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July 2020

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the U.S. Department of Energy
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Executive Summary

Between 2017 and 2018, 10 powered air-purifying respirator (PAPR) cartridge tests were performed on headspace vapors from three Hanford tanks (BY-108 2018, SX-101, and SX-104) and two Hanford tank farm exhausters (AP 2018 and AX). All tests were conducted under static conditions absent waste-disturbing activities in the subject tanks or tank farms. Multipurpose high-efficiency PAPR cartridges, MSA-TL (TL1) (MSA Safety Inc., Pittsburgh, Pennsylvania) and 3M FR-57 (TL2) (3M Company, Maplewood, Minnesota), were tested on each of the five tanks or exhausters. Out of 61¹ Chemicals of Potential Concern (COPCs), only ammonia and 2,5-dimethylfuran exhibited breakthroughs with outlet concentrations that were greater than 10% of their Occupational Exposure Limits (OEL). For 2,5-dimethylfuran, elevated concentrations found in blank tube samples made the elevated outlet measurements for this COPC questionable. Further details and recommendations based on each of these breakthrough signatures are provided below:

- Ammonia exhibited breakthrough² for 7 of the 10 cartridge tests. Breakthrough was not observed for either PAPR cartridge in the AX exhauster tests or for the MSA-TL (TL1) cartridge in the AP exhauster test. Breakthrough between 0 and 6 hours was observed with the MSA-TL (TL1) cartridge in SX-101 and SX-104 testing where inlet concentrations were 628% and 1126% of the OEL, respectively. Breakthrough in the BY-108 test occurred between 4 and 6 hours with a maximum ammonia inlet concentration of 767% of the OEL. Much lower maximum inlet concentrations of 19% and 102% of the OEL were observed in the AX and AP exhauster testing, respectively, where no indication of breakthrough was observed.
- The 3M FR-57 (TL2) cartridge had the shortest breakthrough times for ammonia, less than 2 hours, during the SX-101, SX-104, and BY-108 tests. These tests had the highest maximum inlet concentrations for the 3M cartridge—greater than 586% of the OEL. Breakthrough was observed between 4 and 6 hours during the AP exhauster testing with inlet concentrations at 97% of the OEL. No breakthrough was observed at inlet concentrations of 17% of the OEL during the AX exhauster testing. For both the MSA and 3M PAPR cartridges in each of the tank/cartridge tests, ammonia breakthrough preceded all other breakthrough observations, indicating that it is a leading candidate for defining the minimum breakthrough times for PAPR cartridges.
- Breakthrough of 2,5-dimethylfuran was observed only in the SX-104 tests. All inlet concentrations of 2,5-dimethylfuran for SX-104 with the MSA-TL (TL1) and 3M FR-57 (TL2) cartridges were less than the detection limit (DL) (approximately 4% of the OEL), except for a single inlet measurement for the 3M FR-57 cartridge of 25% of the OEL. Despite low inlet concentrations for both cartridges, two outlet measurements for each of the MSA-TL and 3M FR-57 cartridges were >10% of the OEL and the reporting limit (RL) (13.5% of OEL). Breakthrough times between 8 and 10 hours and between 2 and 4 hours were observed for the MSA-TL and 3M FR-57 cartridges, respectively. However, several 2,5-dimethylfuran measurements from the blank and baseline sample tubes also reported concentrations greater than the RL. The combination of low cartridge inlet concentrations and elevated blank and baseline concentrations makes the breakthrough observation suspect. The single available historical measurement of the SX-104 headspace was less than the RL (25% of the OEL).

¹ Way KJ, September 21, 2017 Letter, Tank Operations Contractor – Chemicals of Potential Concern Rev. 1, WRPS-1604188.1. Washington River Protection Solutions, Richland, Washington.

² Breakthrough is defined as measuring outlet concentrations that were >10% of their Hanford Occupational Exposure Limit established in WRPS-1604188.1 or RPP-22491 Rev. 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. http://www.hanford.gov/tocpmm/files.cfm/IHTechBasis_RPP-22491Rev1.pdf).

Eight additional COPCs—mercury, formaldehyde, furan, 2-methylfuran—and four nitrosamines—N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosomethylethylamine (NMEA), and N-nitrosomorpholine—had inlet concentrations greater than 10% of the OELs in one or more of the 10 PAPR cartridge tests, but with no indication of breakthrough above 10% of their OELs or DLs in the cartridge outlets.

- Maximum mercury inlet concentrations for the PAPR cartridges ranged from 26% to 90% of the OEL, with maximum outlet concentrations all below the RL (<8% of the OEL), despite the fact neither the MSA-TL or 3M FR-57 cartridges are rated for mercury removal.
- The maximum formaldehyde inlet concentrations ranged from 3% to 17% of the OEL, with maximum outlet concentrations ranging from 2% to 9% of the OEL. The highest outlet readings were observed with the 3M FR-57 cartridge tested on the AX exhauster; however, no breakthrough above 10% of the OEL was observed.
- Furan maximum inlet concentrations ranged from 57% to 576% of the OEL. Maximum outlet concentrations were all below DL (<14% to <40% of the OEL); therefore, there was no indication of furan breakthrough for either cartridge for the conditions tested.
- Inlet concentrations of 2-methylfuran were measured above 10% of the OEL only during the BY-108 tests, during which a maximum inlet concentration of approximately 17% of the OEL was observed. All measured outlet concentrations were less than the analytical DL (between 9% and 21% of the OEL), indicating no breakthrough for either cartridge.
- No breakthroughs were observed for any of the nitrosamine COPCs during PAPR cartridge testing. NDMA inlet concentrations ranged from 63% to 6935% of the OEL with the highest concentration observed in SX-104, followed by SX-101 at 3,358%. NDEA inlet concentrations ranged from 13% to 79% of its OEL with the highest concentrations observed in SX-104. NMEA inlet concentrations ranged from 5% to 188% of the OEL with the highest concentrations observed in BY-108 test. N-nitrosomorpholine inlet concentrations ranged from 1% to 51% of its OEL with the highest concentrations observed in the AX exhauster. All outlet concentrations of the four nitrosamine COPCs were below their RLs (<2% to <13%).

Estimations for the MSA-TL PAPR cartridge are based on the Cartridge Life Expectancy Calculator³ from the MSA Response Guide.⁴ Service life results obtained from the Cartridge Life Expectancy Calculator were near or below the measured breakthrough values for each of the MSA-TL cartridge tests. This indicates that the manufacturer's estimator is consistent with and frequently conservative for ammonia and may be used as a reference by Industrial Hygienists in future service life estimations.

The 3M Service Life Software⁵ does not allow for evaluation of ammonia with the FR-57 (TL2) cartridge despite National Institute of Occupational Safety and Health (NIOSH) ammonia certification. 3M recommended the interpolation of the NIOSH testing certification results for estimation of a lower limit on the cartridge service life using a simple algorithm as shown in Appendix F. Data obtained from the interpolation of the NIOSH testing certification results were consistently near or below the measured breakthrough values. However, this interpolation algorithm is not considered as comprehensive as manufacturers' service life calculators (e.g., MSA Cartridge Life Expectancy Calculator or 3M Service Life Software) that relate experimental and model-derived performance data to important variables. Therefore, greater uncertainty exists in results obtained from the interpolation algorithm for the 3M FR-

³ <http://webapps.msasafety.com/responseguide/ChemicalCalculator.aspx>

⁴ <http://webapps.msasafety.com/responseguide/>

⁵ <http://extra8.3m.com/SLSWeb/chemicalInformationSLife.html?page=serviceLife&disclaimerPageFlag=Y>

57 cartridge. For effective evaluation of service life, a robust service life calculator from the manufacturer should be available that is applicable to the relevant work environment.⁶

A comparison of the respirator cartridge inlet COPC concentrations was made against historical concentrations for each tank/exhauster to assess whether the cartridge testing bounded historic maximum concentrations. Sampling and analysis of 59 of the 61 COPCs was performed in the air purifying respirator cartridge testing.⁷ Most of the 59 COPCs evaluated either had maxima (historical and cartridge inlet) that were below 10% of the OEL or had maximum cartridge inlet concentrations that did not significantly exceed historical maxima. In particular, mercury, formaldehyde, NDMA, NDEA, and NMEA all had maximum cartridge-inlet concentrations that exceeded the historical maxima and were greater than 10% of the OEL. 2-Methylfuran and 2,5-dimethylfuran had cartridge inlet maxima that were >10% of the OEL but could not be compared with historical maxima because all the historical data were below the reporting limits.

Eight COPCs were found to have historical maximum concentrations that were either moderately higher than the cartridge-testing inlet concentrations, defined as $2\times$ – $5\times$ the cartridge inlet value, or significantly higher, defined as greater than $5\times$ the cartridge inlet value. The COPCs discussed below were identified as having relevant differences between cartridge inlet and maximum historic source concentrations. The maximum historic concentrations for all of these COPCs except N-nitrosomorpholine were from BY-108 headspace samples.

- Four COPCs—1,3-butadiene, 1-butanol, furan, and acetonitrile—had historic maxima more than $10\times$ higher than maximum inlet concentrations measured in these recent cartridge tests. Two other COPCs—2-heptylfuran and 2-fluoropropene—also were found to have historical maxima significantly higher than the maximum cartridge inlets. However, in both cases, the historical maxima were from 1994 BY-108 sampling and were either suspect data (2-heptylfuran) or represent a single high data point and COPC detection that has not been replicated in any subsequent sampling. Breakthrough was not observed for any of these six COPCs.
- The maximum 1,3-butadiene historical concentration was measured in BY-108 (338% of the OEL) and exceeded the maximum cartridge inlet concentration of ~4% of the OEL measured in the AP exhauster by a factor of approximately $80\times$. It should be noted that the highest butadiene concentration measured in 973 area samples was 12% of the OEL, higher than the maximum cartridge-inlet concentration.
- Historical maxima for furan and 1-butanol both come from 1994 BY-108 headspace measurements and are greater than $70\times$ the maximum cartridge inlet concentrations. However, in both cases, maxima from more recent measurements are substantially lower but still greater than cartridge inlets by factors ranging from $3\times$ to $6\times$.
- The maximum historic acetonitrile concentration was a recent measurement from BY-108 (94% of the OEL) and was approximately $30\times$ the maximum cartridge inlet concentration. Cartridge inlet and outlet measurements of acetonitrile have been variable, but generally <10% of the OEL with few

⁶ The 3M Service Life Software does allow for ammonia evaluation with specific 3M APR and PAPR cartridges other than the FR-57 cartridge used in Hanford testing. The 3M FR-57 cartridge used with the 3M Breathe Easy™ PAPR system was originally selected for cartridge testing in 2017 because it was being used at the Hanford site. As of spring 2020, this PAPR system and FR-57 cartridge are no longer available for Hanford tank farm use. 3M representatives indicated they have conducted ammonia service life testing on several PAPR cartridges and are in the process of adding their newer line of cartridges for the Versaflo™ TR-600 PAPR systems into their Service Life Software (E. W. Johnson, 3M, personal communication, May 8, 2020).

⁷ Sampling for two COPCs—nitrous oxide and dimethyl mercury—was not performed in the PAPR tests. The basis for exclusion of these COPCs is provided in Section 1.3.

exceptions. Historic source and area measurements of acetonitrile have also been highly variable, with no reported measurements exceeding the OEL.

- Two COPCs—ammonia and N-nitrosomorpholine—had historic maxima that were moderately higher (2×–5×) than their maximum cartridge inlet concentrations. Ammonia maximum historic concentrations from BY-108 (2576% of the OEL) are approximately 2× the maximum cartridge inlet concentration of 1213% of the OEL from SX-104 tests. The maximum historic N-nitrosomorpholine concentration (151% of the OEL) is approximately 3× the maximum cartridge inlet concentration (52% of the OEL), with both maxima coming from the AX exhauster. Of these two COPCs, breakthrough behavior has only been observed with ammonia, and testing results support use of the manufacturer’s service life methods for estimation of ammonia service life.

Additional testing or analysis may be warranted for specific COPCs where the cartridge test conditions may not have achieved an adequate performance basis. One option recommended for future testing is to include the ability to artificially elevate the concentrations of COPCs, such as furan, with historically higher concentrations so respirator cartridge performance can be assessed against concentrations that challenge the cartridge and more closely bound historic maximums. Alternatively, a recommendation to test tanks during waste-disturbing activities was implemented in 2017 for 702-AZ 2017 exhauster testing with air purifying respirator cartridges. Elevated concentrations for some COPCs were observed during that testing, thereby leading to better assessment of cartridge performance.

Revision History

Revision Number	Interim Change No.	Effective Date	Description of Change
0	0	July 2020	Initial issue for Release

Acronyms and Abbreviations

APR	air-purifying respirators
BBI	Best Basis Inventory
CAS	Chemical Abstracts Service
COPC	Chemical of Potential Concern
DBBP	dibutyl butylphosphonate
DL	detection limit
EPA	Environmental Protection Agency
GC	gas chromatography
HMS	Hanford Metrological Station
IH	Industrial Hygiene
MS	mass spectroscopy
NDEA	N-nitrosodiethylamine
NDMA	N-Nitrosodimethylamine
NIOSH	National Institute for Occupational Safety and Health
NMEA	N-nitrosomethylethylamine
OEL	Occupational Exposure Limit
OSHA	Occupational Safety and Health Administration
PAPR	powered air-purifying respirator
ppmv	parts per million on a volume basis (also shown as ppm in report)
RL	reporting limit
SureLife [®] calculator	Scott SureLife [®] Cartridge Calculator
SWIHD	Site-Wide Industrial Hygiene Database
TWINS	Tank Waste Information Network System
WRPS	Washington River Protection Solutions

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1.0 Overview of Respirator Cartridge Testing

Between 2017 and 2018, Washington River Protection Solutions conducted a series of tests using two types of chemical cartridges for use in powered air-purifying respirators (PAPR) at Hanford. The purpose of the testing was to determine the period of time that the cartridges would provide adequate performance for air-purifying respirators to protect workers when exposed to a mixture of Chemicals of Potential Concern (COPC) from vapors emanating from the headspace of tanks or exiting the exhausters from Hanford waste storage tanks. The Occupational Safety and Health Administration (OSHA) identifies cartridge testing as a valid approach for establishing cartridge service life. Testing is commonly applied in situations where mixtures of COPCs exist and where other approaches, such as manufacturer recommendations and modeling, are less reliable. The tests were designed and conducted to ensure measurement and/or control of the key variables OSHA identified as important to estimate cartridge service life, including temperature, humidity, COPC concentration, worker breathing rate, and cartridge adsorption capacity. Multipurpose high-efficiency PAPR cartridges, MSA OptiFilter TL⁸ (TL1) (MSA Safety Inc., Pittsburgh, Pennsylvania) and 3M FR-57⁹ (TL2) (3M Company, Maplewood, Minnesota), were assessed over 16-hour periods on separate days using vapor streams from three Hanford tank headspaces and two exhausters in separate tests. Both exhausters were sampled under static (i.e., non-waste-disturbing) conditions. The source vapors were fed to the PAPR cartridge test stand developed by Washington River Protection Solutions in collaboration with HiLine Engineering (Richland, Washington).

Table 1 identifies the 10 test conditions and starting times for each of the cartridges tested. Pacific Northwest National Laboratory was tasked with conducting an independent analysis of the analytical results and making recommendations based on the results for respiratory cartridge performance and breakthrough time. Breakthrough times from testing provide input data to Industrial Hygiene professionals to support respirator cartridge service life determinations.

Individual reports for tests conducted in each of the tank farms have been prepared and submitted to Washington River Protection Solutions. These reports provide detailed summaries of the test conditions, data analysis, and results for each individual test [1–4]. This report integrates the PAPR results from the 2017 and 2018 cartridge tests to provide a more comprehensive understanding of cartridge performance under the range of test conditions. This report includes results for three Hanford tanks (BY-108 2018, SX-101, and SX-104) and two Hanford tank farm exhausters (AP 2018 and AX).

⁸ MSA OptiFilter TL (Part number 10143421; Reorder Number 10080456) is a multipurpose PAPR respirator cartridge for use with the OptimAir[®] TL PAPR, with NIOSH approval for AM/CL/CD/FM/HC/HS/MA/SD/HE/HF application. <https://us.msasafety.com/Air-Purifying-Respirators-%28APR%29/Powered-Air-Purifying-Respirators-%28PAPR%29/OptimAir%C2%AE-TL-PAPR/p/000100003000001600>

⁹ 3M FR-57 (Part number 453-03-02R06) is a multipurpose PAPR respirator cartridge for use with the 3M RRPAS 6000 series facepieces or BE-10 series hood powered supplied air respirator systems, with National Institute of Occupational Safety and Health (NIOSH) approval for OV/SD/HC/CL/CK/HF/AM/MA/FM/HE applications. https://www.3m.com/3M/en_US/company-us/all-3m-products/~/3M-High-Efficiency-Cartridge-FR-57-453-03-02R06-6-EA-Case/?N=5002385+3294780228&rt=rud

Table 1. Summary of 2017 through 2018 PAPR Cartridge Testing

Tank Farm	Headspace or Exhauster		Cartridge Test Start Date and Time	
	Tank Headspace	Exhauster	MSA-TL (TL1)	3M FR-57 (TL2)
241-SX	241-SX-101		06/16/2017 11:23 AM	06/17/2017 11:07 AM
241-SX	241-SX-104		06/23/2017 10:52 AM	06/24/2017 10:17 AM
241-AX		AX Exhauster	08/25/2017 11:20 AM	08/26/2017 10:09 AM
241-BY	241-BY-108		02/23/2018 11:29 AM	02/24/2018 10:55 AM
241-AP		AP Exhauster	03/23/2018 12:16 AM	03/24/2018 10:12 AM

1.1 Use of Alternate Furan Measurements

Two sorbent tubes are currently used in both vapor source characterization and cartridge testing that support quantitation of the furans class of COPCs, which includes furan (Chemical Abstract Service number 110-00-9) and 13 other substituted furans. Prior to 2018, the preferred sorbent tube has been the Tenax TA TDU “Furans” tube, which uses a modified Environmental Protection Agency TO-17 method with gas chromatography (GC)/mass spectroscopy (MS) for quantitation of furan and eight of the 13 substituted furans COPCs. A separate sorbent tube, also used to measure furans, is the Carbotrap 300 TDU tube, analyzed with a modified TO-17 method with GC/MS for quantitation. An evaluation of furan methods was conducted (see details in Appendix F of Freeman et.al [19]) that recommended the use of the Carbotrap 300 TDU tube for its three calibrated furan COPCs: furan; 2,5-dihydrofuran; and 2-methylfuran. All analytical results from cartridge testing documented for these three furan COPCs in this report derive from the Carbotrap 300 TDU sampling. Historic measurements for these three furan COPCs also are derived from the Carbotrap 300 TDU sampling and analysis, as noted in Appendix C.

1.2 Comparison of Source Concentrations for Cartridge Testing and Historical Analysis

The measurements of 59 of 61 COPCs¹⁰ were the primary focus of the cartridge testing. The 61 COPCs shown in Table 2 represent a set of tank vapor chemicals that have been found in a tank farm source at or >10% of the relevant Occupational Exposure Limits (OEL),¹¹ or are considered “known” or “probable” carcinogens by the International Agency for Research Cancer or other regulatory agencies [5,6].

To fully assess respirator cartridge performance for COPC removal, historical headspace and exhauster data were reviewed to determine if the cartridge inlet concentrations were representative of typical source concentrations. Historical headspace and exhauster data from the Tank Waste Information Network System (TWINS) and the Site-Wide Industrial Hygiene Database (SWIHD) were used for this

¹⁰ In 2017, dimethylmercury and 2-propenal (acrolein) were added per Way, KJ, September 21, 2017 Letter, Tank Operations Contractor – Chemicals of Potential Concern Rev. 1, WRPS-1604188.1. Washington River Protection Solutions, Richland, Washington. Sampling for two COPCs—nitrous oxide and dimethyl mercury—was not performed in the PAPR tests. The basis for exclusion of these COPCs is provided in Section 1.3.

¹¹ OELs accepted for Hanford tank farm use are based on OELs established by a U.S. governmental agency or national professional organization (e.g., OSHA, NIOSH, American Conference of Governmental Industrial Hygienists), or if no U.S. OEL exists, standard toxicological practices are applied to develop OELs based on the best available science. The OEL for NDMA was established in 2005 based on the MAK (Maximale Arbeitsplatzkonzentration) Commission standard adopted in Europe.

assessment. Table 2 lists the historical maximum concentrations obtained from SWIHD and/or TWINS for the various headspace and exhauster sources, and the corresponding maximum respirator inlet concentrations. The five tank headspace or tank farm exhauster sources tested are summarized in Table 2 in groups representing tests involving individual tanks (almost all passively ventilated) and their corresponding headspace vapors, and tests involving actively ventilated tank farm exhauster slip streams vapors.

It is recognized that the data set of historical concentration maxima has limitations in terms of using it to determine if the tested cartridge inlet concentrations are high enough to include all potential release concentrations. Historical data are sparse; therefore, their maxima might be lower than actual maxima that existed but were not sampled. On the other hand, some of the historical maxima date back to the 1990s when concentrations could be expected to be higher. Ventilation flow rates, waste organic inventories, and sampling locations also could have changed between the time¹² of historical sampling and the time of cartridge testing. To the extent that historical records permitted, these features of the data have been considered for the comparisons that are made in subsequent sections.

Of the three tank headspace vapor tests, BY-108 2018 is presented separately in Table 2 from the remaining SX-101 and SX-104 headspace tests because the BY tank represents much higher concentrations of many COPCs and it had been included for testing as a higher bounding case for 2016 air-purifying respirator (APR) cartridge tests. The remaining columns in Table 2 address the two exhausters tests; 2018 AP exhauster and AX exhauster tests. More detailed historical information and analyses are provided in Appendices C and D for each of the individual tanks and tank farms.

In general, respirator cartridge inlet concentrations during testing were representative of historical headspace and exhauster concentrations. In some cases, conditions during an individual tank or exhauster tests were not representative of the highest historical concentrations in that specific tank farm, but another test (often BY-108 2018) provided a higher test concentration than observed in an individual test. For many COPCs, concentrations from the tested tanks and exhausters were historically much lower than the 50% of the OEL action level or 10% of the OEL threshold. In these cases, any differences between cartridge tests and historical maxima were not considered significant. All the PAPR cartridges were tested under non-waste-disturbing tank and tank farm exhauster conditions; therefore, care was taken in analyzing the historical analysis results to consider whether the tanks were sampled under similar conditions.

