366 R.1 report was 0.0026 ppm, measured on 6/15/1995, but this was before the AX-101 stabilization that ended in 2003.
2-Heptylfuran, 3777-71-7	0.0612	10/27/1994, BY-108, TWINS HS	The maximum given here is the highest measurement from the same group of BY-108 data whose average provided the 0.044 ppm value given in the PNNL-13366 R.1 report.
2-Propylfuran, 4229-91-8	n/a	n/a	The BY-109 maximum in the 2004 PNNL-13366 R.1 report was 0.590 ppm, measured on 9/22/1994, but this was before the BY-109 stabilization that ended in 1997. No data found for this COPC in the current NUCON-relevant database.

COPC	Maximum for Test-Applicable Concentrations over All Sources (ppm)	Date, Tank, and Database (Plus Survey Title, for TWINS IH)	Notes from Historical Databases
2-Octylfuran, 4179-38-8	n/a	n/a	The BY-106 maximum in the 2004 PNNL-13366 R.1 report was 0.00081 ppm, measured on 7/8/1994, but this was before the BY-106 stabilization that ended in 2003. No data found for this COPC in the current NUCON-relevant database.
3-(2-furanyl)-1-phenyl-2-propen-1-one, 717-21-5	n/a	n/a	The SX-106 maximum in the 2004 PNNL-13366 R.1 report was 0.00058 ppm, measured on 3/24/1995, but this was before the SX-106 stabilization that ended in 2000. No data found for this COPC in the current NUCON-relevant database.
6-(2-furanyl)-6-methyl-2-heptanone, 51595-87-0	n/a	n/a	The C-105 maximum in the 2004 PNNL-13366 R.1 report was 0.00052 ppm, measured on 2/16/1994, but this was before the C-105 retrieval that ended in 2017. No data found for this COPC in the current NUCON-relevant database.
NITRILES			
Acetonitrile, 75-05-8	18.8	10/18/2016, BY-108, SWIHD HS	This BY-108 maximum was measured after the PNNL-13366 R.1 report was published in July 2004 and both supersedes and exceeds the 13 ppm given there for C-103.
Propanenitrile, 107-12-0	0.517	8/1/1996, BX-103, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 5.3 ppm, but this was before the C-103 retrieval that ended in 2006.
Butanenitrile, 109-74-0	0.69	8/1/1996, BX-103, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 2.562 ppm, but this was before the C-103 retrieval that ended in 2006.
Pentanenitrile, 110-59-8	0.251	8/1/1996, BX-103, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 1.078 ppm, but this was before the C-103 retrieval that ended in 2006.

COPC	Maximum for Test-Applicable Concentrations over All Sources (ppm)	Date, Tank, and Database (Plus Survey Title, for TWINS IH)	Notes from Historical Databases
Hexanenitrile, 628-73-9	0.314	8/1/1996, BX-103, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 0.854 ppm, but this was before the C-103 retrieval that ended in 2006.
Heptanenitrile, 629-08-3	0.129	8/1/1996, BX-103, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 0.645 ppm, but this was before the C-103 retrieval that ended in 2006.
2-Methylene-butanenitrile, 1647-11-6	n/a	n/a	No maximum was given in the PNNL-13366 R.1 report. No data found for this COPC in the current NUCON-relevant database.
2,4-Pentadienenitrile, 1615-70-9	0.00085	12/6/1996, U-112, TWINS HS	The maximum given here is the same U-112 value that provided the 0.00085 ppm value given in the PNNL-13366 R.1 report.
AMINES			
Ethanamine, 75-04-7	0.78	11/11/2005, A-105, "A-105 Breather Filter", TWINS IH	No maximum was given in the PNNL-13366 R.1 report. The present maximum was measured after the report.
NITROSAMINES			
N-methyl-N-nitroso-methanamine, (NDMA) 62-75-9	0.0621	10/12/1995, TX-111, TWINS HS	The U-108 maximum in the 2004 PNNL-13366 R.1 report was 0.082 ppm, but this was measured on 8/29/1995 before the U-108 stabilization that ended in 2003.
N-ethyl-N-nitroso-ethanamine, (NDEA) 55-18-5	0.00006	7/17/2015, A-101, SWIHD HS	No maximum was given in the PNNL-13366 R.1 report. The present maximum was measured after the report.
N-methyl-N-nitroso-ethanamine, (NMEA) 10595-95-6	0.000086	8/6/2015, TX-114, SWIHD HS	No maximum was given in the PNNL-13366 R.1 report. The present maximum was measured after the report.

COPC	Maximum for Test-Applicable Concentrations over All Sources (ppm)	Date, Tank, and Database (Plus Survey Title, for TWINS IH)	Notes from Historical Databases
N-nitrosomorpholine, 59-89-2	0.00495	12/22/2014, AX-102, SWIHD HS	The U-108 maximum in the 2004 PNNL-13366 R.1 report was 0.0097 ppm, but this was measured on 8/29/1995 before the U-108 stabilization that ended in 2003.
PYRIDINES			
Pyridine, 110-86-1	0.147	1/23/1996, BY-108, TWINS HS	The maximum given here is the highest measurement from the same group of BY-108 data whose average provided the 0.122 ppm value given in the PNNL-13366 R.1 report. In TWINS HS data, the next highest measurement was 0.121 ppm in BX-104, 1994. The highest concentrations in more recent data were 0.012 ppm (C-201, 2006, TWINS IH, VOC Summa method) and 0.003 ppm (A-102, 2016, SWIHD HS, VOC method)
2,4-dimethylpyridine, 108-47-4	0.0338	11/21/1995, BY-102, TWINS HS	The C-103 maximum in the 2004 PNNL-13366 R.1 report was 0.105 ppm, but this was before the C-103 retrieval that ended in 2006. In TWINS HS data, the next highest (and only other) measurement was 0.00080 ppm in TX-118, 1994. The highest measurement in more recent data was in TWINS IH, 0.019 ppm (C-201, 6/20/2006, VOC Summa method). The highest measurement in SWIHD HS is 0.004 ppm (BY-108, 2016, pyridines method).

4.0 References

10 CFR 830, *Energy/Nuclear Safety Management*. U.S. Code of Federal Regulations, as amended.

ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications.* American Society of Mechanical Engineers, New York, New York.

DOE Order 414.1D, *Quality Assurance.* U.S. Department of Energy, Washington, D.C.

Hoppe EW, LA Mahoney, J Cole, KS Rohlfing. 2016. *Hanford Tank Vapors COPCs Update*. PNNL-25880, September 2016, Pacific Northwest National Laboratory, Richland, Washington.

Meier K. 2018. *NUCON Vapor Abatement Unit Testing Quality Assurance Plan*. 71248-QA-001, Rev. 0. February 2018. Pacific Northwest National Laboratory, Richland, Washington.

Stock LM and JL Huckaby. 2004. *A Survey of Vapors in the Headspaces of Single-Shell Waste Tanks*. PNNL-13366, Rev. 1, July 2004, Pacific Northwest National Laboratory, Richland, Washington.

Swaney SL. 2005. *Single-Shell Tank Interim Stabilization Record*. HNF-SD-RE-TI-178, Rev. 9, July 2005, Babcock Services, Inc., Richland, Washington.

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