Most of the 61 COPCs evaluated either had maxima (historical and cartridge inlet) that were below 10% of the OEL or had maximum cartridge inlet concentrations that were not significantly exceeded by historical maxima. In particular, mercury, formaldehyde, N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), and N-nitrosomethylethylamine (NMEA) all had maximum cartridge-inlet concentrations that exceeded the historical maxima and were >10% of their OELs. 2-Methylfuran and 2,5-dimethylfuran had cartridge-inlet maxima that were >10% of their OELs but could not be compared with historical maxima because all the historical data were below the reporting limits.

¹² Headspace vapors are produced, in part from radiolytic-degradation of various tank waste constituents. The radiation dose and source concentration of key organic wastes was higher earlier in the waste storage timeline and may account for higher concentrations observed in some earlier sampling campaigns.

Table 2. Hanford Tank Vapor COPCs with Maximum Concentrations from Both the Historical Sampling and the FY 2017–2018 PAPR Cartridge Testing Data

COPC Number & Name	CAS Number	Occupational Exposure Limit (OEL)	Headspace Concentration, % of OEL (2018 BY-108)		Headspace Concentrations, % of OEL (SX-101, SX-104)		Exhauster Concentrations, % of OEL (2018 AP, AX)		
			Max. Historical ¹	Max. Cartridge Inlet	Max. Historical ¹	Max. Cartridge Inlet	Max. Historical ¹	Max. Cartridge Inlet	
Inorganic									
1	Ammonia	7664-41-7	25 ppm	2576	767	1572	1213	412	102
2	Nitrous Oxide	10024-97-2	50 ppm	1662 (4)	NM	35	NM	NM	NM
3	Mercury	7439-97-6	25 µg/m ³	68	27	32	26	<50 (32)	90
Hydrocarbons									
4	1,3-Butadiene	106-99-0	1 ppm	338	<4	29	<2	<1	4
5	Benzene	71-43-2	0.5 ppm	<11 (2)	0.5	0.8	0.5	<2	0.1
6	Biphenyl	92-52-4	0.2 ppm	<5	<0.03	<0.1	<0.3	<0.6	0.05
Alcohols									
7	1-Butanol	71-36-3	20 ppm	318 (22)	3*	0.6	0.4	0.2	0.02
8	Methanol	67-56-1	200 ppm	<0.8 (0.01)	0.6	NM	<1	NM	<1 (0.6)
Ketones									
9	2-Hexanone	591-78-6	5 ppm	0.9	0.3	0.2	0.4	<0.2	0.005
10	3-Methyl-2-butene-2-one	814-78-8	0.02 ppm	NM	n/a	NM	n/a	NM	n/a
11	4-Methyl-2-hexanone	105-42-0	0.5 ppm	<0.8 (0.4)	0.2	NM	0.1	<0.4	<0.02
12	6-Methyl-2-heptanone	928-68-7	8 ppm	NM	0.02	NM	n/a	NM	n/a
13	3-Buten-2-one	78-94-4	0.2 ppm	<29	4	5	1	<5 (2)	0.2
Aldehydes									
14	Formaldehyde	50-00-0	0.3 ppm	6	3	5	5	11	17
15	Acetaldehyde	75-07-0	25 ppm	11	0.5	0.9	0.6	0.5	0.3
16	Butanal	123-72-8	25 ppm	0.5	0.5	0.5	0.05	<0.04 (0.01)	0.004
17	2-Methyl-2-butenal	1115-11-3	0.03 ppm	NM	n/a	NM	n/a	NM	n/a
18	2-Ethyl-hex-2-enal	645-62-5	0.1 ppm	NM	n/a	NM	n/a	NM	n/a
New ²	2-Propenal	107-02-8	0.1 ppm	<11	<0.9	<0.9	<0.9	<12	<0.9
Furans and Substituted Furans									
19	Furan	110-00-9	1 ppb	54700 (1840)	576	<310 (143)	100	715	57
20	2,3-Dihydrofuran	1191-99-7	1 ppb	<47	<3	<34	7	<73	<8
21	2,5-Dihydrofuran	1708-29-8	1 ppb	<5660*	<24	<980	<53	<290	<25
22	2-Methylfuran	534-22-5	1 ppb	<4840*	17	<1800	<20	<247	<10 (7)
23	2,5-Dimethylfuran	625-86-5	1 ppb	<34	<3	<25	25	<53	<4
24	2-Ethyl-5-methylfuran	1703-52-2	1 ppb	NM	n/a	NM	n/a	NM	n/a
25	4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	1 ppb	NM	n/a	NM	n/a	NM	n/a
26	3-(1,1-Dimethylethyl)-2,3-dihydrofuran	34314-82-4	1 ppb	NM	n/a	NM	n/a	NM	n/a
27	2-Pentylfuran	3777-69-3	1 ppb	<24	<3	<17	7	<37	<3
28	2-Heptylfuran	3777-71-7	1 ppb	6120* (<20)	<3	<14	<3	<31	<3
29	2-Propylfuran	4229-91-8	1 ppb	<30	<2	<21	<3	<47	<3
30	2-Octylfuran	4179-38-8	1 ppb	NM	n/a	NM	n/a	NM	n/a
31	2-(3-Oxo-3-phenylprop-1-enyl)furan	717-21-5	1 ppb	NM	n/a	NM	n/a	NM	n/a
32	2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	1 ppb	NM	n/a	NM	n/a	NM	n/a
Phthalates									
33	Diethylphthalate	84-66-2	5 mg/m ³	<1	0.02	<0.02	<0.1 (0.04)	<0.1	0.02
Nitriles									
34	Acetonitrile	75-05-8	20 ppm	94	0.9	14	3	<5 (0.3)	0.4
35	Propanenitrile	107-12-0	6 ppm	<0.8 (0.5)	0.1	<0.08 (0.05)	0.08	<0.04	0.02
36	Butanenitrile	109-74-0	8 ppm	<0.7 (0.4)	0.2	<0.3 (0.08)	0.06	<0.04	0.01
37	Pentanenitrile	110-59-8	6 ppm	<0.8 (0.2)	0.04	<0.2	0.05	<0.04	0.003
38	Hexanenitrile	628-73-9	6 ppm	<0.7 (0.1)	0.03	<0.1 (0.02)	0.02	<0.03	<0.002
39	Heptanenitrile	629-08-3	6 ppm	NM	n/a	NM	n/a	NM	n/a
40	2-Methylene butanenitrile	1647-11-6	0.3 ppm	NM	n/a	NM	n/a	NM	n/a
41	2,4-Pentadienenitrile	1615-70-9	0.3 ppm	NM	n/a	NM	n/a	NM	n/a

Table 2. (continued)

COPC Number & Name	CAS Number	Occupational Exposure Limit (OEL)	Headspace Concentration, % of OEL [2018 BY-108]		Headspace Concentrations, % of OEL [SX-101, SX-104]		Exhauster Concentrations, % of OEL [2018 AP, AX]		
			Max. Historical ¹	Max. Cartridge Inlet	Max. Historical ¹	Max. Cartridge Inlet	Max. Historical ¹	Max. Cartridge Inlet	
Amines									
42	Ethylamine	75-04-7	5 ppm	<0.3	0.9	<0.7	0.3	<0.3 (0.2)	<0.09
Nitrosamines									
43	N-Nitrosodimethylamine	62-75-9	0.3 ppb	2063	721	9300	6935	5267	3130*
44	N-Nitrosodiethylamine	55-18-5	0.1 ppb	<1030 (8)	13	<37	79	<48 (17)	20
45	N-Nitrosomethylethylamine	10595-95-6	0.3 ppb	<413 (8)	188	<14	100	49	40
46	N-Nitrosomorpholine	59-89-2	0.6 ppb	<153 (8)	<2	<6	29	151	51
Organophosphates									
47	Tributyl phosphate	126-73-8	0.2 ppm	<3	<0.03	<0.06	<0.3	<0.3	<0.05
48	Dibutyl butylphosphonate	78-46-6	0.007 ppm	<91	<0.4	<1	<5	<10	<0.6
Halogenated Hydrocarbons									
49	Chlorinated Biphenyls	Varies	1 mg/m ³	NM	n/a	NM	n/a	NM	n/a
50	2-Fluoropropene	1184-60-7	0.1 ppm	530 (n/a)	n/a	<3	n/a	NM	n/a
Pyridines									
51	Pyridine	110-86-1	1 ppm	<5 (0.3)	0.2	0.2	0.1	<0.3	<0.05 (0.01)
52	2,4-Dimethylpyridine	108-47-4	0.5 ppm	<8 (0.8)	0.07	<0.4	<0.04	<0.4	<0.05
Organonitriles									
53	Methyl nitrite	624-91-9	0.1 ppm	NM	n/a	NM	n/a	NM	n/a
54	Butyl nitrite	544-16-1	0.1 ppm	NM	n/a	NM	n/a	NM	n/a
Organonitrates									
55	Butyl nitrate	928-45-0	2.5 ppm	NM	n/a	NM	0.02	NM	n/a
56	1,4-Butanediol, dinitrate	3457-91-8	0.05 ppm	NM	n/a	NM	n/a	NM	n/a
57	2-Nitro-2-methylpropane	594-70-7	0.3 ppm	NM	n/a	NM	2	NM	n/a
58	1,2,3-Propanetriol, 1,3-dinitrate	623-87-0	0.05 ppm	NM	n/a	NM	n/a	NM	n/a
Isocyanates									
59	Methyl Isocyanate	624-83-9	20 ppb	NM	n/a	NM	n/a	NM	n/a
Organometallics									
New ²	Dimethylmercury	593-74-8	0.010 mg/m ³ (as Hg)	NM	NM	NM	NM	3	NM

¹ ^c indicates the maximum is from a nonreport (<RL) analysis result, and reported (>RL) values for the COPC were not obtained or are less than 0.01% of the OEL. Value in parentheses, if present, indicates the maximum reported (detected) value >RL.

² 2-propenal and dimethylmercury were added to the COPC List in September, 2017.

* Suspect data due to sample quality issue discussed in Appendix C (e.g., low sample volume, more than one significant data quality flag, etc) Value in parentheses, (#), if present, indicates the maximum reported (detected) value >RL, or best estimate of true value.

italics Indicates that the historic concentration data is pre-2006 TWINS headspace results (often 1994-1997 data). Where more recent data are 10% or less of the 1990s maximum, the more recent maximum is included in parentheses without italics, using only the above-report maximum if available.

n/a Indicates that sampling and analysis have been performed but the analyte has not been detected above thresholds for reporting of tentatively identified compounds (TICs).

NM Not measured or not reported (cartridge inlet) or no measurement reported in databases (historic maximum).

Values highlighted in red indicate cartridge inlet concentrations that were significantly lower than the applicable historical maximum (<20% of historical). Values are highlighted only if 1) the historic maximum represented an above-report or above detect value, 2) either the cartridge or historical maximum was higher than tank farm action level of 50% of OEL, 3) the historic maximum was not bounded by another test inlet concentration, and 4) the historic maximum was measured during undisturbed tank headspace conditions for undisturbed cartridge tests, or measured during any tank conditions for disturbed cartridge tests.

Values highlighted in yellow indicate cartridge inlet concentrations that were lower than the applicable historical maximum (<50% but >20% of historical). Values are highlighted only if 1) the historic maximum represented an above-report or above detect value, 2) either the cartridge or historical maximum was higher than tank farm action level of 50% of OEL, 3) the historic maximum was not bounded by another test inlet concentration, and 4) the historic maximum was measured during undisturbed tank headspace conditions for undisturbed cartridge tests, or measured during any tank conditions for disturbed cartridge tests.

Only eight COPCs were found to have historical maximum concentrations that were either moderately higher (factors in the 2–10 range) or significantly higher (factor >10) than the cartridge-testing inlet concentrations. These COPCs are highlighted in Table 2 and listed below with the differences described. Comparisons are made to available area-sampling data for all tank farms between 2008 and 2018.¹³

- *Ammonia* – The maximum ammonia cartridge inlet concentration of 1213% of the OEL, which was measured in SX-104 under non-disturbed conditions, was slightly less than half of the historical maximum of 2576% of the OEL in the BY-108 headspace. For comparison, the highest ammonia concentration measured in more than 1500 area samples was ~1% of the OEL.
- *1,3-Butadiene* – The maximum butadiene cartridge inlet concentration, like the maximum historical concentration, was measured in BY-108 under non-disturbed conditions. The maximum historical and cartridge inlet concentrations were respectively 338% and <4% of the OEL, so the historical maximum concentration was less than 80× the highest cartridge inlet concentration. For comparison, the highest butadiene concentration measured in 973 area samples was 12% of the OEL.
- *1-Butanol* – The maximum butanol cartridge inlet concentration was in the 2018 AP tests, while the maximum historical concentration was measured in BY-108. Both were measured under non-disturbed conditions. The historical and cartridge inlet concentrations were respectively 318% and 4% of the OEL, so the historical maximum concentration was more than 70× the highest cartridge inlet concentration. For comparison, the highest 1-butanol concentration measured in 914 area samples was only 0.1% of the OEL.
- *Furan* – The maximum cartridge inlet furan concentration was 576% of the OEL, measured in the BY-108 2018 headspace. It was significantly lower than the historical maximum concentration of 54,700% of the OEL, which also was measured in the BY-108 headspace. The historical maximum concentration was more than 90× the highest cartridge inlet concentration. Out of 915 furan area samples, all were non-detects; therefore, no quantitative comparison to area samples can be made.
- *2-Heptylfuran* – The maximum 2-heptylfuran cartridge inlet concentration was less than ~3% of the OEL in all PAPR tests. The historical maximum concentration was 6120% of the OEL in the BY-108 headspace; however, this measurement is considered to have come from misidentification of the chemical. The next highest historical concentration from a cartridge-tested source was below the reporting limit of 31% of the OEL, and there were no above-report historical concentrations. The relation between the cartridge inlet and historical maxima is unclear. There are no area-sampling data for 2-heptylfuran.
- *Acetonitrile* – The maximum acetonitrile cartridge inlet concentration of 3% of the OEL was measured in the SX-104 headspace, while the maximum historical concentration of 94% of the OEL was measured in BY-108. The historical maximum concentration was more than 30× the highest cartridge inlet concentration. For comparison, the highest acetonitrile concentration measured in 1080 area samples was 24% of the OEL, and there were eight measurements that exceeded 3% of the OEL.
- *N-nitrosomorpholine* – The maximum cartridge inlet nitrosomorpholine concentration, from the AX exhauster, was 51% of the OEL. The historical maximum concentration was also measured in the AX exhauster and was 151% of the OEL, which is less than 3× the cartridge inlet maximum. Out

¹³ Area-sampling data typically represent time weighted average concentrations comparable to source and cartridge testing samples, but may not represent instantaneous or short duration concentrations, if present. In addition, area sampling represents only a portion of the data potentially available. WRPS industrial hygiene performs more extensive analysis on vapor concentrations in the breathing zone using additional data sets.

of approximately 1500 nitrosomorpholine area samples, all were non-detects; therefore, no quantitative comparison to area samples can be made.

- *2-Fluoropropene* – There were no measurable concentrations of 2-fluoropropene in cartridge-inlet data; it was consistently a tentatively identified compound. The maximum historical concentration was 530% of the OEL, in BY-108. However, the next highest historical concentration from a cartridge-tested source was below the reportable limit of 3% of the OEL, and there were no above-report historical concentrations. The relation between the cartridge inlet and historical maxima is unclear. There are no area-sampling data for 2-fluoropropene.

1.3 Summary of Cartridge-Testing Results

Table 3 includes the maximum inlet (source) and maximum cartridge outlet concentrations of all of the COPCs measured in the respirator cartridge tests. Because of testing and analytical limitations, measurements of nitrous oxide and dimethylmercury were not included in the tests. Nitrous oxide is not susceptible to respirator filtration, and there are no known respirator filtration cartridges approved by the NIOSH for nitrous oxide. Dimethyl mercury was not measured because it requires special sampling and analysis methods.

A total of 10 COPCs were detected in the cartridge inlets above 10% of their OELs and above their reporting limits (RL) or detection limits (DL) in any of the tests. Those COPCs that were observed at least once in the cartridge inlet at levels above the action level (50% of their OELs), and representing the breakthrough concerns, included furan, nitrosamines (NDMA, NMEA, NDEA, and N-nitrosomorpholine), ammonia, and mercury.

Time to breakthrough for any COPC was defined as the time from the onset of cartridge exposure to the tank vapors to the time at which the outlet cartridge concentration becomes >10% of the OEL.¹⁴ Sustained increases in cartridge outlet concentrations during testing also provided an indication of breakthrough behavior. Further discussion of the breakthrough criteria is provided in Appendix A. Table 3 identifies those COPCs that exhibited breakthrough behavior with an orange highlight.

Several of the PAPR cartridge tests indicated breakthrough of ammonia. In addition, for one source (SX-104), outlet concentrations of 2,5-dimethylfuran >10% of the OEL suggested potential breakthrough. However, the combination of low cartridge inlet concentrations and elevated blank and baseline concentrations makes the breakthrough observation suspect. Despite elevated inlet concentrations for mercury, furan, and all nitrosamines, there was no indication of breakthrough for any of these COPCs. The most complete analysis and discussion of the breakthrough data is provided in Chapter 2.0.

¹⁴ For COPCs with DL or RL values greater than 10% of the OELs, an alternate breakthrough criteria was applied. For example, furan and several substituted furans required use of 50% of the OEL criteria for breakthrough to distinguish between breakthrough and analytical scatter around the DL.

Table 3. Hanford Tank Vapor COPCs with Maximum Respirator Cartridge Inlet and Outlet Concentrations

COPC Number & Name	CAS Number	Occupational Exposure Limit (OEL)	Headspace Concentration, % of OEL (2018 BY-108)		Headspace Concentrations, % of OEL (SX-101, SX-104)		Exhauster Concentrations, % of OEL (2018 AP, AX)		
			Max. Cartridge Inlet ¹	Max. Cartridge Outlet	Max. Cartridge Inlet ¹	Max. Cartridge Outlet	Max. Cartridge Inlet ¹	Max. Cartridge Outlet	
Inorganic									
1	Ammonia	7664-41-7	25 ppm	767	718	1213	1163	102	57
2	Nitrous Oxide	10024-97-2	50 ppm	NM		NM		NM	
3	Mercury	7439-97-6	25 µg/m ³	27	<7	26	<8	90	<7
Hydrocarbons									
4	1,3-Butadiene	106-99-0	1 ppm	<4	<4	<2	<2	4	2
5	Benzene	71-43-2	0.5 ppm	0.5	0.2	0.5	0.07	0.1	0.1
6	Biphenyl	92-52-4	0.2 ppm	<0.03	<0.03	<0.3	0.09	0.05	0.05
Alcohols									
7	1-Butanol	71-36-3	20 ppm	3*	<0.004	0.4	0.02	0.02	<0.02 (0.01)
8	Methanol	67-56-1	200 ppm	0.6	0.3	<1	<1	<1 (0.6)	<1
Ketones									
9	2-Hexanone	591-78-6	5 ppm	0.3	<0.001	0.4	<0.003	0.005	<0.002
10	3-Methyl-3-butene-2-one	814-78-8	0.02 ppm	n/a		n/a		n/a	
11	4-Methyl-2-hexanone	105-42-0	0.5 ppm	0.2	<0.02	0.1	<0.03	<0.02	<0.02
12	6-Methyl-2-heptanone	928-68-7	8 ppm	0.02	n/a	n/a		n/a	
13	3-Buten-2-one	78-94-4	0.2 ppm	4	0.1	1	<0.2	0.2	<0.2 (0.08)
Aldehydes									
14	Formaldehyde	50-00-0	0.3 ppm	3	2	5	2	17	9
15	Acetaldehyde	75-07-0	25 ppm	0.5	0.3	0.6	0.4	0.3	0.5
16	Butanal	123-72-8	25 ppm	0.5	0.002	0.05	<0.001	0.004	<0.002 (0.001)
17	2-Methyl-2-butanal	1115-11-3	0.03 ppm	n/a		n/a		n/a	
18	2-Ethyl-hex-2-enal	645-62-5	0.1 ppm	n/a		n/a		n/a	
New ²	2-Propenal	107-02-8	0.1 ppm	<0.9	<1	<0.9	<0.9	<0.9	<1
Furans and Substituted Furans									
19	Furan	110-00-9	1 ppb	576	<14	100	<28	57	<40
20	2,3-Dihydrofuran	1191-99-7	1 ppb	<3	<3	7	4	<8	<8
21	2,5-Dihydrofuran	1708-29-8	1 ppb	<24	<24	<53	<53	<25	<26
22	2-Methylfuran	534-22-5	1 ppb	17	<9	<20	<21	<10 (7)	<11
23	2,5-Dimethylfuran	625-86-5	1 ppb	<3	<3	25	34* (<4)	<4	<4
24	2-Ethyl-5-methylfuran	1703-52-2	1 ppb	n/a		n/a		n/a	
25	4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	1 ppb	n/a		n/a		n/a	
26	3-(1,1-Dimethylethyl)-2,3-dihydrofuran	34314-82-4	1 ppb	n/a		n/a		n/a	
27	2-Pentylfuran	3777-69-3	1 ppb	<3	<3	7	5	<3	<3
28	2-Heptylfuran	3777-71-7	1 ppb	<3	<3	<3	<3	<3	3
29	2-Propylfuran	4229-91-8	1 ppb	<2	<2	<3	<3	<3	<3
30	2-Octylfuran	4179-38-8	1 ppb	n/a		n/a		n/a	
31	2-(3-Oxo-3-phenylprop-1-enyl)furan	717-21-5	1 ppb	n/a		n/a		n/a	
32	2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	1 ppb	n/a		n/a		n/a	
Phthalates									
33	Diethylphthalate	84-66-2	5 mg/m ³	0.02	0.01	<0.1 (0.04)	<0.04	0.02	<0.02
Nitriles									
34	Acetonitrile	75-05-8	20 ppm	0.9	3	3	3	0.4	4
35	Propanenitrile	107-12-0	6 ppm	0.1	<0.003	0.08	<0.006	0.02	<0.006
36	Butanenitrile	109-74-0	8 ppm	0.2	0.01	0.06	<0.003	0.01	0.002
37	Pentanenitrile	110-59-8	6 ppm	0.04	0.002	0.05	0.003	0.003	<0.003
38	Hexanenitrile	628-73-9	6 ppm	0.03	<0.001	0.02	<0.003	<0.002	<0.002
39	Heptanenitrile	629-08-3	6 ppm	n/a		n/a		n/a	
40	2-Methylene butanenitrile	1647-11-6	0.3 ppm	n/a		n/a		n/a	
41	2,4-Pentadienenitrile	1615-70-9	0.3 ppm	n/a		n/a		n/a	

Table 3. (continued)

COPC Number & Name	CAS Number	Occupational Exposure Limit (OEL)	Headspace Concentration, % of OEL (2018 BY-108)		Headspace Concentrations, % of OEL (SX-101, SX-104)		Exhauster Concentrations, % of OEL (2018 AP, AX)		
			Max. Cartridge Inlet ¹	Max. Cartridge Outlet	Max. Cartridge Inlet ¹	Max. Cartridge Outlet	Max. Cartridge Inlet ¹	Max. Cartridge Outlet	
Amines									
42	Ethylamine	75-04-7	5 ppm	0.9	0.6	0.3	<0.09	<0.09	<0.09
Nitrosamines									
43	N-Nitrosodimethylamine	62-75-9	0.3 ppb	721	<5	6935	<5	3130*	<7
44	N-Nitrosodiethylamine	55-18-5	0.1 ppb	13	<11	79	<12	20	<13
45	N-Nitrosomethylethylamine	10595-95-6	0.3 ppb	188	<4	100	<5	40	<5
46	N-Nitrosomorpholine	59-89-2	0.6 ppb	<2	<2	29	<2	51	<2
Organophosphates									
47	Tributyl phosphate	126-73-8	0.2 ppm	<0.03	<0.03	<0.3	<0.07	<0.05	<0.06
48	Dibutyl butylphosphonate	78-46-6	0.007 ppm	<0.4	<0.4	<5	<1	<0.6	<0.6
Halogenated Hydrocarbons									
49	Chlorinated Biphenyls	Varies	1 mg/m ³	n/a		n/a		n/a	
50	2-Fluoropropene	1184-60-7	0.1 ppm	n/a	n/a	n/a		n/a	
Pyridines									
51	Pyridine	110-86-1	1 ppm	0.2	<0.008 (0.007)	0.1	<0.04	<0.05 (0.01)	<0.04
52	2,4-Dimethylpyridine	108-47-4	0.5 ppm	0.07	<0.01	<0.04	<0.04	<0.05	<0.05
Organonitrites									
53	Methyl nitrite	624-91-9	0.1 ppm	n/a		n/a		n/a	
54	Butyl nitrite	544-16-1	0.1 ppm	n/a		n/a		n/a	
Organonitrates									
55	Butyl nitrate	928-45-0	2.5 ppm	n/a		0.02	n/a	n/a	
56	1,4-Butanediol, dinitrate	3457-91-8	0.05 ppm	n/a		n/a		n/a	
57	2-Nitro-2-methylpropane	594-70-7	0.3 ppm	n/a		2	n/a	n/a	
58	1,2,3-Propanetriol, 1,3-dinitrate	623-87-0	0.05 ppm	n/a		n/a		n/a	
Isocyanates									
59	Methyl isocyanate	624-83-9	20 ppb	n/a		n/a		n/a	
Organometallics									
New ²	Dimethylmercury	593-74-8	0.010 mg/m ³ (as Hg)	NM		NM		NM	
¹ "<" indicates the maximum is from a nonreport (<RL) analysis result, and reported (>RL) values for the COPC were not obtained or are less than 0.01% of the OEL. Value in parentheses, if present, indicates the maximum reported (detected) value >RL.									
² 2-propenal and dimethylmercury were added to the COPC List in September, 2017.									
[*] Suspect data due to sample quality issue discussed in Appendix C (e.g., low sample volume, more than one significant data quality flag, etc). Value in parentheses, (#), if present, indicates the maximum reported (detected) value >RL, or best estimate of true value.									
n/a Indicates that sampling and analysis have been performed but the analyte has not been detected above thresholds for reporting of tentatively identified compounds (TICs).									
NM Not measured or not reported.									
Obvious breakthrough above 10% of OEL observed, or suspected breakthrough behavior inferred based on sustained increases in cartridge outlet concentrations.									
Values highlighted in red indicate cartridge inlet concentrations that were significantly lower than the applicable historical maximum (<20% of historical). Values are highlighted only if 1) the historic maximum represented an above-report or above detect value, 2) either the cartridge or historical maximum was higher than tank farm action level of 50% of OEL, 3) the historic maximum was not bounded by another test inlet concentration, and 4) the historic maximum was measured during undisturbed tank headspace conditions for undisturbed cartridge tests, or measured during any tank conditions for disturbed cartridge tests.									
Values highlighted in yellow indicate cartridge inlet concentrations that were lower than the applicable historical maximum (<50% but >20% of historical). Values are highlighted only if 1) the historic maximum represented an above-report or above detect value, 2) either the cartridge or historical maximum was higher than tank farm action level of 50% of OEL, 3) the historic maximum was not bounded by another test inlet concentration, and 4) the historic maximum was measured during undisturbed tank headspace conditions for undisturbed cartridge tests, or measured during any tank conditions for disturbed cartridge tests.									

2.0 Analysis of Powered Air-Purifying Respirator Cartridge Breakthrough Data

2.1 PAPR Manufacturer Service Life Estimators

Estimations for the MSA-TL (TL1) cartridge are based on the Cartridge Life Expectancy Calculator¹⁵ from the MSA Response Guide;¹⁶ both references were used for calculations based on the web version available from August through September 2019. Manufacturer version information was not provided on the web pages. The running average concentration of the COPC (usually ammonia), the running average temperature, relative humidity up to the breakthrough point, and the available flow rate were used to calculate the service life without adding any safety factor. The formula used in the MSA cartridge calculator for ammonia does not incorporate the effects of temperature and humidity per manufacturer's clarification (see Appendix F).

The 3M Service Life Software¹⁷ does not allow for evaluation of ammonia with the FR-57 (TL2) cartridge despite NIOSH ammonia certification. 3M's engineering group recommended interpolation of the NIOSH testing certification results to predict cartridge service life. The effects of relative humidity and temperature were neglected in the 3M interpolation method. Although the 3M method is a conservative interpolation based on a minimum service life NIOSH requirement (25 minutes), the resulting service life estimates are not as comprehensive as manufacturers' service life calculators that relate experimental and model-derived performance data to important variables. Therefore, greater uncertainty exists in results obtained from the interpolation algorithm for the 3M FR-57 cartridge.

2.2 COPCs with Cartridge Breakthrough Signatures

COPCs determined to exhibit breakthrough behavior are identified in Table 3. Only two COPCs exhibited breakthrough with outlet concentrations that reached or became >10% of their corresponding OELs. These COPCs were ammonia and 2,5-dimethylfuran, both of which were identified in earlier reports for each of the individual tank/respirator cartridge analyses. Plots of the cartridge outlet concentrations versus time for both of these COPCs are shown in Figure 1. Formaldehyde exhibited evidence of breakthrough behavior but at outlet concentrations that were relatively low—all <10% of their corresponding OELs.

Further discussion of the COPC breakthroughs with outlet concentrations of 10% of the OELs are provided in the following sections. For these analyses, more precise estimates of the breakthrough times, at 10% of the OELs at cartridge outlets, were calculated by interpolating the data shown in Figure 1. This interpolation procedure is described in Appendix B.

¹⁵ <http://webapps.msasafety.com/responseguide/ChemicalCalculator.aspx>

¹⁶ <http://webapps.msasafety.com/responseguide/>

¹⁷ <http://extra8.3m.com/SLSWeb/chemicalInformationSLife.html?page=serviceLife&disclaimerPageFlag=Y>,

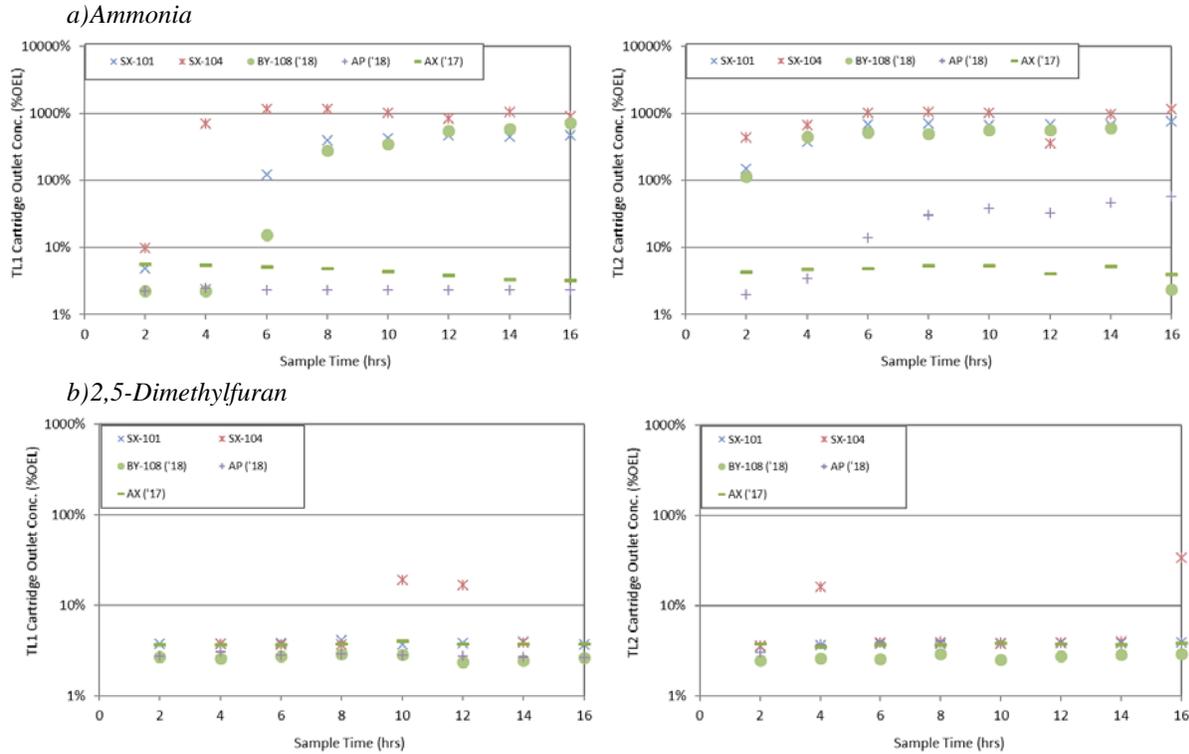


Figure 1. COPCs with Tank Vapor Cartridge Breakthroughs Corresponding to Outlet Concentrations >10% of Their OELs. PAPP cartridge MSA-TL (TL1) on the left and 3M FR-57 (TL2) on the right.

2.3 Ammonia

The ammonia breakthrough time versus inlet concentration are plotted in Figure 2. The black dashed curves in Figure 2 also show service life estimations as a function of inlet ammonia concentration using the MSA calculator and 3M estimation method. Apparent breakthrough of ammonia >10% of the OEL at the cartridge outlet was observed in less than 16 hours in the SX-101 tests, SX-104 tests, BY-108 tests, and the AP exhaustor 3M FR-57 (TL2) test. Breakthrough was not observed for either the two AX exhaustor tests or the AP exhaustor MSA-TL (TL1) cartridge test.

The MSA-TL cartridge had breakthrough times of 0 to 6 hours during the SX-101¹⁸ and SX-104 tests with the highest inlet concentrations¹⁹ of 628% and 1126% of the OEL, respectively. During the BY-108 test, the highest MSA-TL cartridge ammonia inlet concentration was 767% of the OEL, and breakthrough was observed between 4 and 6 hours. No breakthrough was observed during the AX exhaustor and AP exhaustor testing with highest inlet ammonia concentrations of 19% and 102% of the OEL, respectively.

¹⁸ Ammonia breakthrough appeared to occur in the SX-101 MSA-TL (TL1) cartridge above 10% of the OEL after 4 hours. However, the 4-hour sample concentration was unusual with a less-than-DL result.

¹⁹ Measured over each 16-hour test period.

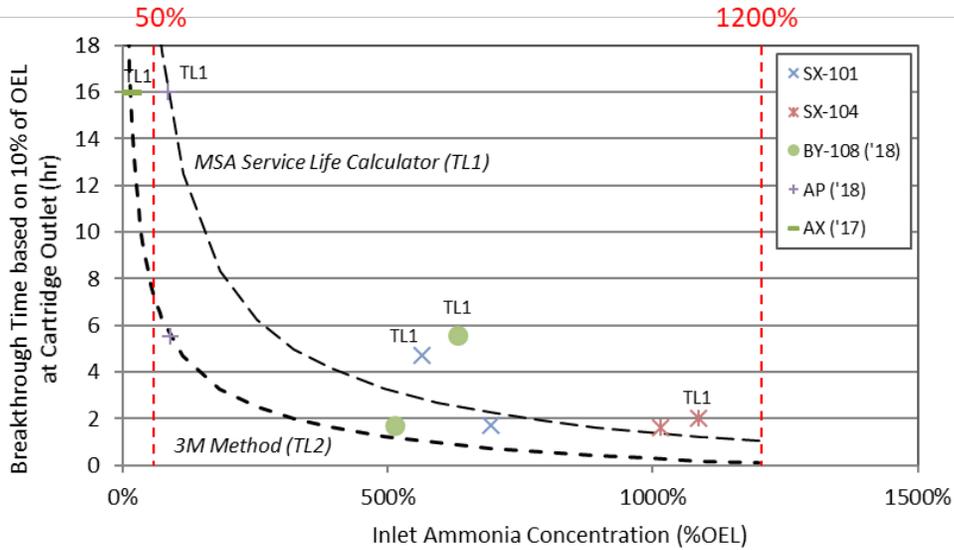


Figure 2. Ammonia Breakthrough Time at Different Inlet Concentrations for the PAPR Cartridge Tests, along with Results from MSA Cartridge Life Expectancy Calculator and 3M Estimation Method for Extreme Environmental Conditions. Breakthrough times of 16 hours or higher should be interpreted as greater than 16 hours. TL1 data points are labeled and all other data points are from TL2. Red dashed lines at 50% and 1200% of OEL mark the tank farm action level and upper bound concentration for PAPR use, respectively.

The 3M FR-57 (TL2) cartridge had the shortest breakthrough times, less than 2 hours, during the SX-101, SX-104, and BY-108 tests. These tests had some of the highest inlet concentrations—ranging from 686% to 1213% of the OEL. The 3M FR-57 cartridge had a breakthrough time of 4 to 6 hours during the AP exhaustor testing with inlet ammonia concentrations of 97% of the OEL. No breakthrough was observed during the AX exhaustor testing with inlet concentrations reaching a maximum of 17% of the OEL.

Ammonia breakthrough data also were compared with service life estimations from the MSA Cartridge Life Expectancy Calculator and 3M estimation method as mentioned in the beginning of this section. This comparison is shown in Figure 3. Here, the service life estimations using the MSA calculator and 3M interpolation algorithm are consistently near or below the measured breakthrough values. The MSA calculator estimates are consistent with and frequently conservative relative to test results and may be used as a reference by the Industrial Hygienist when estimating service life for the MSA PAPR cartridges. Estimated service lives of the 3M FR-57 (TL2) cartridges were also consistent or lower than test results. However, the 3M interpolation algorithm is not as comprehensive as manufacturers' calculators with potentially greater uncertainty in the results.

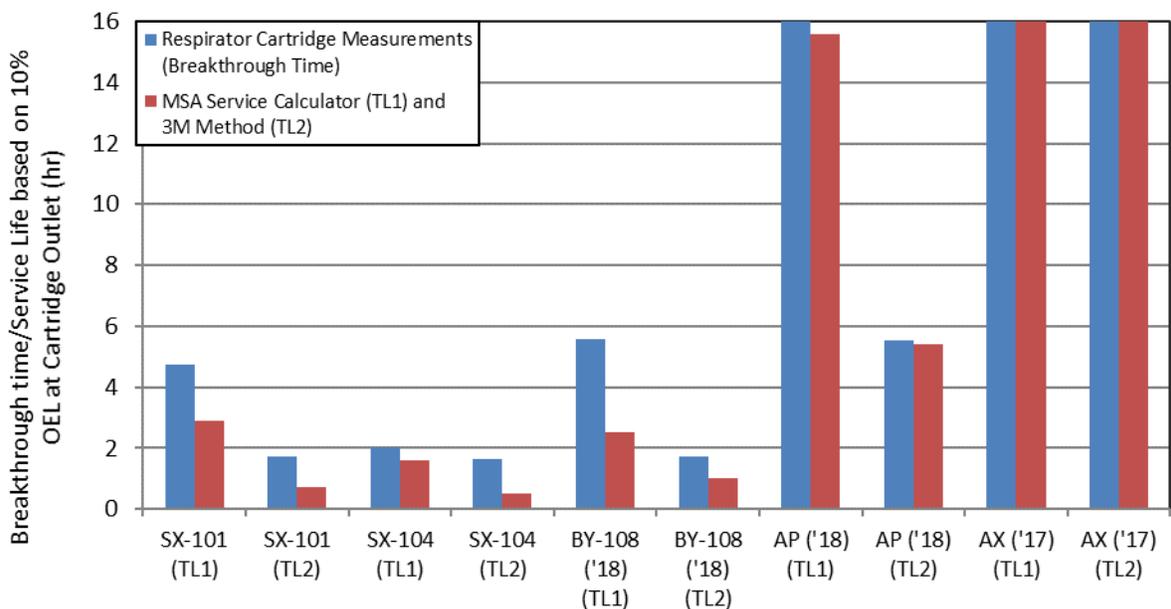


Figure 3. Comparison of Ammonia Breakthrough Time Estimates from Testing and Service Life from MSA’s Cartridge Life Expectancy Calculator and 3M Estimation Method (both based on 10% of the OEL at cartridge outlet). MSA-TL (TL1) and the 3M FR-57 (TL2) cartridges were used in the comparison.

2.4 2,5-Dimethylfuran

Breakthrough of 2,5-dimethylfuran was observed only in the SX-104 tests (see Figure 4). All inlet concentrations of 2,5-dimethylfuran for SX-104 with the MSA-TL (TL1) and 3M FR-57 (TL2) cartridges were less than the DL (approximately 4% of the OEL), except for a single inlet measurement for the 3M FR-57 cartridge of 25% of the OEL.²⁰ Despite low inlet concentrations for both cartridges, two outlet concentrations for each of the MSA-TL and 3M FR-57 cartridges measured >10% of the OEL and the RL (13.5% of OEL). The interpolated experimental breakthrough times of 9.2 and 3.4 hours are shown in Figure 4 for the MSA-TL and 3M FR-57 cartridges, respectively. However, several 2,5-dimethylfuran measurements from the blank and baseline sample tubes also reported concentrations greater than the RL, which puts the elevated inlet and outlet measurements for this COPC into question (see Appendix D). The single available historical measurement of the SX-104 headspace was less than the RL (25% of the OEL).

²⁰ The inlet 2,5-dimethylfuran concentration shown in Fig. 4 represents the average inlet concentration up to the point of observed breakthrough, which is lower than the maximum inlet measurement for the 3M FR-57 (TL2) cartridge.

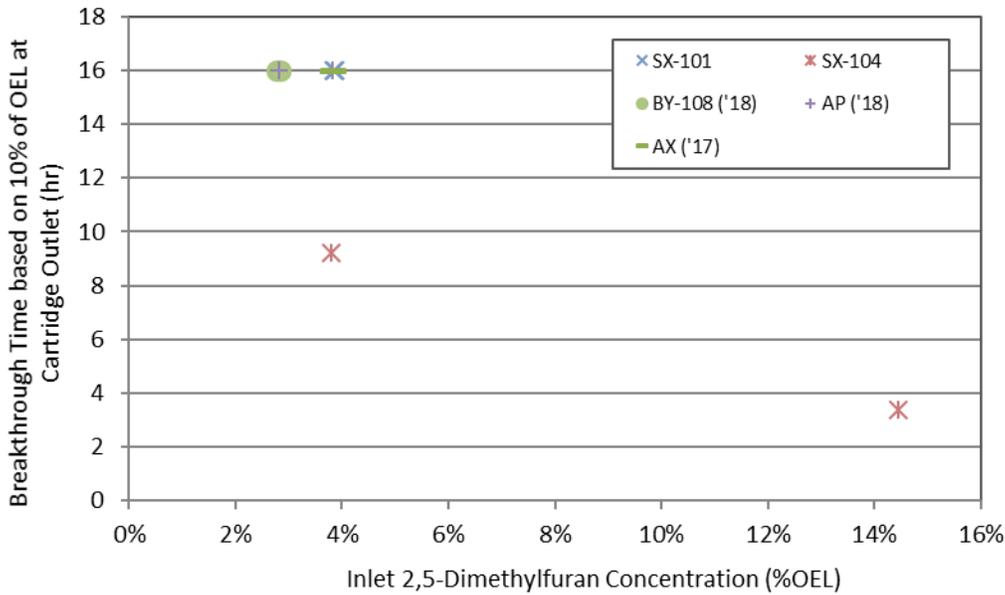


Figure 4. 2,5-dimethylfuran Breakthrough Data for Respirator Cartridge Tests. Breakthrough times of 16 hours or higher should be interpreted as greater than 16 hours.

2.5 Lower Concentration COPCs with Potential Breakthrough Signatures

One of the COPCs, formaldehyde, did not have outlet concentrations that were >10% of its OEL but still exhibited signatures that would indicate potential breakthrough if inlet concentrations were to increase. The outlet concentration data were plotted against the corresponding inlet concentrations for formaldehyde as shown in Figure 5. The results show that outlet concentrations appear to increase with corresponding increased inlet concentrations, especially for the 3M FR-57 (TL2) cartridge, which indicates limited retention of formaldehyde. Therefore, if the inlet concentrations were to exceed 20% of the OELs, it appears PAPR cartridge breakthrough could occur.

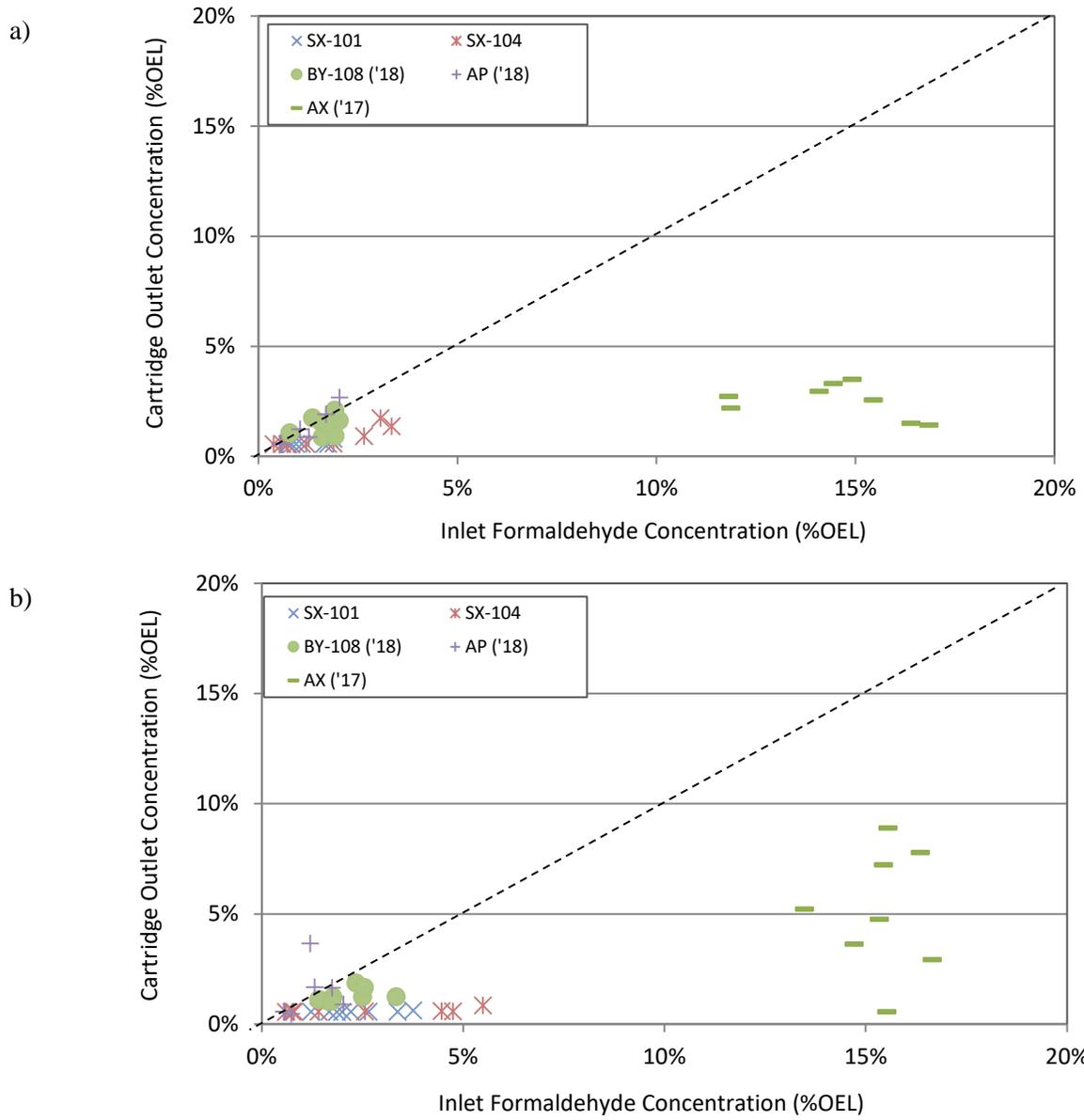


Figure 5. Plots of Outlet Concentrations versus Inlet Concentrations for Formaldehyde for Cartridge Tests with a) MSA-TL (TL1) and b) 3M FR-57 (TL2).

3.0 Cartridge Performance Outside of Tested Ranges

The conditions represented in the multiple tank tests span a range of compositions and environmental conditions. The important factors for respirator cartridge performance and the extent to which testing assessed the known ranges of those factors are discussed in this chapter.

3.1 Factors that Can Impact Cartridge Performance

Mathematical relationships are often used to estimate breakthrough time for adsorption systems [7-9]. These relationships include the Dubinin-Klotz equation [10] and the Wheeler-Jonas equation [10,11]. The Wheeler-Jonas equation is used by OSHA in the Gerry O. Wood Mathematical Model and many respirator cartridge manufacturers for respirator cartridge modeling [11]. A typical form of the Wheeler-Jonas equation is shown below:

$$t_b = \frac{W_e W}{C_o Q} - \frac{W_e \rho_B}{k_v C_o} \ln \left(\frac{C_o - C}{C} \right)$$

where t_b (minutes) is the breakthrough time; W (g) is the weight of activated carbon; ρ_B (g/cm³) is the packed density in the cartridge; C_o (g/cm³) is the inlet vapor concentration; C (g/cm³) is the breakthrough concentration; Q (cm³/min) is the flow rate; k_v (minutes⁻¹) is the adsorption rate coefficient; and W_e (g/g carbon) is the adsorption capacity at C_o [12]. Other factors such as relative humidity, temperature, and competitive adsorption can affect these parameters. Also, this model depends on the Dublin-Radushkevich isotherm equation, which is not thermodynamically consistent in the Henry's law regions; that is, the Dublin-Radushkevich equation does not reduce to Henry's law when vapor concentrations are very low, such as in sub-ppb levels [16]. Therefore, errors can result when using the Wheeler-Jonas equation to predict breakthrough times in these regions.

Note that the Polanyi Adsorption Theory [13] and the Ideal Adsorbed Solution Theory [14] are the two most common equations used to describe multicomponent adsorption, especially binary adsorption. Both of these theories predict that previously adsorbed vapor molecules will be displaced by more strongly adsorbed vapor molecules. The adsorption rate coefficients also will be affected by competitive adsorption. Wood [15] reported that the correction factors of the adsorption rate coefficient for second eluting vapors averaged 85% and those for third and fourth eluting vapors averaged 56%. The contribution of the adsorption rate coefficient to breakthrough time is usually much smaller compared with the effect of equilibrium adsorption capacity.

Table 4 shows a summary of factors that can impact breakthrough times for respirator cartridges, based on published theoretical and empirical relationships. Here, the factors are grouped into cartridge design factors, which are unique to the respirator cartridge being tested; vapor or gas factors, which are related to the specific compositions of the streams being measured; and environmental factors, which are relevant to the testing conditions, but can change with atmospheric conditions.

Table 4. Factors that Can Impact Breakthrough Time of Chemical Vapor Adsorption on Respirator Cartridges (see Appendix E for details)

Factors	Typical Impact on Breakthrough Time
<i>Cartridge Design Factors</i>	
Micropore volume	Larger micropore volumes will typically lead to higher adsorption capacities and longer breakthrough times.
Packed density	Larger packed density will typically increase the breakthrough time for a fixed volume.
Granule size	Smaller particles will typically increase adsorption rate and increase breakthrough time when pressure drop is acceptable.
Flowrate of vapor or gas stream through cartridge	Higher flow rates will reduce the breakthrough times.
<i>Vapor or Gas Factors</i>	
Molecular weight of vapor or gas constituent	Heavier molecules tend to have higher affinity adsorption and have longer breakthrough times.
Inlet concentration of vapor or gas constituent	Higher inlet concentrations typically lead to shorter breakthrough times.
Competitive adsorption from other vapor or gas constituents	In mixtures, molecules with lower adsorption affinities will have reduced breakthrough times comparatively.
<i>Environmental Factors^a</i>	
Relative humidity of vapor or gas stream	Higher relative humidity levels will typically increase breakthrough times for hydrophilic molecules (those able to hydrogen bond with water) and decrease breakthrough times for non-polar molecules.
Temperature of vapor or gas stream	Higher temperatures will generally decrease equilibrium adsorption capacities and reduce the breakthrough times.
Pressure of vapor or gas stream	Pressure drops will lead to underestimation of the concentrations of target chemicals. If not corrected, calculated breakthrough times will be overestimated.

^a See Appendix E for details on Environmental Factors.

3.2 Sensitivity Analysis

A sensitivity analysis of cartridge performance was conducted on the factors identified in Table 4 as in the multitank APR summary report [16]. The MSA Response Guide Cartridge Life Expectancy Calculator and the TL PAPR cartridge from MSA were used for this analysis. Relative humidity, temperature, and inlet concentration were the three variables assessed. Only five of the tank vapor COPCs—ammonia, pyridine, acetonitrile, 1-butanol, and acetaldehyde—could be assessed using the MSA calculator. One chemical is evaluated at a time using the MSA calculator, and this also applies when the service life was estimated for the MSA PAPR cartridge on ammonia (Figure 3). More details about using the manufacture’s calculators to estimate the service life of the selected cartridge are provided in Appendix F.

The analysis involved calculating relative cartridge service lives (relative to a reference point, 500% OEL inlet concentration, 77°F, 50% relative humidity, and 102.5 L/min flow rate) for ranges of each factor. In each sensitivity analysis, only the targeted factor is varied, with the other factors fixed. Cartridge service life means the period of time that a filter or sorbent in a specified respirator or other respiratory equipment provides adequate protection to the wearer. No safety factor was applied in the MSA calculator to

estimate the service life of the cartridge. More information about the relationship and difference between cartridge service life and breakthrough time is provided in Appendix A, Section A.5. Figure 6 shows plots of the resulting sensitivity analysis for each of the four factors assessed.

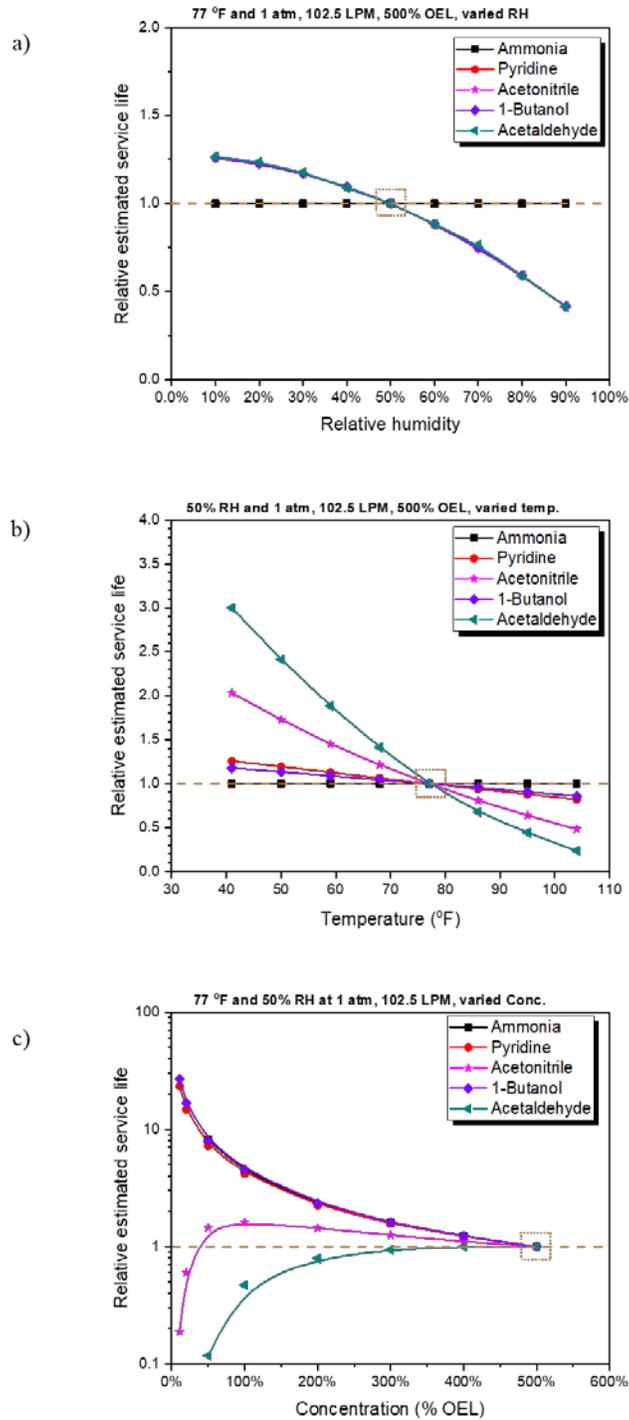


Figure 6. Sensitivity Plots for Variables that Affect Cartridge Performance. Data in these plots were obtained from the MSA Response Guide Cartridge Life Expectancy Calculator for an MSA-TL respirator cartridge.

3.2.1 Impact of Relative Humidity

Figure 6a shows predicted cartridge performance as a function of relative humidity. In general, service life decreases with increasing relative humidity for most constituents, except for polar chemical species such as ammonia, that have strong interactions with water. However, the results in Figure 6a suggest that the service life of the cartridge for ammonia adsorption is not sensitive at all to relative humidity. According to MSA, the formula used for ammonia specifically on the MSA cartridge calculator does not incorporate the effects of temperature, relative humidity, or breathing rate (see Appendix F).

The relative humidity data recorded for the cartridge tests ranged between 35 and 91%.²¹ Unlike the strong correlations between meteorological temperatures and testing temperatures, the analysis provided in Appendix E showed only a weak relationship between atmospheric humidity data and the cartridge testing humidity measurements. This is likely due to the influence of the humidity from the tank itself. However, the meteorological data should more closely represent the humidity conditions in the breathing zones for workers.

The meteorological relative humidity range during the cartridge tests ranged from 10% to 90%. The meteorological relative humidity range for calendar year 2017 ranged from 6% to 100%. Based on the breakthrough sensitivities shown in Figure 6a lower humidity values should result in higher breakthrough times compared to those tested, which should be a conservative effect on the cartridge breakthrough times measured.

Year-round meteorological data provided in Appendix E show slightly higher relative humidity levels than the ranges tested. Ammonia was predicted to have equivalent breakthrough times at the higher relative humidity conditions. However, the breakthrough times for the other (non-polar) constituents are predicted to significantly decrease, such that conditions at relative humidity levels greater than 84% should be deemed as uncertain with respect to cartridge performance until further testing can be conducted at the higher humidity levels.

3.2.2 Impact of Temperature

Figure 6b shows a consistent decrease in relative breakthrough times with increasing temperatures, which is consistent with theoretical understanding.

Temperatures recorded for the cartridge tests ranged between 36 and 103°F.²² Appendix E shows meteorological data including the points in time when cartridge testing occurred. The meteorological temperature range during cartridge testing was from 20 to 90°F. During 2017, temperatures from the whole year ranged from -7 to 106°F. For several of the constituents is shown in Figure 6b, the potential impact of reduced breakthrough times with historically higher temperatures (106°F versus 94°F) could be significant, such that cartridge use should not be inferred at temperatures greater than 94°F. Correspondingly, based on the sensitivity data shown in Figure 6b, it is expected that lower temperature conditions should result in longer breakthrough times, meaning that the conditions tested should represent conservative cartridge performance compared to the temperature ranges tested.

²¹ MSA TL1 cartridge tests ranged from 36% to 84% relative humidity. The 3M FR-57 TL2 cartridge tests ranged from 35% to 91% relative humidity. Relative humidity for the test periods are calculated from the average of the relative humidity measured at the start and end of each test.

²² Temperatures for the MSA TL cartridge tests ranged from 36 to 100°F. Temperatures for the 3M FR-57 TL2 cartridge tests ranged from 52 to 103°F. Temperatures for the test periods are calculated from the average of the temperatures measured at the start and end of each test.

3.2.3 Impact of Inlet Concentration

Figure 6c shows a consistent decrease in relative cartridge performance with increasing COPC inlet concentrations. Acetaldehyde and acetonitrile show an opposite effect. A similar trend was observed for acetaldehyde using the SCOTT (3M) SureLife calculator for an APR application.[16] Based on the Wheeler-Jonas equation shown earlier, this uncommon opposite concentration effect can be observed when the ratio of the adsorption capacity (W_e) to the inlet concentration (C_o) increases as the inlet concentration increases. Based on a conversation with a 3M engineer, this phenomenon can be explained by the competitive adsorption from water moisture in air for organic vapors [15]. More importantly, the competition of water loading is more severe when the chemical concentration is low as in the tank vapor field test. Water molecules will replace acetaldehyde molecules easier at lower concentrations than at higher concentration due to the adsorption isotherm trend²³ of acetaldehyde on activated carbon [17]. This will lead to a shorter stoichiometric time (i.e., the time when the outlet concentration equals the inlet concentration) and cause a shorter breakthrough time (i.e., when the outlet concentration reaches the permissible concentration) at a lower concentration. Because source concentrations were used to challenge the respirator cartridges, this should indicate conservatively low breakthrough times compared to actual tank farm breathing space conditions. See Appendix A, Section A.2, for additional discussion of differences in typical tank farm source and area concentrations.

²³ Figure 2 of reference 17.

4.0 Conclusions and Recommendations

Between 2017 and 2018, 10 PAPR cartridge tests were performed on headspace vapors from three Hanford tanks (BY-108, SX-101, and SX-104) and two Hanford tank farm exhausters (AP and AX). All tests were conducted under static conditions absent waste-disturbing activities in the subject tanks or tank farms. Multipurpose high-efficiency PAPR cartridges, MSA-TL (TL1) (MSA Safety Inc., Pittsburgh, Pennsylvania) and 3M FR-57 (TL2) (3M Company, Maplewood, Minnesota), were tested on each of the five tanks or exhausters. Out of 61²⁴ COPCs, only ammonia and 2,5-dimethylfuran exhibited breakthrough with outlet concentrations that were >10% of their OELs. For 2,5-dimethylfuran, elevated concentrations found in blank tube samples put the elevated outlet measurements for this COPC into question. Further details and recommendations based on each of these breakthrough signatures are provided below:

- Ammonia exhibited breakthrough²⁵ for 7 of the 10 cartridge tests. Breakthrough was not observed for either PAPR cartridge in the AX exhauster tests or for the MSA-TL (TL1) cartridge in the AP exhauster test. Breakthrough between 0 and 6 hours was observed with the MSA-TL (TL1) cartridge in the SX-101 and SX-104 testing where inlet concentrations were 628% and 1126% of the OEL, respectively. Breakthrough in the BY-108 2018 MSA-TL (TL1) test occurred between 4 and 6 hours with a maximum ammonia inlet concentration of 767% of the OEL. Much lower maximum inlet concentrations of 19% and 102% of the OEL were observed in the AX and AP 2018 exhauster testing, respectively, where no indication of breakthrough was observed.

The 3M FR-57 (TL2) cartridge had the shortest breakthrough times for ammonia, less than 2 hours, during the SX-101, SX-104, and BY-108 tests. These tests had the highest maximum inlet concentrations for the 3M cartridge (>586% of the OEL). Breakthrough was observed between 4 and 6 hours during the AP exhauster testing with inlet concentrations at 97% of the OEL. No breakthrough was observed at inlet concentrations of 17% of the OEL during the AX exhauster testing. For both the MSA and 3M PAPR cartridges in each of the tank/cartridge tests, ammonia breakthrough preceded all other breakthrough observations, indicating that it is a leading candidate for defining the minimum breakthrough times for PAPR cartridges.

- Breakthrough of 2,5-dimethylfuran was observed only in the SX-104 tests. All inlet concentrations of 2,5-dimethylfuran for SX-104 with the MSA-TL (TL1) and 3M FR-57 (TL2) cartridges were less than the DL (approximately 4% of the OEL), except for a single inlet measurement for the 3M FR-57 cartridge of 25% of the OEL. Despite low inlet concentrations for both cartridges, two outlet measurements for each of the MSA-TL and 3M FR-57 cartridges were >10% of the OEL and the RL (13.5% of OEL). Breakthrough times between 8 and 10 hours and between 2 and 4 hours were observed for the MSA-TL and 3M FR-57 cartridges, respectively. However, several 2,5-dimethylfuran measurements from the blank and baseline sample tubes also reported concentrations greater than the RL. The combination of low cartridge inlet concentrations and elevated blank and baseline concentrations makes the breakthrough observation suspect. The single available historical measurement of the SX-104 headspace was less than the RL (25% of the OEL).

²⁴ Way, KJ, September 21, 2017 Letter, Tank Operations Contractor – Chemicals of Potential Concern Rev. 1, WRPS-1604188.1. Washington River Protection Solutions, Richland, Washington.

²⁵ Breakthrough is defined as measuring outlet concentrations that were >10% of their Hanford OEL established in WRPS-1604188.1 or RPP-22491 Rev. 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. http://www.hanford.gov/tocpmm/files.cfm/IHTechBasis_RPP-22491Rev1.pdf).

Eight additional COPCs—mercury, formaldehyde, furan, 2-methylfuran, NDMA, NDEA, NMEA, and N-nitrosomorpholine—had inlet concentrations >10% of the OEL in one or more of the 10 PAPR cartridge tests, but with no indication of breakthrough above 10% of their OELs or DLs in the cartridge outlets.

- Maximum mercury inlet concentrations for the PAPR cartridges ranged from 26% to 90% of the OEL, with maximum outlet concentrations all below the RL (<8% of the OEL), despite the fact neither the MSA-TL or 3M FR-57 cartridges are rated for mercury removal.
- The maximum formaldehyde inlet concentrations ranged from 3% to 17% of the OEL, with maximum outlet concentrations ranging from 2% to 9% of the OEL. The highest outlet readings were observed with the 3M FR-57 cartridge tested on the AX exhaustor; however, no breakthrough above 10% of the OEL was observed.
- Furan maximum inlet concentrations ranged from 57% to 576% of the OEL. Maximum outlet concentrations were all below the DL (<14% to <40% of the OEL); therefore, there was no indication of furan breakthrough for either cartridge for the conditions tested.
- Inlet concentrations of 2-methylfuran were measured above 10% of the OEL only during the BY-108 tests, during which a maximum inlet concentration of ~17% of the OEL was observed. All measured outlet concentrations were less than the analytical DL (between 9% and 21% of the OEL), indicating no breakthrough for either cartridge.
- No breakthroughs were observed for any of the nitrosamine COPCs during PAPR cartridge testing. NDMA inlet concentrations ranged from 63% to 6935% of the OEL with the highest concentration observed in SX-104, followed by SX-101 at 3358%. NDEA inlet concentrations ranged from 13%–79% of the OEL with the highest concentrations observed in SX-104. NMEA inlet concentrations ranged from 5% to 188% of the OEL with the highest concentration observed in BY-108 test. N-nitrosomorpholine inlet concentrations ranged from 1% to 51% of the OEL, with the highest concentrations observed in the AX exhaustor. All outlet concentrations of the four nitrosamine COPCs were below the RL (<2%–<13%).

Estimations for the MSA-TL PAPR cartridge are based on the Cartridge Life Expectancy Calculator²⁶ from the MSA Response Guide²⁷. Service life results obtained from the Cartridge Life Expectancy Calculator were near or below the measured breakthrough values for each of the MSA-TL cartridge tests. This indicates that the manufacturer's estimator is consistent with and frequently conservative for ammonia and may be used as a reference by Industrial Hygienists in future service life estimations.

The 3M Service Life Software²⁸ does not allow for evaluation of ammonia with the FR-57 (TL2) cartridge despite NIOSH ammonia certification. 3M recommended the interpolation of the NIOSH testing certification results for estimation of a lower limit on the cartridge service life using a simple algorithm as shown in Appendix F. Data obtained from interpolating the NIOSH testing certification results were consistently near or below the measured breakthrough values. However, this interpolation algorithm is not considered as comprehensive as manufacturers' service life calculators (e.g., MSA Cartridge Life Expectancy Calculator or 3M Service Life Software) that relate experimental and model-derived performance data to important variables. Therefore, greater uncertainty exists in results obtained from the interpolation algorithm for the 3M FR-57 cartridge. For effective evaluation of service life, a robust service life calculator from the manufacturer should be available that is applicable to the relevant work

²⁶ <http://webapps.msasafety.com/responseguide/ChemicalCalculator.aspx>

²⁷ <http://webapps.msasafety.com/responseguide/>

²⁸ <http://extra8.3m.com/SLSWeb/chemicalInformationSLife.html?page=serviceLife&disclaimerPageFlag=Y>

environment.²⁹ A comparison of the respirator cartridge inlet COPC concentrations was made against historical concentrations for each tank/exhauster to assess whether the cartridge testing bounded historic maximum concentrations. Sampling and analysis of 59 of the 61 COPCs was performed during PAPR cartridge testing.³⁰ Most of the 59 COPCs evaluated either had maxima (historical and cartridge inlet) that were <10% of the OEL or had maximum cartridge inlet concentrations that were not significantly exceeded by historical maxima. In particular, mercury, formaldehyde, NDMA, NDEA, and NMEA had maximum cartridge-inlet concentrations that exceeded the historical maxima and were >10% of their OELs. 2-Methylfuran and 2,5-dimethylfuran had cartridge-inlet maxima that were >10% of their OELs but could not be compared with historical maxima because all the historical data were below the RLs.

Eight COPCs were found to have historical maximum concentrations that were either moderately higher than the cartridge-testing inlet concentrations, defined as 2×–5× the cartridge inlet value, or significantly higher, defined as greater than 5× the cartridge inlet value. The COPCs discussed below were identified as having relevant differences between cartridge inlet and maximum historic source concentrations. The maximum historic concentrations for these COPCs except N-nitrosomorpholine were from BY-108 headspace samples.

- Four COPCs—1,3-butadiene, 1-butanol, furan, and acetonitrile—had historic maximum concentrations that were more than 10× higher than maximum inlet concentrations measured in these recent cartridge tests. Two other COPCs—2-heptylfuran and 2-fluoropropene—also were found to have historical maximum concentrations that were significantly higher than the maximum cartridge inlet concentrations. However, in both cases the historical maximum concentrations were from 1994 BY-108 sampling and were either suspect data (2-heptylfuran) or a single high data point and COPC detection that has not been replicated in any subsequent sampling. Breakthrough was not observed for any of these six COPCs.
- The maximum 1,3-butadiene historical concentration was measured in BY-108 2018 (338% of the OEL) and exceeded the maximum cartridge inlet concentration of ~4% of the OEL measured in the AP exhauster by a factor of approximately 80×. It should be noted that the highest butadiene concentration measured in 973 area samples was 12% of the OEL, higher than the maximum cartridge-inlet concentration.
- Historical maxima for furan and 1-butanol both come from 1994 BY-108 headspace measurements and are more than 70× the maximum cartridge inlet concentrations. However, in both cases, maximum concentrations from more recent measurements are substantially lower but still greater than cartridge inlets by factors ranging from 3×–6×.
- The maximum historic acetonitrile concentration was a recent measurement from BY-108 (94% of the OEL) and was approximately 30× the maximum cartridge inlet concentration. Cartridge inlet and outlet measurements of acetonitrile have been variable, but generally <10% of the OEL with few exceptions. Historic source and area measurements of acetonitrile have also been highly variable, with no reported measurements exceeding the OEL.

²⁹ The 3M Service Life Software does allow for ammonia evaluation with specific 3M APR and PAPR cartridges other than the FR-57 cartridge used in Hanford testing. The 3M FR-57 cartridge used with the 3M Breathe Easy™ PAPR system was originally selected for cartridge testing in 2017 because it was being used at the Hanford site. As of spring 2020, this PAPR system and FR-57 cartridge are no longer available for Hanford tank farm use. 3M representatives indicate they have conducted ammonia service life testing on several PAPR cartridges and are adding their newer line of cartridges for the Versaflo™ TR-600 PAPR system into their Service Life Software (E. W. Johnson, 3M, personal communication, May 8, 2020).

³⁰ Sampling for two COPCs—nitrous oxide and dimethyl mercury—was not performed in the PAPR tests. The basis for exclusion of these COPCs is provided in Section 1.3.

- Two COPCs—ammonia and N-nitrosomorpholine—had historic maxima that were moderately higher (2×–5×) than their maximum cartridge inlet concentrations. Ammonia maximum historic concentrations from BY-108 (2576% of the OEL) are approximately 2× the maximum cartridge inlet concentration of 1213% of the OEL from SX-104 tests. The maximum historic N-nitrosomorpholine concentration (151% of the OEL) is approximately 3× the maximum cartridge inlet concentration (52% of the OEL), with both maximum concentrations coming from the AX exhauster. Of these two COPCs, breakthrough behavior has only been observed with ammonia, and testing results support the use of the manufacturer’s service life methods for estimation of ammonia service life.

Additional testing or analysis may be warranted for specific COPCs where the cartridge test conditions may not have achieved an adequate performance basis. One option recommended for future testing is to include the ability to artificially elevate the concentrations of COPCs, such as furan, with historically higher concentrations so respirator cartridge performance can be assessed against concentrations that challenge the cartridge and more closely bound historic maximums. Alternatively, the recommendation to test tanks during waste-disturbing activities was implemented in 2017 for 702-AZ 2017 exhauster testing with APR cartridges. Elevated concentrations for some COPCs were observed during that testing, thereby leading to better assessment of cartridge performance.

5.0 References

1. Nune, SK, CK Clayton, J Liu, CJ Freeman, TM Brouns, and LA Mahoney, 2020. *Analysis of Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on Hanford Tanks SX-101 and SX-104*, PNNL-27558 Vol. 1, Rev. 0., Pacific Northwest National Laboratories, Richland, Washington.
2. Nune, SK, CK Clayton, J Liu, CJ Freeman, TM Brouns, and LA Mahoney, 2020. *Analysis of Air-Purifying Respirator (APR) and Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on a Hanford AX Tank Farm Exhauster Slipstream*, PNNL-27860 Vol. 1, Rev. 0., Pacific Northwest National Laboratories, Richland, Washington.
3. Nune, SK, CL Bottenus, J Liu, LA Mahoney, CJ Freeman, and TM Brouns. 2020. *Analysis of Air-Purifying Respirator (APR) and Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on Hanford Tanks BY-108 and BY-110*, PNNL-28334 Vol. 1, Rev. 0, Pacific Northwest National Laboratories, Richland, Washington.
4. Nune, SK, CL Bottenus, J Liu, LA Mahoney, CJ Freeman, and TM Brouns. 2020. *Analysis of Air-Purifying Respirator (APR) and Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on Hanford AP Tank Farm Exhauster*, PNNL-28680 Vol. 1, Rev. 0, Pacific Northwest National Laboratories, Richland, Washington.
5. 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. http://www.hanford.gov/tocpmm/files.cfm/IHTechBasis_RPP-22491Rev1.pdf.
6. Industrial Hygiene Exposure Assessment Strategy, TFC-PLN-34, REV E-6, Feb 22, 2013.
7. Ruthven DM. 1984. *Principles of Adsorption and Adsorption Processes*. John Wiley & Sons, Inc. New York
8. Wood GO. 1992. "Activated Carbon Adsorption Capacities for Vapors." *Carbon* 30(4):593–599. DOI: 10.1016/0008-6223(92)90177-X.
9. Lodewyckx P, GO Wood, and SK Ryu. 2004. "The Wheeler-Jonas Equation: A Versatile Tool for the Prediction of Carbon Bed Breakthrough Times." *Carbon* 42(7):1351–1355. DOI: 10.1016/j.carbon.2004.01.016.
10. Xiang YC, JC Zeng, and SQ Yan. 1998. "A Simplified Equation for Predicting Breakthrough Time of a Fixed Carbon Bed." *Carbon* 36(7):1057–1060. DOI: 10.1016/S0008-6223(98)00077-3.
11. Respiratory Protection eTool. Occupational Safety and Health Administration. <https://www.osha.gov/SLTC/etools/respiratory/>.
12. Wood GO and JL Snyder. 2007. "Estimating Service Lives of Organic Vapor Cartridges III: Multiple Vapors at All Humidities." *Journal of Occupational and Environmental Hygiene* 4(5):363–374. DOI: 10.1080/15459620701277468.
13. Grant RJ and M Manes. 1966. "Adsorption of Binary Hydrocarbon Gas Mixtures on Activated Carbon." *Industrial and Engineering Chemistry Fundamentals* 5(4):490. DOI: 10.1021/i160020a010.
14. Myers AL and JM Prausnitz. 1965. "Thermodynamics of Mixed-Gas Adsorption." *AIChE Journal* 11(1):121–127. DOI: 10.1002/aic.690110125.

15. Wood GO. 2002. "A Review of the Effects of Covapors on Adsorption Rate Coefficients of Organic Vapors Adsorbed onto Activated Carbon from Flowing Gases." *Carbon* 40(5):685–694.
DOI: 10.1016/S0008-6223(01)00185-3.
16. Freeman, CJ, J Liu, C Clayton, SK Nune, LA Mahoney, CL Bottenus, TM Brouns, P Humble, and MJ Minette. 2020. *Overview of 2016 Through 2018 Testing of Air-Purifying Respirator Cartridge Performance on Multiple Hanford Tank Headspace and Exhausters*, PNNL-26821, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.
17. Wang HY, Wang BD, Li JH, and Zhu TL. 2019. "Adsorption Equilibrium and Thermodynamics of Acetaldehyde/Acetone on Activated Carbon." *Separation and Purification Technology* 209:535-541.
DOI: 10.1016/j.seppur.2018.07.076

Appendix A

Testing Assumptions and Approach

Appendix A

Testing Assumptions and Approach

A.1 Testing Program

Based on the Occupational Safety and Health Administration (OSHA) guidance, a sample testing approach was pursued for quantifying respirator cartridge effectiveness for Hanford tank vapors. Washington River Protection Solutions (WRPS) developed a sampling approach documented in individual Industrial Hygiene Sampling and Analysis Plans.

The powered air-purifying respirator (PAPR) cartridge-testing setup developed by WRPS was used to collect vapor samples from the tank headspaces and tank farm exhausters listed in Table 1 of this report. The test system and methodology were developed in consultation with recognized subject matter experts to follow the example of tank farm headspace field sampling for the purposes of cartridge testing. The design of the PAPR cartridge test rig was modified to accommodate higher flow rates than those encountered by the original air-purifying respirator (APR) cartridge test rig.

The Sampling and Analysis Plan was developed under the direction and oversight of the Industrial Hygienist in conjunction with the Tank Farms Operations Contractor Retrieval and Closure, Tank Farms Project, and/or Production Operations Project Management Team, as applicable. Trained Industrial Hygiene Technicians under the direction of a qualified Industrial Hygienist collected chemical vapor samples from the influent and effluent sides of the cartridge test apparatus. Before the test stands were transported to the tank farms, WRPS Sampling Equipment Operators, Industrial Hygiene Technicians, and Field Work Supervisors underwent training at HiLine Engineering (Richland, Washington).

The PAPR cartridge test was designed and constructed to operate without negative effects on performance to the following environmental conditions:

- Temperature: 32 to 115°F
- Relative Humidity: 5 to 100%
- Precipitation: Up to 4 inches in 6 hours
- Wind: Up to 20 mph with blowing dust.

To better evaluate the performance of the cartridges,³¹ WRPS developed a testing program with the following conservative conditions to support robust cartridge service life estimates:

- The flow rate through the PAPR cartridges was set at approximately 90 to 100 L/min, which is equivalent to 180 to 200 L/min for a two-cartridge unit, or 270 to 300 L/min for a three-cartridge unit. These test flow rates are significantly higher than the minimum PAPR flow rate requirements.³² The

³¹ The multipurpose cartridges are part of a PAPR system. The MSA OptiFilter TL cartridge is used with the MSA OptimAir® TL PAPR and the 3M FR-57 is used with the 3M RRPAS 6000 Series facepieces or BE-10 Series hood powered supplied air respirator systems. The cartridge is part of a system that must be evaluated for the activity being planned by the Industrial Hygiene staff.

³² PAPR cartridges have a minimum flow rate requirement of 115 L/min for a tight-fitting mask and 170 L/min for a loose-fitting hood [26]. The MSA PAPR uses two TL1 cartridges, and the 3M PAPR uses three FR-57 (TL2) cartridges. Testing at ~95 L/min provided a conservatively high flow rate for the MSA cartridge (equivalent to 190 L/min = 12% higher than minimum for a loose-fitting hood), and the 3M cartridge (equivalent to 285 L/min = 68% higher than minimum for a loose-fitting hood).

flow rate also is conservative relative to the 3M-specified flow rate of 220 L/min for use in service life estimates of their Breathe Easy PAPR with 3M FR-57 cartridge,³³ and slightly below MSA-specified flow rate of 205 L/min assigned in their Response Guide Cartridge Life Expectancy Calculator for the MSA OptiFilter TL PAPR with hood [17].

- Tank farm vapor source sampling was performed on headspace vapors rather than from Hanford Tank Farm atmospheric concentrations (i.e., source sampling versus the area sampling).
- A threshold concentration of 10% of the Occupational Exposure Limits (OEL for each Chemical of Potential Concern (COPC) was chosen.

Using the PAPR cartridge-testing setup described later, separate test surveys were performed on two National Institute for Occupational Safety and Health (NIOSH)-approved respiratory protection cartridges: the MSA OptiFilter TL (TL1)³⁴ and 3M FR-57 (TL2)³⁵ using the PAPR test rig. These cartridges were chosen because they are suitable for capturing organic vapors, acid gases, ammonia, formaldehyde, and particulates [17,18].

Vapor concentrations upstream and downstream of the cartridges were monitored with an array of sorbent tubes. Influent (upstream) and effluent (downstream) sorbent tubes were changed out every 2 hours until each experiment was finished. A measured quantity of sample air was drawn in through the sorbent tube. Compounds from the sorbent tubes were extracted and analyzed using analytical methods referenced Table A.1.

³³ Email exchange on October 27, 2017, between J. Liu (PNNL scientist) and E.W. Johnson (3M Technical Service Specialist). See Appendix F, Figure F.1

³⁴ MSA OptiFilter TL (Part number 10143421; Reorder Number 10080456) is a multipurpose PAPR respirator cartridge for use with the OptimAir® TL PAPR, with NIOSH approval for AM/CL/CD/FM/HC/HS/MA/SD/HE/HF applications. <https://us.msasafety.com/Air-Purifying-Respirators-%28APR%29/Powered-Air-Purifying-Respirators-%28PAPR%29/OptimAir%C2%AE-TL-PAPR/p/000100003000001600>

³⁵ 3M FR-57 (Part number 453-03-02R06) is a multipurpose PAPR respirator cartridge for use with the 3M RRPAS 6000 Series facepieces or BE-10 Series hood powered supplied air respirator systems, with NIOSH approval for OV/SD/HC/CL/CK/HF/AM/MA/FM/HE application. https://www.3m.com/3M/en_US/company-us/all-3m-products/~3M-High-Efficiency-Cartridge-FR-57-453-03-02R06-6-EA-Case/?N=5002385+3294780228&rt=rud

Table A.1. Information on Sorbent Media used to Capture Contaminants, Flow Rates used, Methods used to Extract Analyte from Sorbent Media, and Methods used to Quantify or Estimate the Concentrations of Hazardous Contaminant

Analyte Category	Media	Flow Rate (mL/min)	Analytical Method ^a	Instrument Used ^b	Analysis Location ^c
Acetonitrile	Charcoal Tube, SKC-226-09	100	NIOSH 1606	GC-FID	ALS
Acetonitrile	Carbotrap 300 TDU Tube	33	EPA TO-17 Modified	GC/MS	WRPS
Furans	TDU Tenax TA	50	EPA TO-17 Modified	GC/MS	WRPS
Semivolatile Organic Compounds	Carbotrap 150 TDU Tube	33	EPA TO-17 Modified	GC/MS	WRPS
Volatile Organic Compounds	Carbotrap 300 TDU tube	33	EPA TO-17 Modified	GC/MS	WRPS
Mercury	Anasorb C300, SKC-226-17-1A	250	NIOSH-6009	CVAA	WHL
Methanol ^d	Silica Gel, SKC-226-51	33	NIOSH-2000	GC-FID	ALS
Ammonia	Anasorb 747 (sulfuric acid), SKC-226-29	200	OSHA-ID-188	IC	WHL
1,3-butadiene	Charcoal, SKC-226-37, (Parts A and B)	200	NIOSH-1024	GC-FID	ALS
Aldehyde	DNPH Treated Silica Gel, SKC-226-119	200	EPA TO-11A	HPLC	ALS
Pyridine	Coconut Shell Charcoal, SKC-226-01	1000	NIOSH-1613	GC-FID	ALS
Nitrosamines	Thermosorb/N	2000	NIOSH-2522 Modified	GC-TEA	CBAL
Ethylamine	XAD-7 (NBD) Chloride), SKC 226-96	100	OSHA-ID-34, 36, 40, and 41	HPLC-UV	ALS

^a Analytical Method

NIOSH: National Institute of Occupation Safety and Health
EPA: U.S. Environmental Protection Agency
OSHA: Occupational Safety and Health Administration

^b Instrument Used

GC-FID: Gas Chromatography-Flame Ionization Detector
GC/MS: Gas Chromatography-Mass Spectrometry
CVAA: Cold Vapor Atomic Absorption
IC: Ion Chromatography
HPLC: High Performance Liquid Chromatography
GC-TEA: Gas Chromatography-Thermal Energy Analyzer
HPLC-UV: High Performance Liquid Chromatography-Ultraviolet Detector

^c Analysis Location

ALS: ALS Environmental Salt Lake City
WRPS-222S: Washington River Protection Solutions, Organic Studies Group
WHL-222S: Wastren Hanford Laboratory
CBAL: Columbia Basin Analytical Laboratory, part of the RJ Lee Group

^d Methanol was also collected and measured using SUMMA Canisters with EPA TO-15 the Analytical Method

The measurement of 61 COPCs were the primary focus of the testing. The 61 COPCs represent a set of tank vapor chemicals found in a tank farm source >10% of the OELs or are considered “known” or “probable” carcinogens by the International Agency for Research Cancer or other regulatory agencies.[19,20] A full listing of these COPCs is provided in Section 1.3.

A.2 Cartridge Selection

The multipurpose high-efficiency PAPR cartridges used in testing were the MSA OptiFilter TL (TL1) (MSA Safety Inc., Pittsburgh, Pennsylvania) and 3M FR-57 (TL2) (3M Company, Maplewood, Minnesota). The MSA OptiFilter TL cartridge (Part number 10143421; reorder number 10080456) is a multipurpose PAPR respirator cartridge for use with the OptimAir® TL PAPR, with NIOSH approval for AM/CL/CD/FM/HC/HS/MA/SD/HE/HF applications. The 3M FR-57 cartridge (part number 453-03-02R06) is a multipurpose PAPR respirator cartridge for use with the 3M RRPAS 6000 Series facepieces or BE-10 Series hood powered supplied air respirator systems, with NIOSH approval for OV/SD/HC/CL/CK/HF/AM/MA/FM/HE applications.

The two cartridges were used to assess Hanford tanks exhauster and headspace vapor streams. These cartridges were chosen because they are suitable for capturing organic vapors, acid gases, ammonia, methylamine, and formaldehyde.

A.3 Testing Source and Setup

Sources for the respirator cartridge testing were selected to ensure that the mixture of COPCs challenging the cartridges represented actual tank farm mixtures. Direct tank vapor sources including tank headspace and tank farm exhauster slip streams were chosen to provide conservatively high concentrations relative to the area concentrations of expected respirator use.

Figure A.1 provides a summary of the 241-AZ tank farm historical area and source monitoring from January 2009 through September 2016, as an example of typical differences between headspace or exhauster source measurements and monitoring of the work area in and around the tank farm.

Area concentrations shown for the AZ tank farm indicate very few detected COPCs above 10% of their OELs within the tank farm. Most samples from area air sampling are non-detects that are less than the reported DL (or RL)³⁶. In contrast, source data from stack or headspace sampling indicates several COPCs detected above 10% of their OELs, and in this specific farm, ammonia, mercury, and N-Nitrosodimethylamine are identified with detected levels >100% of their OELs. None of these three COPCs were detected at elevated source concentrations during area sampling. Only ammonia was detected at a concentration near 1% of its OEL. Only 2-heptylfuran is identified in Figure A.1 as being detected near 100% of its OEL during area sampling, whereas source measurements for that compound were all non-detects with an RL at or <10% of the OEL. In general, area concentrations for COPCs are substantially lower (e.g., 10× or more) than source concentrations. However, there are exceptions, such as 2-heptylfuran. Several other COPCs—specifically formaldehyde, acetonitrile, and acetaldehyde—are shown as detects in area sampling at levels comparable to or higher than source concentrations. All of these COPCs are at concentrations well below 10% of their OELs. Tank farm area sampling also may result in detection of COPCs that did not originate from the sources in that farm. They could be from other nearby farms or from non-tank farm sources entirely including ambient background concentrations.

³⁶ Area-sampling data typically represent time weighted average concentrations comparable to source and cartridge testing samples but may not represent instantaneous or short duration concentrations, if present. In addition, area sampling represents only a portion of the data potentially available. WRPS Industrial Hygiene performs more extensive analysis on vapor concentrations in breathing zones using additional data sets.

They could be from other nearby farms or from non-tank farm sources entirely including ambient background concentrations.

AZ Farm Air Sampling Results Relative to OEL - Chemicals of Potential Concern
 1/20/2009 to 12/13/2016 (Data Reviewed as of July 2017)

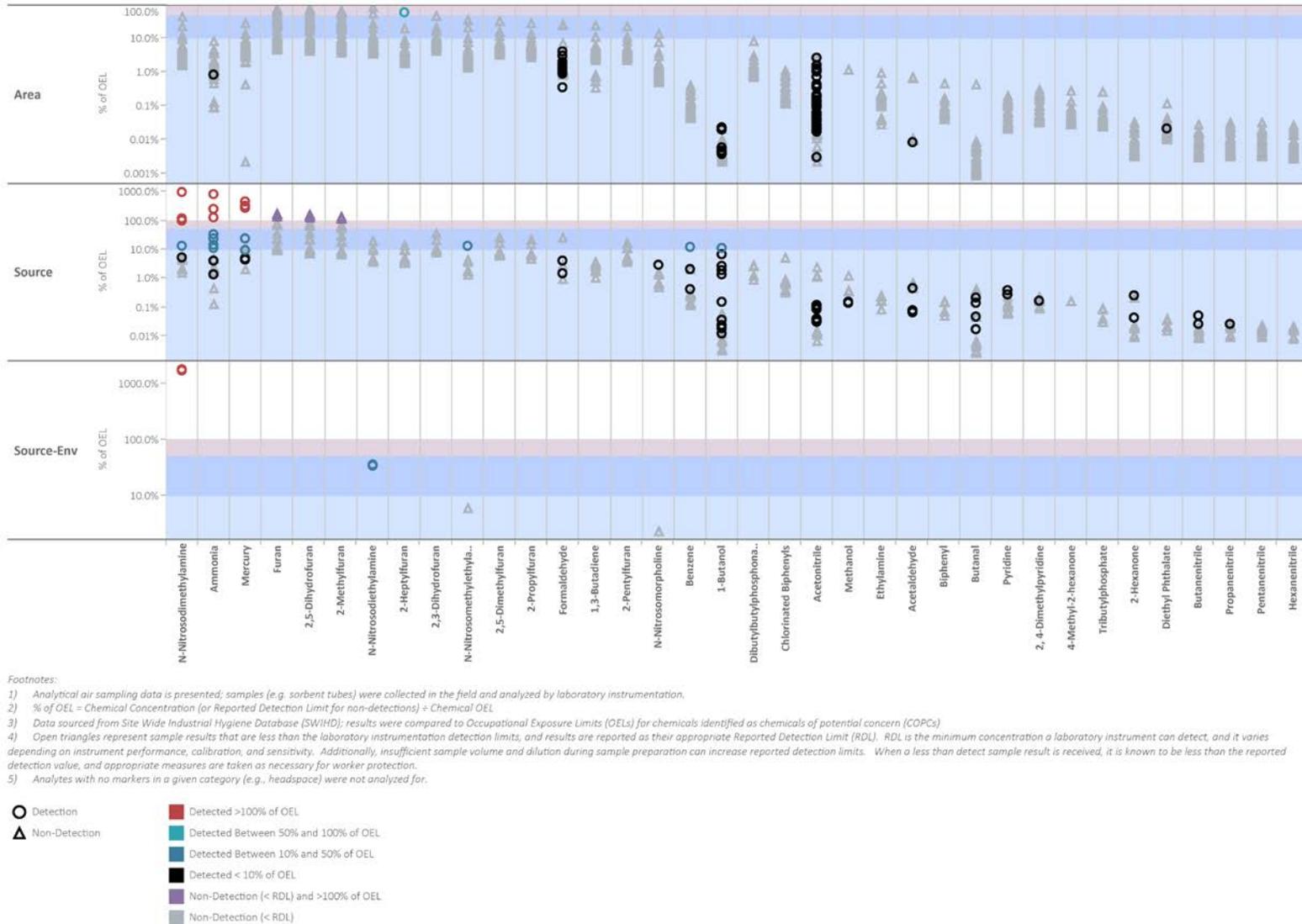


Figure A.1. Comparison of Source and Area Air Sampling in the AZ Farm³⁷

³⁷ The figure is adapted from hanfordvapors.com (https://hanfordvapors.com/wp-content/uploads/2017/05/percent_oel_nonpersonal_az_farm-1.pdf). Additional data and sampling results from other tank farms and time periods are also available.

A.4 PAPR Respirator Cartridge Test Rig

The primary COPCs present at source concentrations to respirator cartridge performance testing (e.g., ammonia, mercury, nitrosamines, etc.) have historically been detected and quantified at much higher concentrations in tank farm sources than in ambient area samples, making testing with actual tank farm source concentrations an appropriately conservative approach for evaluating cartridge performance.

The respirator cartridge-testing system was developed by WRPS and HiLine Engineering (Richland, Washington) as a means to comprehensively test respirator cartridge performance with actual Hanford tank headspace or exhauster slip stream gases. Tank headspace or exhauster slip stream vapors are pulled directly from the source through a flexible hose connecting the tank or exhauster sampling port within the tank farm/exhauster fence line to the respirator cartridge-testing system outside the farm [1-4]. Multiple in-line particulate filters are installed in the line between the tank/exhauster and test system to remove potential radioactive particulates. Each filter unit contains a hydrophobic Fluoropore™ polytetrafluoroethylene filter (Millipore Sigma, Billerica, Massachusetts) that is required in accordance with the radiological work permit. This polytetrafluoroethylene filter medium is the same material used for routine tank vapor area monitoring as well as sampling and analysis of sources (headspace and exhausters) and was selected because of its broad chemical compatibility that minimizes sorption of, or reactions with, chemical compounds. The filter medium is not expected to adversely impact the test objectives because all tank farm vapor sampling uses this type of filter medium.

The hose was wrapped in heat tape to maintain in-tank vapor temperatures as near as possible as vapors were transferred to the testing system.³⁸ Other benefits of maintaining the vapor temperature during transfer are reducing condensation of water, which can act as a sink for chemicals, and preventing potential condensation of other chemicals, including COPCs. There were two connection hoses:

1. The hose from the riser to the inlet of the respirator cartridge-testing system was a Centurion Process, LLC 1-in. RFRTP polytetrafluoroethylene Teflon-lined hose with an ethylene propylene diene monomer rubber cover with 1-in. 316 stainless steel male national pipe thread ends.
2. The return hose was a Centurion Process, LLC 1-in. RT smoothbore fluorinated ethylene propylene lined hose with an ethylene propylene diene monomer rubber cover and 1-in. 316 stainless steel male national pipe thread ends.

The test equipment enables sampling of the vapor stream both before and after the cartridge so performance for a given COPC can be quantified. Sorbent media tubes were used to capture the COPCs and other hazardous contaminants. After a given test segment, the sorbent tubes were removed and analyzed. Sampling of the inlet and exhaust gas was performed every 2 hours, but this timing can be modified as necessary.

The PAPR cartridge test rig had been modified from older systems to include:

- An enlarged cartridge housing and a mounting compatible with the larger PAPR cartridge.
- An additional sampling line and control valve to accommodate 12 simultaneous inlet and outlet sorbent tubes versus the 11 sorbent tubes used in the original APR test stand. The inlet and effluent portion of the test stand were used during the comparison testing.

³⁸ Across all ten tests, the measured in-tank thermocouple temperatures ranged between 59.7 and 69.8°F during the sampling. The tent surrounding the cartridge test rig was kept as near the in-tank temperatures as possible.

- Additional instruments to directly measure pressure, temperature, and relative humidity immediately after the cartridge filter.

Figure A.2 is a general schematic diagram for the respirator cartridge test apparatus, and Figure A.3 shows photographs of the actual equipment. The test system uses vacuum to draw tank gases/vapors into the unit so the potential for leakage to atmosphere is minimized until the gases/vapors are under positive pressure downstream of the vacuum pumps. By the time gases reach the vacuum pump, COPCs are essentially captured or removed by either the sorbent tubes or the respirator cartridge [1-4].

Flows through the respirator cartridge and through each sorbent tube were set and controlled/maintained using manual flow control valves on the outlet of each rotameter, and rotameters were calibrated against DryCal primary flow calibrators before and after testing. DryCal flow meters also were used downstream of the sorbent tubes to measure the flow through each sorbent tube. All equipment connections were leak tested prior to initiation of the test. Temperature, relative humidity, and pressure of the inlet gas/vapor stream were monitored by calibrated instrumentation.

Using Industrial Hygiene-approved materials, cartridge test equipment was constructed so it would not influence/interfere with vapor analysis. Stainless steel or Teflon™ tubing and fittings are used where possible because of their relatively inert nature to the vapors being analyzed. Limited portions of the assembly used acrylic, Viton™, glass, and Masterflex C-flex tubing, which are commonly used for various vapor-sampling applications.

The vacuum sources for the PAPR cartridge test rig are two large vacuum pumps that are set to a combined slipstream flow rate of 30 to 50 L/min. Test operations would start at 30 L/min and monitor the flows throughout testing to be sure they stayed in the range of 30 to 50 L/min. Rotameters control flow rates for each tube. The flow rates were checked nominally every 15 minutes during testing.

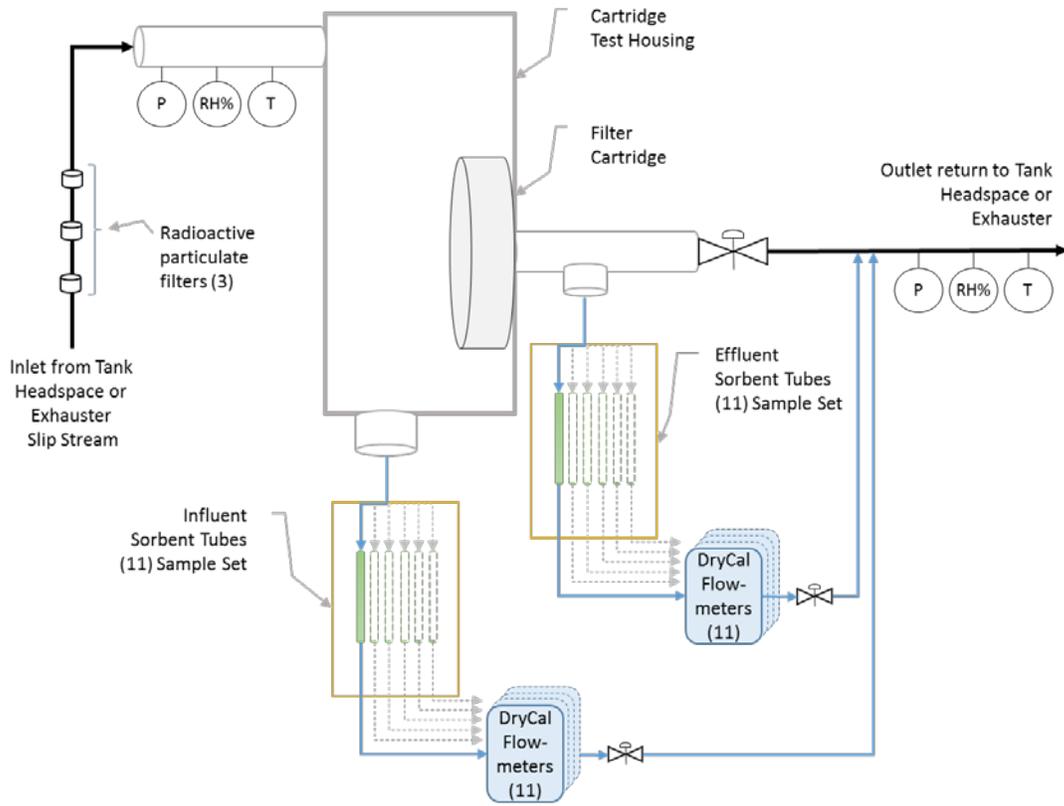


Figure A.2. General Schematic of Respirator Cartridge Test Apparatus

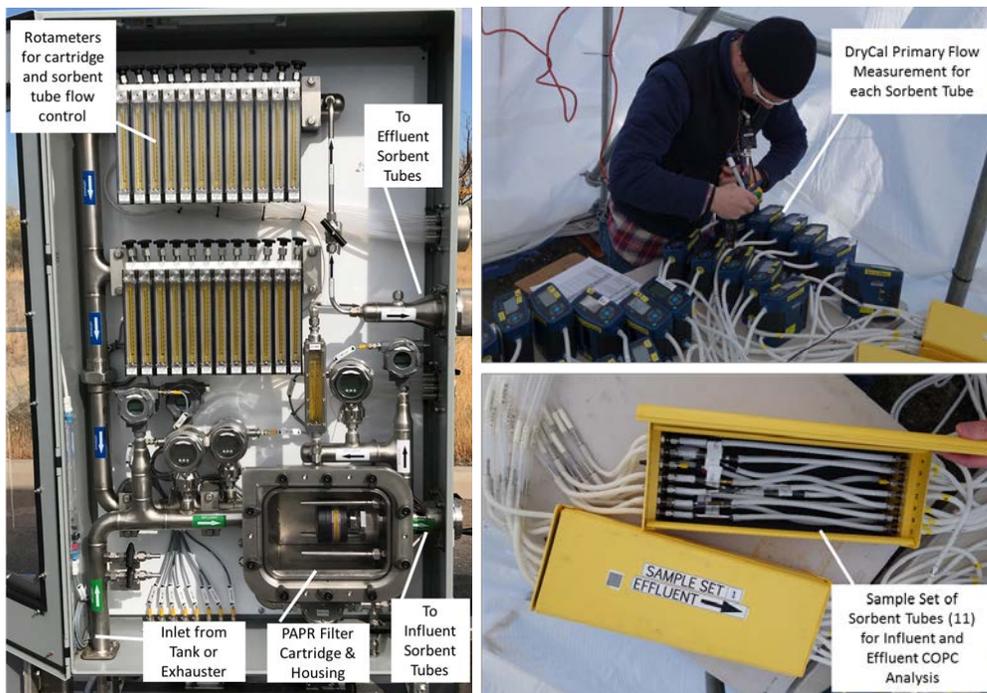


Figure A.3. Photographs of the PAPR Respirator Cartridge Test Equipment

A.5 Breakthrough Criteria

A general definition of breakthrough time is the time at which the effluent concentration reaches its maximum permissible level [5]. Within the adsorption research community, researchers use different definitions of breakthrough time based on specific needs. Some researchers choose the time when the first detectable concentration is captured as the breakthrough time [6], some choose a time when the effluent concentration reaches a percentage of the influent concentration [7], and others choose a time when the effluent concentration matches the influent concentration to assess the equilibrium breakthrough capacity and to compare with adsorption isotherm results [8].

There is a difference between cartridge service life and breakthrough time. According to OSHA, service life means the period of time that a respirator, filter or sorbent, or other respiratory equipment provides adequate protection to the wearer [9]. To prevent any contamination, cartridges ideally should be changed before expected breakthrough. Therefore, a safety factor, such as changing cartridges before 90% of the estimated breakthrough, needs to be applied to the breakthrough time to estimate the service life of the cartridge. To estimate the cartridge service life, the most common practice is to use the time when the effluent concentration reaches a percentage of either the OEL or influent concentration for a specific chemical. OSHA suggests the software package “MultiVapor” based on Gerry Wood’s model (provided by NIOSH) to estimate the service life of a cartridge [10,11]. Here, the time at which the effluent concentration reaches 10% of the influent concentration is chosen as the breakthrough time. In a field method developed to determine the service lives of respirator cartridges, the time when the effluent concentration reaches ~10% of the influent concentration is used as the breakthrough time [12]. Respirator manufacturers such as Honeywell (North Safety) have used similar breakthrough criteria [13]. However, other respirator manufacturers such as 3M and MSA use the time when the effluent concentration reaches a certain percentage of an OEL to determine the breakthrough time and to estimate the cartridge service life [14,15]. Some literature on service life indicator deemed that this 50% of the OEL is actually a common breakthrough time determination criterion to estimate cartridge service life [16].

There is no universal standard for determining breakthrough time or service life; therefore, for the cartridge performance tests, we defined breakthrough as the time when the effluent concentration reaches 10% of the OEL. When the influent concentration of the chemical is higher than its OEL, the 10% of the OEL criterion is more conservative than 10% of the influent concentration. This works particularly well for ammonia and nitrosamine compounds. When the influent concentration is lower than the OEL, the 10% of the OEL criterion is not as conservative as 10% of the inlet concentration. However, when the influent concentration is less than the OEL, 10% of the OEL is still conservative because the effluent concentration is substantially less than the limit of the acceptable concentration of a hazardous substance in the workplace.

A.6 References

1. Nune, SK, CK Clayton, J Liu, CJ Freeman, TM Brouns, and LA Mahoney, 2020. *Analysis of Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on Hanford Tanks SX-101 and SX-104*, PNNL-27558 Vol. 1, Rev. 0., Pacific Northwest National Laboratories, Richland, Washington.
2. Nune, SK, CK Clayton, J Liu, CJ Freeman, TM Brouns, and LA Mahoney, 2020. *Analysis of Air-Purifying Respirator (APR) and Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on a Hanford AX Tank Farm Exhauster Slipstream*, PNNL-27860 Vol. 1, Rev. 0., Pacific Northwest National Laboratories, Richland, Washington.

3. Nune, SK, CL Bottenus, J Liu, LA Mahoney, CJ Freeman, and TM Brouns. 2020. *Analysis of Air-Purifying Respirator (APR) and Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on Hanford Tanks BY-108 and BY-110*, PNNL-28334 Vol. 1, Rev. 0, Pacific Northwest National Laboratories, Richland, Washington.
4. Nune, SK, CL Bottenus, J Liu, LA Mahoney, CJ Freeman, and TM Brouns. 2020. *Analysis of Air-Purifying Respirator (APR) and Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on Hanford AP Tank Farm Exhauster*, PNNL-28680 Vol. 1, Rev. 0, Pacific Northwest National Laboratories, Richland, Washington.
5. Ruthven DM. 1984. *Principles of Adsorption and Adsorption Processes*. John Wiley & Sons, Inc. New York.
6. Zhao Y, X Liu, KX Yao, and Y Han. 2012. “Superior Capture of CO₂ Achieved by Introducing Extra-framework Cations into N-doped Microporous Carbon.” *Chemistry of Materials* 24:4725–4734. DOI: 10.1021/cm303072n.
7. Li Z, Y Liu, X Yang, Y Xing, C-J Tsai, M Meng, RT Yang. 2017. “Performance of Mesoporous Silicas and Carbon in Adsorptive Removal of Phenanthrene as a Typical Gaseous Polycyclic Aromatic Hydrocarbon.” *Microporous and Mesoporous Materials*, 239:9–18. DOI: 10.1016/j.micromeso.2016.09.027.
8. Danmaliki GI and TA Saleh. 2017. “Effects of Bimetallic Ce/Fe Nanoparticles on the Desulfurization of Thiophenes Using Activated Carbon.” *Chemical Engineering Journal* 307:914–927. DOI: 10.1016/j.cej.2016.08.143.
9. Occupational Safety and Health Administration (OSHA). 2017. “Respiratory Protection eTool.” https://www.osha.gov/SLTC/etools/respiratory/change_schedule_testing.html.
10. Occupational Safety and Health Administration (OSHA): 29 CFR Parts 1910 and 1926 Respiratory Protection: Final Rule. Federal Register 63(5):1278–1279. Washington, D.C.: U.S. Government Printing Office, Office of the Federal Register, January 8, 1998. http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=12716.
11. Wood GO and JL Snyder. 2007. “Estimating Service Lives of Organic Vapor Cartridges III: Multiple Vapors at All Humidities.” *Journal of Occupational and Environmental Hygiene* 4(5):363–374. DOI: 10.1080/15459620701277468.
12. Cohen HJ, SP Levine, and RP Garrison. 1991. “Development of a Field Method for Determining the Service Lives of Respirator Cartridges—Part IV: Results of Field Validation Trials.” *The American Industrial Hygiene Association Journal* 52(7):263–270. DOI: 10.1080/15298669191364712.
13. Honeywell North. 2017. <http://ezguide.northsafety.com/help/html/esLifeMain.aspx>.
14. 3M. 2017. “3M Select & Service Life Software.” <http://extra8.3m.com/SLWeb/home.html>.
15. MSA. 2017. “MSA Response Guide.” <http://webapps2.msasafety.com/ResponseGuide/Home.aspx>.

16. Checky M, K Frankel, D Goddard, E Johnson, JC Thomas, M Zelinsky, and C Javner. 2016. "Evaluation of a Passive Optical Based End of Service Life Indicator (ESLI) for Organic Vapor Respirator Cartridges." *Journal of Occupational and Environmental Hygiene* 13(2):112–120. <http://multimedia.3m.com/mws/media/1142921O/esli-article-in-joe.pdf?fn=EvaluationofaPassiveOpticalBased>.
17. MSA Safety, Inc. Response® Guide Cartridge Life Expectancy Calculator. <http://webapps2.msasafety.com/ResponseGuide/ChemicalCalculator.aspx>
18. Scott Air-Purifying Respirators (742 Twin Cartridges), https://www.scottsafety.com/en/us/DocumentandMedia1/Poster_742SelectionGuide_HS_6411_0313.pdf
19. 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. http://www.hanford.gov/tocpmm/files.cfm/IHTechBasis_RPP-22491Rev1.pdf.
20. Industrial Hygiene Exposure Assessment Strategy, TFC-PLN-34, REV E-6, Feb 22, 2013.

Appendix B
Data Analysis

Appendix B

Data Analysis

Each Chemical of Potential Concern (COPC) with observed breakthrough signatures (outlet concentration >10% of the Occupational Exposure Limit [OEL]) was further assessed to infer when the point of breakthrough occurred at a higher resolution than the 2-hour collection times. An interpolation was used to determine the time when 10% of the OEL concentration at the outlet would have occurred. Once the interpolated breakthrough time was determined, the average inlet concentrations and measured gas stream properties were determined up until that point for use in subsequent statistical analyses. The results of the interpolation procedures are shown in Tables B.1 and B.2. Note that the data sources are from the Appendix D and Appendix C data given in each of the prior tank analysis reports.

Table B.1. Calculation of Breakthrough Times for Ammonia

Tank	Cartridge	Breakthrough Time at 10% of OEL Concentration in Outlet - interpolated (hour)	Breakthrough Time at 10% of OEL Concentration in Outlet - estimated (hour)	Averages for Period Up to Calculated Breakthrough				
				Cartridge Inlet Concentration (ppm)	Cartridge Inlet Concentration (% of OEL)	Stream Temperature (F)	Inlet Pressure (Torr)	Relative Humidity (%)
SX-101	TL1	4.7	2.9	141	564%	77.4	675	77.8
SX-101	TL2	1.7	0.7	174	694%	84.6	670	80.5
SX-104	TL1	2.0	1.6	272	1087%	92.7	667	49.5
SX-104	TL2	1.6	0.5	254	1015%	96.1	669	60.8
BY-108 ('18)	TL1	5.6	2.5	158	632%	45.8	709	75.6
BY-108 ('18)	TL2	1.7	1.0	128	514%	54.3	681	76.6
AP ('18)	TL1	> 16	15.6	22	86%	52.8	698	73.0
AP ('18)	TL2	5.5	5.4	23	90%	57.4	700	87.6
AX ('17)	TL1	> 16	>16	4.3	17%	79.8	693	52.7
AX ('17)	TL2	> 16	>16	3.8	15%	87.3	693	44.7

Table B.2. Calculation of Breakthrough Times for 2,5-Dimethylfuran

Tank	Cartridge	Breakthrough Time at 10% of OEL Concentration in Outlet - interpolated (hour)	Averages for Period Up to Calculated Breakthrough				
			Cartridge Inlet Concentration (ppm)	Cartridge Inlet Concentration (% of OEL)	Stream Temperature (F)	Inlet Pressure (Torr)	Relative Humidity (%)
SX-101	TL1	> 16	3.85E-05	4%	69.3	678	79.9
SX-101	TL2	> 16	3.86E-05	4%	78.5	680	80.9
SX-104	TL1	9.2	3.80E-05	4%	93.8	668	51.2
SX-104	TL2	3	1.44E-04	14%	98.9	671	56.2
BY-108 ('18)	TL1	> 16	2.76E-05	3%	41.6	704	73.3
BY-108 ('18)	TL2	> 16	2.84E-05	3%	53.1	681	77.7
AP ('18)	TL1	> 16	2.82E-05	3%	52.8	698	73.0
AP ('18)	TL2	> 16	3.81E-05	4%	55.3	700	76.3
AX ('17)	TL1	> 16	3.87E-05	4%	79.8	693	52.7
AX ('17)	TL2	> 16	3.76E-05	4%	87.3	693	44.7

Appendix C

Historical COPC Data Comparisons to Respirator Testing Conditions

Appendix C

Historical Data Comparisons to Respirator Cartridge-Testing Conditions

The historical headspace-characterization data and Industrial Hygiene data—referred to in this report as “TWINS HS”³⁹ and “TWINS IH”⁴⁰—were obtained from the Tank Characterization Database via the Tank Waste Information Network System. Pre-2006 vapor analysis results, stored in TWINS HS,⁴¹ were obtained via a TWINS query on June 20, 2016, for all the tanks and exhaust systems in this report. The TWINS IH data were downloaded on the following dates as cartridge test reporting progressed.

- March 8, 2017, for the headspaces of SX-101 and SX-104
- December 7, 2017, for the AX exhauster data from the Site-Wide Industrial Hygiene Database (SWIHD) Source database
- May 9, 2018, for the AP exhauster (2018 tests) and the headspace of BY-108 (2018 tests).

Post-2014 headspace vapor data were obtained from the SWIHD by a query that produced a data set referred to as “SWIHD HS.” There were several different download dates for these data as well, which are the same as for the TWINS IH data downloads.

Although surveys that occurred later than those listed above might provide higher historical maxima, the double-shell tank exhauster data in the downloads that were used cover a period going back to 2005 and include a variety of double-shell tank activities. These data are expected to provide a sufficiently complete basis for comparison to cartridge data. In the case of single-shell tank headspaces, activity and surveys have been infrequent or nonexistent since the download dates and, again, the data in the downloads is expected to be sufficiently complete.

For the TWINS IH and SWIHD HS data sets, each line of data in the set represents a measurement made on the contents of a single sorbent tube (or other collector). In many cases, a single sample air stream passed through a series of two or more collectors, which meant the actual sample concentration was the sum of the contributions from all the collectors in the series. The intent of this sample collection method was to have most or all of the vapor deposited in the first collector, with a relatively small degree of breakthrough into the second collector.

The TWINS IH and SWIHD HS data sets currently do not contain explicit information to denote which data came from collectors in series or to identify which collectors belong in a set. This absence causes some difficulty in identifying which data should be summed to obtain the true concentration for the sample stream. For the purpose of providing a historical data set for comparison to cartridge data, use of the uncombined raw data was considered to be adequate. Therefore, uncombined data were used for some of the data analyses.⁴² As a result, some historical concentration maxima and averages will be

³⁹ TWINS HS is the acronym for Tank Waste Information Network System Headspace.

⁴⁰ TWINS IH is the acronym of Tank Waste Information Network System Industrial Hygiene.

⁴¹ No data have been added to TWINS HS since April 2005, so the June 2016 download does not require updating.

⁴² A method for combining historical collector concentrations for SWIHD HS data, though not for SWIHD Source or TWINS IH data, was developed partway through the cartridge testing project. Consequently, the impact of collectors installed in series is accounted for (SWIHD HS collector concentrations were combined) only for the SX-101, SX-104, and BY-108 headspaces. The 2017 tank vapor COPC report describes the approach [1].

underestimated in those analyses; the underestimates are expected to be within a factor of 2 of the true (summed) concentration value, because in almost all cases, there are no more than two collectors in series. Preliminary examination of the data suggests that when data combination is not performed, it is rare to underestimate concentrations of Chemicals of Potential Concern (COPC) by 40% or more.

Some historical concentration data were removed from consideration because they were flagged as having certain measurement quality issues. TWINS HS data were eliminated from consideration if they were:

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

TWINS IH and SWIHD HS data were eliminated from consideration if they:

- Were associated with a contaminant in a blank (Data Qualifier Flag b or B), a laboratory control sample that was out of range (Data Qualifier Flag a), a low-level standard with percent recovery outside the specified range (Data Qualifier Flag L)⁴³
- Had an excessive relative percent difference between duplicates (Data Qualifier Flag c)
- Were marked with a laboratory-defined flag whose meaning was not generically defined and might indicate a serious data-quality issue (Data Qualifier Flag Y).

TWINS HS results associated with chemicals that were ambiguously identified (e.g., “alkane,” “unknown,” “C6 ketone”) were deleted unless the molecular weight of one of the chemicals could be unambiguously specified (e.g., “octanenitrile and others” was kept). In these mixture cases, where the Chemical ID consisted of a Chemical Abstracts Service (CAS) number followed by M, the molecular weight of the identified chemical was added to the data record, the CAS number was used for the Chemical ID, and the concentration expressed in parts per million (absent from the downloaded database) was calculated from the concentration in milligrams per cubic meter at 25°C and the molecular weight.

A number of chemicals in the TWINS IH data set had “needs conversion” notes in the concentration (mg/m³ and ppm) columns rather than numbers so calculations were required to supply these concentrations. Values already in the database were used in the calculations: the molecular weight, the reported value and its units, and the sample volume and its units. Here, a temperature of 25°C and a pressure of 1 atm were assumed.

The method described above was consistent with that used in the 2016 and 2017 tank vapor COPC reports [1, 2] except that non-reports—measurements that were less than the reporting limit (RL) for the analyte—were excluded from the 2016 COPC analysis but were not excluded in this study. In addition, Data Quality Flags for TWINS IH and SWIHD HS data have been updated since the 2016 COPC report.⁽⁴⁴⁾

⁴³ Data with the q flag were not excluded, although this flag was temporarily used by the 222-S Laboratory to signify the same thing that L currently signifies. There were relatively few data for which q flag was present. Such data were few enough, and low enough in concentration, that they would have had no effect on historical maxima and little effect on historical averages if they had been excluded.

⁴⁴ The current data qualifier flags are defined in the 222-S Laboratory Guidance Document, AT5-GD-1048, Rev. A-7, effective November 16, 2016.

The databases were further examined to make sure that the concentration data subsets used in analyses, for each cartridge-testing source, were consistent with the location where the cartridge-testing sample was taken.

- *AP Stack, 2018 tests:* The TWINS HS database contained data identified as having the location “AP Ventilation.” These data were included as part of this analysis. The SWIHD HS database contained no data for the AP stack. AP Farm data whose Survey Titles indicated sampling from valve pits, motor housings, or other non-stack sources were excluded from this analysis. All of the TWINS IH data that were analyzed were listed in the database as having the location “Primary Exhauster.” Data where the location was an individual tank name, “CAM Cabinet,” or “Inside Farm” were not used. They may have been relevant to in-stack concentrations, but their apparent location made that unclear. Almost all data that were used had “stack” or “exhauster” somewhere in the survey title. TWINS HS and TWINS IH data from before September 8, 2016, the date when the AP exhauster upgrade was completed, were used for comparison to FY 2016 cartridge data. TWINS IH data from after that date were used for comparison to FY 2018 cartridge data.
- *BY-108 Headspace, 2018 tests:* TWINS HS and SWIHD HS data for BY-108 were used without special selection. The SWIHD HS data for BY-108 were from three dates in October 2016. All BY Farm data in the TWINS IH database were attributed to individual tank locations; that is, there were no location designations such as “Inside Farm,” “Outside Farm,” etc. Of the data that had BY-108 as a location, all had Survey Titles that included phrases such as “BY-108 BF COPC Sampling,” “BY-108 COPC Sampling,” or “BY-108 BF COPC Make-up.” Because the location was specified as BY-108, and many of the surveys contained BF (i.e., “Breather Filter”) in the title, all TWINS IH BY-108 data were considered appropriate for comparison to cartridge-testing samples from the tank headspace.
- *AX Exhauster:* The only data available for the AX exhauster were two Industrial Hygiene surveys that were carried out at the POR127 stack in October 2017. No headspace or other data for the AX farm were used because the data predated the addition of the AX exhauster.
- *SX-101 and SX-104 Headspace:* The TWINS HS database contained headspace data for SX-101 and SX-104 measurements. All TWINS HS data for organic compounds and ammonia in these two SX tanks were from measurements made in 1999 or before. However, these data were taken while a sludge cooler (active ventilation) was in place. Active ventilation ended in 2003,⁴⁵ and only data later than 2003 are relevant to the current passively ventilated conditions. The SWIHD HS database contained no headspace data for SX-101; however, SWIHD HS data for SX-104, based on measurements taken in July 2015, were present. All TWINS IH data that had “SX101” or “SX104” noted in the “Location” field of the database were used. These data had Survey Titles that alluded to “BF” (breather filter) and “S-complex COPC summa sampling” and were taken in 2006.

⁴⁵ Email from JE Meacham to LA Mahoney, “RE: Exhauster system changes”, December 21, 2017, 3:11:18 PM.

Maximum and average⁴⁶ exhaust concentrations were found for each analyte for the combined TWINS IH and SWIHD⁴⁷ databases, as were counts of the number of measurements.⁴⁸ These maxima are given in Table C.1 and Table C.2,⁴⁹ together with Occupational Exposure Limits (OEL). Average concentrations were routinely affected by a number of non-reports and were deemed to be less valuable than historical maxima for comparison to cartridge inlet concentrations. Therefore, they are not presented in the tables, but only in the individual cartridge-testing reports [3-7]. Maximum cartridge inlet concentrations are presented as the first value in each cell, and maximum historical concentrations are presented following a “/”.

Because the TWINS HS data were older and in many cases did not represent the current source from which cartridge test samples were taken, they were considered to be not as representative of the vapors present during cartridge testing, and the default decision was to omit them from calculations. However, in some cases, the maximum and average concentrations for an analyte were considerably different if they were determined from a combination of all three databases. When this was the case, the results for the three-database combination are tabulated in individual cartridge-testing reports along with those for the default two-database combination. That is, Table F.1 in each of the individual cartridge-testing reports contains two rows for such a chemical instead of one, with the upper row (the default two-database combination) in normal font and the lower row (the three-database combination) in italic. The two criteria for tabulating this extra information were 1) that at least one concentration for the chemical exceeded the OEL and 2) that there was a significant difference between the value obtained from the two-database combination and that from the three-database combination. The significant difference could be either that there were data for the three-database set but no data for the two-database set (i.e., data only in TWINS HS), or that there was a difference of a factor of 3 or more, in either direction, between the value obtained from the two-database combination and that from the three-database combination. In Table C.1 and Table C.2, TWINS HS data (maxima indicated by italics) were used only when more recent data were not available, and when it was judged that the waste generating the vapor had not permanently changed so that early measurements were not applicable.

Because the RLs on concentrations in the historical database were generally higher than the RLs or detection limits (DL) in the cartridge tests, it was necessary to analyze data in a way that would let the effect of <RL historical data be recognized. To do this, it was assumed that all of the non-reports in the databases had concentrations equal to the measurements' RLs. If a maximum value was a non-report, it was marked with “<” in Table C.1 and Table C.2.

⁴⁶ Arithmetic average.

⁴⁷ This evaluation used the concentration data in SWIHD and converted them to %OEL, rather than directly using the %OEL data in SWIHD. Although this approach was consistent with the methods used on the other two data sets, there are cases where it gave a %OEL value smaller than that found in the SWIHD database. This difference occurs because concentrations in SWIHD may be truncated to one or two significant figures, while the %OEL values in SWIHD are calculated from concentrations before truncation. The difference between %OEL based on truncated and non-truncated concentrations is small enough to have no effect on conclusions about whether cartridge maxima are consistent with historical maxima.

⁴⁸ The TWINS IH data were the only concentrations present in the two-database combination for the AP stack, AN stack, and 702-AZ cases because the SWIHD HS database contained no data for those stacks.

⁴⁹ All %OEL values were calculated from concentration data that had been rounded to a minimum of three significant figures.

Table C.1. Comparison of Maximum Cartridge Inlet Concentrations to Historical Tank Headspace Maximum Concentrations

COPC Number & Name	CAS Number	Occupational Exposure Limit (OEL)	Cartridge Inlet / Historic Headspace Concentration (% of OEL / % of OEL) ¹			
			SX-101	SX-104	2018 BY-108	
			Maximum	Maximum	Maximum	
Inorganic						
1	Ammonia	7664-41-7	25 ppm	796/25	1213/1572	767/2576
2	Nitrous Oxide	10024-97-2	50 ppm	NM/4	NM/35	NM/1662 (4)
3	Mercury	7439-97-6	25 µg/m ³	26/<0.2	16/32	27/68
Hydrocarbons						
4	1,3-Butadiene	106-99-0	1 ppm	<2/<0.2	<2/29	<4/338
5	Benzene	71-43-2	0.5 ppm	0.4/<0.6	0.5/0.8	0.5/<11 (2)
6	Biphenyl	92-52-4	0.2 ppm	<0.08/<0.1	<0.3/<0.09	<0.03/<5
Alcohols						
7	1-Butanol	71-36-3	20 ppm	0.1/0.05	0.4/0.6	3*/318 (22)
8	Methanol	67-56-1	200 ppm	<1/NM	<1/NM	0.6/<0.8 (0.01)
Ketones						
9	2-Hexanone	591-78-6	5 ppm	0.2/<0.08	0.4/0.2	0.3/0.9
10	3-Methyl-3-butene-2-one	814-78-8	0.02 ppm	n/a/NM	n/a/NM	n/a/NM
11	4-Methyl-2-hexanone	105-42-0	0.5 ppm	0.1/NM	0.06/NM	0.2/<0.8 (0.4)
12	6-Methyl-2-heptanone	928-68-7	8 ppm	n/a/NM	n/a/NM	0.02/NM
13	3-Buten-2-one	78-94-4	0.2 ppm	0.6/<3	1/5	4/<29
Aldehydes						
14	Formaldehyde	50-00-0	0.3 ppm	4/5	5/5	3/6
15	Acetaldehyde	75-07-0	25 ppm	0.3/NM	0.6/0.9	0.5/11
16	Butanal	123-72-8	25 ppm	0.01/0.04	0.05/0.5	0.5/0.5
17	2-Methyl-2-butenal	1115-11-3	0.03 ppm	n/a/NM	n/a/NM	n/a/NM
18	2-Ethyl-hex-2-enal	645-62-5	0.1 ppm	n/a/NM	n/a/NM	n/a/NM
New ²	2-Propenal	107-02-8	0.1 ppm	<0.9/NM	<0.9/<0.9	<0.9/<11
Furans and Substituted Furans						
19	Furan	110-00-9	1 ppb	<28/<230	100/<310 (143)	576/54700 (1840)
20	2,3-Dihydrofuran	1191-99-7	1 ppb	<2/NM	7/<34	<3/<47
21	2,5-Dihydrofuran	1708-29-8	1 ppb	<52/<730	<53/<980	<24/<5660*
22	2-Methylfuran	534-22-5	1 ppb	<12/<1300	<20/<1800	17/<4840*
23	2,5-Dimethylfuran	625-86-5	1 ppb	<4/NM	25/<25	<3/<34
24	2-Ethyl-5-methylfuran	1703-52-2	1 ppb	n/a/NM	n/a/NM	n/a/NM
25	4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	1 ppb	n/a/NM	n/a/NM	n/a/NM
26	3-(1,1-Dimethylethyl)-2,3-dihydrofuran	34314-82-4	1 ppb	n/a/NM	n/a/NM	n/a/NM
27	2-Pentylfuran	3777-69-3	1 ppb	7/NM	6/<17	<3/<24
28	2-Heptylfuran	3777-71-7	1 ppb	<3/NM	<3/<14	<3/6120* (<20)
29	2-Propylfuran	4229-91-8	1 ppb	<2/NM	<3/<21	<2/<30
30	2-Octylfuran	4179-38-8	1 ppb	n/a/NM	n/a/NM	n/a/NM
31	2-(3-Oxo-3-phenylprop-1-enyl)furan	717-21-5	1 ppb	n/a/NM	n/a/NM	n/a/NM
32	2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	1 ppb	n/a/NM	n/a/NM	n/a/NM
Phthalates						
33	Diethylphthalate	84-66-2	5 mg/m ³	<0.04/<0.02	<0.1 (0.04)/<0.01	0.02/<1
Nitriles						
34	Acetonitrile	75-05-8	20 ppm	2/<0.02	3/14	0.9/94
35	Propanenitrile	107-12-0	6 ppm	0.05/<0.06	0.08/<0.08 (0.05)	0.1/<0.8 (0.5)
36	Butanenitrile	109-74-0	8 ppm	0.05/<0.2	0.06/<0.3 (0.08)	0.2/<0.7 (0.4)
37	Pentanenitrile	110-59-8	6 ppm	0.05/<0.2	0.02/<0.2	0.04/<0.8 (0.2)
38	Hexanenitrile	628-73-9	6 ppm	0.02/<0.09	0.02/<0.1 (0.02)	0.03/<0.7 (0.1)
39	Heptanenitrile	629-08-3	6 ppm	n/a/NM	n/a/NM	n/a/NM
40	2-Methylene butanenitrile	1647-11-6	0.3 ppm	n/a/NM	n/a/NM	n/a/NM
41	2,4-Pentadienenitrile	1615-70-9	0.3 ppm	n/a/NM	n/a/NM	n/a/NM
Amines						
42	Ethylamine	75-04-7	5 ppm	<0.09/NM	0.3/<0.7	0.9/<0.3
Nitrosamines						
43	N-Nitrosodimethylamine	62-75-9	0.3 ppb	3358/<2	6935/9300	721/2063
44	N-Nitrosodiethylamine	55-18-5	0.1 ppb	44/<5	79/<37	13/<1030 (8)
45	N-Nitrosomethylethylamine	10595-95-6	0.3 ppb	31/<2	100/<14	188/<413 (8)
46	N-Nitrosomorpholine	59-89-2	0.6 ppb	11/<0.8	29/<6	<2/<153 (8)
Organophosphates						
47	Tributyl phosphate	126-73-8	0.2 ppm	<0.07/<0.06	<0.3/<0.06	<0.03/<3
48	Dibutyl butylphosphonate	78-46-6	0.007 ppm	<1/<1	<5/<1	<0.4/<91
Halogenated Hydrocarbons						
49	Chlorinated Biphenyls	Varies	1 mg/m ³	n/a/NM	n/a/NM	n/a/NM
50	2-Fluoropropene	1184-60-7	0.1 ppm	n/a/<2	n/a/<3	n/a/530 (n/a)

Table C.1. (continued)

COPC Number & Name	CAS Number	Occupational Exposure Limit (OEL)	Cartridge Inlet / Historic Headspace Concentration (% of OEL / % of OEL) ¹			
			SX-101	SX-104	2018 BY-108	
			Maximum	Maximum	Maximum	
Pyridines						
51	Pyridine	110-86-1	1 ppm	0.04/<0.1	0.1/0.2	0.2/<5 (0.3)
52	2,4-Dimethylpyridine	108-47-4	0.5 ppm	<0.04/<0.4	<0.04/<0.4	0.07/<8 (0.8)
Organonitrites						
53	Methyl nitrite	624-91-9	0.1 ppm	n/a/NM	n/a/NM	n/a/NM
54	Butyl nitrite	544-16-1	0.1 ppm	n/a/NM	n/a/NM	n/a/NM
Organonitrates						
55	Butyl nitrate	928-45-0	2.5 ppm	0.02/NM	n/a/NM	n/a/NM
56	1,4-Butanediol, dinitrate	3457-91-8	0.05 ppm	n/a/NM	n/a/NM	n/a/NM
57	2-Nitro-2-methylpropane	594-70-7	0.3 ppm	2/NM	n/a/NM	n/a/NM
58	1,2,3-Propanetriol, 1,3-dinitrate	623-87-0	0.05 ppm	n/a/NM	n/a/NM	n/a/NM
Isocyanates						
59	Methyl Isocyanate	624-83-9	20 ppb	n/a/NM	n/a/NM	n/a/NM
Organometallics						
New ²	Dimethylmercury	593-74-8	0.010 mg/m ³ (as Hg)	NM/NM	NM/NM	NM/NM
¹ "<" indicates the maximum is from a nonreport (<RL) analysis result, and reported (>RL) values for the COPC were not obtained or are less than 0.01% of the OEL. Value in parentheses, if present, indicates the maximum reported (detected) value >RL.						
² 2-propenal and dimethylmercury were added to the COPC List in September, 2017.						
[*] Suspect data due to sample quality issue discussed in Appendix C (e.g., low sample volume, more than one significant data quality flag, etc). Value in parentheses, (#), if present, indicates the maximum reported (detected) value >RL, or best estimate of true value.						
<i>italics</i>	Indicates that the historic concentration data is pre-2006 TWINS headspace results (often 1994-1997 data). Where more recent data are 10% or less of the 1990s maximum, the more recent maximum is included in parentheses without italics, using only the above-report maximum if available.					
n/a	Indicates that sampling and analysis have been performed but the analyte has not been detected above thresholds for reporting of tentatively identified compounds (TICs).					
NM	Not measured or not reported (cartridge inlet) or no measurement reported in databases (historic maximum).					
	Values highlighted in red indicate cartridge inlet concentrations that were significantly lower than the applicable historical maximum (<20% of historical). Values are highlighted only if 1) the historic maximum represented an above-report or above detect value, 2) either the cartridge or historical maximum was higher than tank farm action level of 50% of OEL, and 3) the historic maximum was one measured during undisturbed headspace conditions, for undisturbed cartridge tests, or any conditions, for tests during disturbance.					
	Values highlighted in yellow indicate cartridge inlet concentrations that were lower than the applicable historical maximum (<50% but >20% of historical). Values are highlighted only if 1) the historic maximum represented an above-report or above detect value, 2) either the cartridge or historical maximum was higher than tank farm action level of 50% of OEL, and 3) the historic maximum was one measured during undisturbed headspace conditions, for undisturbed cartridge tests, or any conditions, for tests during disturbance.					
	Heavy-line cell border indicates the bounding cartridge-inlet maximum concentration over all tests; border is applied only if there was at least one test in which measurement was performed for the COPC (not nitrous oxide, for example), and an above-report concentration (historic or cartridge) was more than 50% of the OEL in any of the tests.					

To better understand the historical maxima, the historical data sets were reviewed to determine which data were taken during planned tank operations that caused waste disturbance or were taken during or just after ventilation system outages. Such maxima are not relevant to the PAPR cartridge tests because they were performed during periods when no disturbances occurred.

Note that procedures already in place prevent air-purifying respirators from being used in downwind areas during certain types of planned operations; for example, waste transfers, other waste-disturbing activities, and ventilation restarts after outages. Tank farm personnel would use more protective equipment such as self-contained breathing apparatus or supplied air. Thus, maxima that come from data taken during these operations need to be recognized as such because they may be less pertinent to the intended purpose of cartridge testing.

Waste transfers, waste recirculation, and addition of water from evaporators are considered to be waste-disturbing activities in the discussion in this appendix. Raw water additions also are discussed when present; however, for dates when they are present without waste transfers, they are not taken as waste-disturbing events.

Table C.2. Comparison of Cartridge Inlet Concentrations to Historical Tank Farm Exhauster Maximum Concentrations

COPC Number & Name		Cartridge Inlet / Historic Headspace Concentration (% of OEL / % of OEL) ¹			
		CAS Number	Occupational Exposure Limit (OEL)	AX Exhauster	2018 AP Exhauster (New Exhauster)
				Maximum	Maximum
Inorganic					
1	Ammonia	7664-41-7	25 ppm	19/13	102/412
2	Nitrous Oxide	10024-97-2	50 ppm	NM/NM	NM/NM
3	Mercury	7439-97-6	25 µg/m ³	90/20	12/<50 (32)
Hydrocarbons					
4	1,3-Butadiene	106-99-0	1 ppm	<2/NM	4/<1
5	Benzene	71-43-2	0.5 ppm	0.09/NM	0.1/<2
6	Biphenyl	92-52-4	0.2 ppm	0.05/NM	<0.03/<0.6
Alcohols					
7	1-Butanol	71-36-3	20 ppm	0.02/NM	<0.02 (0.01)/0.2
8	Methanol	67-56-1	200 ppm	<1/NM	0.6/NM
Ketones					
9	2-Hexanone	591-78-6	5 ppm	0.005/NM	0.003/<0.2
10	3-Methyl-3-butene-2-one	814-78-8	0.02 ppm	n/a/NM	n/a/NM
11	4-Methyl-2-hexanone	105-42-0	0.5 ppm	<0.02/NM	<0.02/<0.4
12	6-Methyl-2-heptanone	928-68-7	8 ppm	n/a/NM	n/a/NM
13	3-Buten-2-one	78-94-4	0.2 ppm	0.2/NM	<0.2 (0.1)/<5 (2)
Aldehydes					
14	Formaldehyde	50-00-0	0.3 ppm	17/11	2/2
15	Acetaldehyde	75-07-0	25 ppm	0.3/0.5	0.05/0.09
16	Butanal	123-72-8	25 ppm	0.004/0.01	0.002/<0.04 (0.008)
17	2-Methyl-2-butenal	1115-11-3	0.03 ppm	n/a/NM	n/a/NM
18	2-Ethyl-hex-2-enal	645-62-5	0.1 ppm	n/a/NM	n/a/NM
New ²	2-Propenal	107-02-8	0.1 ppm	<0.9/<1	<0.9/<12
Furans and Substituted Furans					
19	Furan	110-00-9	1 ppb	<39/<6	57/715
20	2,3-Dihydrofuran	1191-99-7	1 ppb	<2/<6	<8/<73
21	2,5-Dihydrofuran	1708-29-8	1 ppb	<17/<6	<25/<290
22	2-Methylfuran	534-22-5	1 ppb	<9/<5	<10 (7)/<247
23	2,5-Dimethylfuran	625-86-5	1 ppb	<4/<4	<4/<53
24	2-Ethyl-5-methylfuran	1703-52-2	1 ppb	n/a/NM	n/a/NM
25	4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	1 ppb	n/a/NM	n/a/NM
26	3-(1,1-Dimethylethyl)-2,3-dihydrofuran	34314-82-4	1 ppb	n/a/NM	n/a/NM
27	2-Pentylfuran	3777-69-3	1 ppb	<3/<3	<3/<37
28	2-Heptylfuran	3777-71-7	1 ppb	<3/<3	<3/<31
29	2-Propylfuran	4229-91-8	1 ppb	<3/<4	<3/<47
30	2-Octylfuran	4179-38-8	1 ppb	n/a/NM	n/a/NM
31	2-(3-Oxo-3-phenylprop-1-enyl)furan	717-21-5	1 ppb	n/a/NM	n/a/NM
32	2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	1 ppb	n/a/NM	n/a/NM
Phthalates					
33	Diethylphthalate	84-66-2	5 mg/m ³	<0.02/NM	0.02/<0.1
Nitriles					
34	Acetonitrile	75-05-8	20 ppm	0.4/NM	0.07/<5 (0.3)
35	Propanenitrile	107-12-0	6 ppm	0.02/NM	<0.005/<0.04
36	Butanenitrile	109-74-0	8 ppm	0.01/NM	<0.002/<0.04
37	Pentanenitrile	110-59-8	6 ppm	0.003/NM	<0.002/<0.04
38	Hexanenitrile	628-73-9	6 ppm	<0.001/NM	<0.002/<0.03
39	Heptanenitrile	629-08-3	6 ppm	n/a/NM	n/a/NM
40	2-Methylene butanenitrile	1647-11-6	0.3 ppm	n/a/NM	n/a/NM
41	2,4-Pentadienenitrile	1615-70-9	0.3 ppm	n/a/NM	n/a/NM
Amines					
42	Ethylamine	75-04-7	5 ppm	<0.09/NM	<0.09/<0.3 (0.2)
Nitrosamines					
43	N-Nitrosodimethylamine	62-75-9	0.3 ppb	72/46	3130 ⁴ /5267
44	N-Nitrosodiethylamine	55-18-5	0.1 ppb	20/<3	<13/<48 (17)
45	N-Nitrosomethylethylamine	10595-95-6	0.3 ppb	40/2	22/49
46	N-Nitrosomorpholine	59-89-2	0.6 ppb	51/151	3/16
Organophosphates					
47	Tributyl phosphate	126-73-8	0.2 ppm	<0.05/NM	<0.03/<0.3
48	Dibutyl butylphosphonate	78-46-6	0.007 ppm	<0.6/NM	<0.4/<10
Halogenated Hydrocarbons					
49	Chlorinated Biphenyls	Varies	1 mg/m ³	n/a/NM	n/a/NM
50	2-Fluoropropene	1184-60-7	0.1 ppm	n/a/NM	n/a/NM

Table C.2. (continued)

COPC Number & Name		Cartridge Inlet / Historic Headspace Concentration (% of OEL / % of OEL) ¹			
		CAS Number	Occupational Exposure Limit (OEL)	AX Exhauster	2018 AP Exhauster (New Exhauster)
				Maximum	Maximum
	Pyridines				
51	Pyridine	110-86-1	1 ppm	0.01/NM	<0.05/<0.3
52	2,4-Dimethylpyridine	108-47-4	0.5 ppm	<0.04/NM	<0.05/<0.4
	Organonitriles				
53	Methyl nitrite	624-91-9	0.1 ppm	n/a/NM	n/a/NM
54	Butyl nitrite	544-16-1	0.1 ppm	n/a/NM	n/a/NM
	Organonitrates				
55	Butyl nitrate	928-45-0	2.5 ppm	n/a/NM	n/a/NM
56	1,4-Butanediol, dinitrate	3457-91-8	0.05 ppm	n/a/NM	n/a/NM
57	2-Nitro-2-methylpropane	594-70-7	0.3 ppm	n/a/NM	n/a/NM
58	1,2,3-Propanetriol, 1,3-dinitrate	623-87-0	0.05 ppm	n/a/NM	n/a/NM
	Isocyanates				
59	Methyl isocyanate	624-83-9	20 ppb	n/a/NM	n/a/NM
	Organometallics				
New ²	Dimethylmercury	593-74-8	0.010 mg/m ³ (as Hg)	NM/NM	NM/3
¹ "<" indicates the maximum is from a nonreport (<RL) analysis result, and reported (>RL) values for the COPC were not obtained or are less than 0.01% of the OEL. Value in parentheses, if present, indicates the maximum reported (detected) value >RL.					
² 2-propenal and dimethylmercury were added to the COPC List in September, 2017.					
[*] Suspect data due to sample quality issue discussed in Appendix C (e.g., low sample volume, more than one significant data quality flag, etc). Value in parentheses, (#), if present, indicates the maximum reported (detected) value >RL, or best estimate of true value.					
<i>italics</i> Indicates that the historic concentration data is pre-2006 TWINS headspace results (often 1994-1997 data). Where more recent data are 10% or less of the 1990s maximum, the more recent maximum is included in parentheses without italics, using only the above-report maximum if available.					
<i>n/a</i> Indicates that sampling and analysis have been performed but the analyte has not been detected above thresholds for reporting of tentatively identified compounds (TICs).					
<i>NM</i> Not measured or not reported (cartridge inlet) or no measurement reported in databases (historic maximum).					
Values highlighted in red indicate cartridge inlet concentrations that were significantly lower than the applicable historical maximum (<20% of historical). Values are highlighted only if 1) the historic maximum represented an above-report or above detect value, 2) either the cartridge or historical maximum was higher than tank farm action level of 50% of OEL, and 3) the historic maximum was one measured during undisturbed headspace conditions, for undisturbed cartridge tests, or any conditions, for tests during disturbance.					
Values highlighted in yellow indicate cartridge inlet concentrations that were lower than the applicable historical maximum (<50% but >20% of historical). Values are highlighted only if 1) the historic maximum represented an above-report or above detect value, 2) either the cartridge or historical maximum was higher than tank farm action level of 50% of OEL, and 3) the historic maximum was one measured during undisturbed headspace conditions, for undisturbed cartridge tests, or any conditions, for tests during disturbance.					
Heavy-line cell border indicates the bounding cartridge-inlet maximum concentration over all tests; border is applied only if there was at least one test in which measurement was performed for the COPC (not nitrous oxide, for example), and an above-report concentration (historic or cartridge) was more than 50% of the OEL in any of the tests.					

Only TWINS IH data were checked for disturbance conditions. Headspace data (TWINS and SWIHD) were not so reviewed because it was expected to be rare for headspace sampling to be conducted during planned operations that caused waste disturbances.

The first type of information used to identify waste-disturbing or ventilation-disturbing activities was the title of the Industrial Hygiene survey in the TWINS IH database. Surveys were considered to reflect waste-disturbing operations if their titles included a reference to “retrieval,” “transfer,” “tank Y to tank Z,” “Z% complete” (referring to a retrieval), ALC (air-lift circulator), recirculation, portable exhausters on single-shell tanks, or the 242-A evaporator (implying an ongoing evaporation campaign). However, if the title also included the words “baseline,” “re,” or “start,” the survey was considered to precede transfer operations and to not include the effects of waste disturbance. Ventilation-disturbing activities were identified by Survey Titles that included a reference to “outage,” “restart of exhauster,” “exhauster startup,” or just “startup” if there was no additional reference to a transfer or retrieval.

The information in the Survey Title was tested and supplemented by consulting the TWINS databases of tank transfers (pre-2001 and post-2000).⁽⁵⁰⁾ These databases are related to Best Basis Inventory (BBI)⁵¹ determinations and focus on activities that change the waste inventories in tanks. They do not include any information about ventilation disturbances, and only include information on in-tank recirculation if it indirectly changed the inventory (e.g., by inducing a gas release).

The cartridge inlet concentrations discussed in the following sections include (as appropriate) above-report concentrations, below-report concentrations (in which case RLs were used for comparison), and below-detects (in which case DLs were used for comparison). The use of below-detect versus below-report depends on the type of sample analysis. For more background, see Appendix D, which discusses the difference between DLs and RLs for furans.

The larger discrepancies, or apparent discrepancies, between historical data and cartridge inlet concentrations are discussed below. Discrepancies are discussed if the maximum historical concentration of a compound was greater than 10% of the OEL and the maximum cartridge inlet concentration was less than 50% of the historical value. However, discrepancies are considered significant only if the maximum historical concentration was greater than 10% of the OEL and the maximum cartridge inlet concentration is less than 20% of the historical value. In some cases other COPCs (even if not discrepant by the above definition) are also discussed. When the cartridge inlet maximum is greater than or equal to the historical, there is usually no discussion.

In cases where the cartridge inlet concentration (maximum or average) was below the RL or the DL, the RL or DL is used as a basis for comparison. The same approach is taken for historical concentrations that were below the RL (“below-report”, or “<RL”).

It is recognized that the data set of historical concentration maxima has limitations in terms of using it to determine if the tested cartridge inlet concentrations are high enough to include all release concentrations. Historical data are sparse; therefore, their maxima might be lower than actual maxima that existed but were not sampled. On the other hand, some of the historical maxima date back to the 1990s when concentrations could be expected to be higher. Ventilation flow rates, waste organic inventories, and sampling locations also could have changed between the time⁵² of historical sampling and the time of cartridge testing. To the extent that historical records permitted, these features of the data have been considered for the comparisons that are made in subsequent sections.

⁵⁰ See the “Tank Transfers” menu item under <https://twins.labworks.org/twinsdata/Forms/About.aspx>. Note that many entries in these databases refer to inventory changes caused not by a waste-affecting operation but by re-baselining, changes in inventory calculation assumptions, changes in level instrumentation, etc. Some (not all) spontaneous gas releases also are included.

⁵¹ The BBI establishes the inventory of the underground waste storage tanks at Hanford by using sample data, process knowledge, surveillance data, and waste stream composition information from the Hanford Defined Waste (HDW) computer model (Agnew SF, J. Boyer, RA Corbin, TB Duran, JR FitzPatrick, KA Jurgensen, TP Ortiz, and BL Young. 1997. *Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 4*. LA-UR-96-3860, Los Alamos National Laboratory, Los Alamos, New Mexico).

⁵² Headspace vapors are produced, in part from radiolytic-degradation of various tank waste constituents. The radiation dose and source concentration of key organic wastes was higher earlier in the waste storage timeline and may account for higher concentrations observed in some earlier sampling campaigns.

C.1 SX-101 Headspace Comparison with Historical Data

The maximum and average COPC concentrations measured during cartridge testing were compared to the maximum and average historical concentrations, and where differences were found, the historical data were examined for explanations in the type or circumstances of sampling.

SX-101 has been almost inactive since 2003. A small volume addition of raw water was made in 2005. The sludge-cooler ventilation was not shut down until 2003. Because of the change in ventilation, headspace and activity data collected prior to 2004 are considered irrelevant.

With respect to waste disturbance, it must be noted that SX farm tanks are arranged in three-tank cascades. Tanks SX-101, SX-102, and SX-103 are connected by overflow lines through which vapors may move from one tank headspace to another (Huckaby et al. 2004). It is physically possible for waste disturbances in SX-102 and SX-103 to have affected vapor concentrations in SX-101. However, there were no waste-disturbing operations in any of the tanks of the SX-101 cascade in 2006, the only year for which post-2003 SX-101 headspace data are available. Hence, none of the available data for SX-101 were taken during waste-disturbing conditions.

The larger discrepancies, or apparent discrepancies, between cartridge inlet and historical concentrations are discussed in the following sections.

C.1.1 Ammonia

The maximum cartridge inlet concentrations was 796% of the OEL for the PAPR cartridges. This cartridge inlet maximum is high compared to the historical maximum concentration of 6.22 ppm (25% of the OEL). This data point comes from the TWINS IH database and was a breather-filter measurement made on August 7, 2006. The historical data apparently do not provide good guidance for the presence of high concentrations under current headspace conditions.

C.1.2 Nitrous Oxide

Nitrous oxide was not measured in cartridge testing. There is one historical concentration in TWINS IH, 2.1 ppm (4.2% of the OEL). The maximum above-report concentration in the TWINS HS database was measured in 1997 and is not relevant.

C.1.3 Mercury

The maximum cartridge inlet concentrations was 25.9% of the OEL for the PAPR cartridges. This cartridge inlet maximum is high compared to the sole historical measurement, a below-report with an RL of 0.000051 mg/m³ (concentration <0.204% of the OEL). This measurement came from TWINS IH; it was a breather-filter measurement made on August 7, 2006. For this chemical, the historical data apparently do not provide good guidance for the presence of high concentrations under current headspace conditions.

C.1.4 Furan and Substituted Furans

For PAPR cartridges, the maximum inlet concentration of furan was below the DL of the Carbotrap 300 TDU method (i.e., <28.5% of the OEL). The maximum PAPR inlet concentration of 2-pentylfuran was 6.85% of the OEL. The other PAPR cartridge inlet concentrations for furans were below the applicable DLs.

None of the furan chemicals had historical concentration data given in the TWINS HS database. The TWINS IH database contained data for only three of these chemicals: furan, 2,5-dihydrofuran, and 2-methylfuran. All three of these were measured only in 2006 and had only two measurements each, all of which were below-reports. These below-report maxima, measured by the Carbotrap 300 TDU method, had RLs of <230% of the OEL for furan, <730% for 2,5-dihydrofuran, and <1300% for 2-methylfuran. There are no above-report historical data for these chemicals, so no conclusion can be drawn about where their cartridge inlet concentrations lie with respect to historical data.

C.1.5 N-nitrosodimethylamine (NDMA)

The maximum cartridge inlet concentration was 3358% of the OEL for the PAPR cartridges, which is very high compared to the sole historical concentration, a below-report datum that had an RL of 0.0070 ppb (<2.3% of the OEL). This value came from the TWINS IH database; it was a breather-filter measurement made on August 7, 2006. There are no TWINS HS data for nitrosamines in this tank. For this chemical, the historical data apparently do not provide good guidance for the presence of high concentrations under current headspace conditions.

C.1.6 N-nitrosodiethylamine (NDEA), N-nitrosomethylethylamine (NMEA), N-nitrosomorpholine

The comparison between the cartridge inlet maxima and the historical maxima gives the same type of results for these nitrosamines as for NDMA. For the PAPR cartridges, the cartridge inlet maxima were 43.8% of the OEL for NDEA, 30.9% of the OEL for NMEA, and 10.6% of the OEL for N-nitrosomorpholine.

The historical maxima were below-reports that had RLs of <5.09% of the OEL for NDEA, <1.97% for NMEA, and <0.75% for N-nitrosomorpholine. These values were from the sole historical sample, which was in the TWINS IH database; it was a breather-filter measurement made on August 7, 2006. There are no TWINS HS data for nitrosamines in this tank. For these chemicals, the historical data apparently do not provide good guidance for the presence of high concentrations under current headspace conditions.

C.1.7 Summary of Historical Data Comparisons

In summary, most cartridge inlet maxima for the chemicals of interest in the SX-101 headspace were substantially higher than the historical maxima. These included ammonia, mercury, NDMA, NDEA, NMEA, and N-nitrosomorpholine.

The cartridge inlet concentrations that were substantially lower than historical data can be described as follows:

- Differences could not be resolved because of the scarcity of above-report historical data: furan, 2,3-dihydrofuran, 2,5-dihydrofuran, 2-methylfuran, 2,5-dimethylfuran, 2-pentylfuran, 2-heptylfuran, and 2-propylfuran.

C.2 SX-104 Headspace Comparison with Historical Data

The maximum and average COPC concentrations measured during cartridge testing were compared to the maximum and average historical concentrations, and where differences were found, the historical data were examined for explanations in the type or circumstances of sampling.

Salt well pumping undertaken in the SX-104 tank during the period 1997–1999 substantially reduced its waste volume from 587 kgal to 466 kgal. This pumping is considered to have changed the waste sufficiently to make pre-2000 data irrelevant, thereby excluding TWINS HS data that were measured in 1995. Furthermore, pre-2004 data are irrelevant because of the change from active to passive ventilation in 2003.

Because SX Farm tanks are arranged in three-tank cascades, tanks SX-104, SX-105, and SX-106 are connected by overflow lines through which vapors may move from one tank headspace to another (Huckaby et al. 2004). It is physically possible for waste disturbances in SX-105 and SX-106 to have affected vapor concentrations in SX-104. There was no activity in SX-104 after 1999. The other tanks in its cascade—SX-105 and SX-106—had no waste-disturbing operations in 1995, 2006, or 2015, the only years for which SX-104 headspace data are available. Hence, none of the available data for SX-104 were taken during waste-disturbing conditions.

The larger discrepancies, or apparent discrepancies, between cartridge inlet and historical concentrations are discussed in the following sections.

C.2.1 Ammonia

The maximum cartridge inlet concentration of 1213% of the OEL (PAPR cartridges) is within a factor of two of the historical maximum concentration of 393 ppm (1572% of the OEL). This data point came from the SWIHD HS database and was measured on July 10, 2015. By contrast, the single ammonia measurement in the TWINS IH database, made in 2006 at the breather filter, was 47 ppm. The more recent historical data are considered to be comparable with the cartridge testing inlet concentrations.

C.2.2 Nitrous Oxide

Nitrous oxide was not measured in cartridge testing, and there are no nitrous oxide data in the SWIHD HS database. There is one historical concentration in TWINS IH, 17.3 ppm (35% of the OEL), measured in 2006.

C.2.3 Mercury

The maximum cartridge inlet concentration was 15.5% of the OEL for the PAPR cartridges. The sole historical measurement was 0.008 mg/m³ (32% of the OEL). This data point came from the SWIHD HS database and was measured on July 10, 2015. The single mercury measurement in the TWINS IH database, made in 2006 at the breather filter, was 0.002 mg/m³. The PAPR cartridge inlet maximum is about 50% of the 2015 historical datum. The cartridge inlet maxima are considered comparable to the available historical datum.

C.2.4 1,3-Butadiene

The maximum cartridge inlet concentration was less than the RL, which was 1.98% OEL for PAPR cartridges). This is low compared to the historical maximum concentration of 0.293 ppm (29% of the OEL). This data point came from the SWIHD HS database and was measured on July 10, 2015. By contrast, the single measurement in the TWINS IH database, made in 2006, was less than the RL of 0.0028 ppm (<0.28% OEL). The cartridge testing inlet concentration was less than 20% of the historical maximum and is considered significantly different.

C.2.5 Furan

For PAPR cartridges, the inlet maximum concentration was 100% of the OEL (Carbotrap 300 TDU method). The historical maximum was a 2006 below-report with an RL of 3.1 ppb (<310% of the OEL). The highest above-report historical concentration was in the SWIHD HS database, measured on July 10, 2015. This concentration was 1.43 ppb (143% of the OEL measured using the Carbotrap 300 TDU method). The PAPR cartridge testing inlet concentration was comparable to the 2015 historical measurement.

C.2.6 Substituted Furans

For PAPR cartridges, substituted furans that were measured by the furans method were 2,3-dihydrofuran (6.55% of the OEL), 2,5-dimethylfuran (25.2% of the OEL), 2-pentylfuran (5.69% of the OEL), 2-heptylfuran (<DL [2.52% of the OEL]), and 2-propylfuran (<DL [2.51% of the OEL]). The substituted furans measured by the Carbotrap 300 TDU method were below their DLs, with concentrations of <52.5% of the OEL for 2,5-dihydrofuran and <21.1% OEL for 2-methylfuran.

The TWINS IH and SWIHD HS databases contained only below-report data for all the substituted furans. The below-report maxima have RLs of <34% of the OEL for 2,3-dihydrofuran (2015 SWIHD HS), <980% of the OEL for 2,5-dihydrofuran (2006 TWINS IH), <1800% of the OEL for 2-methylfuran (2006 TWINS IH), <25% of the OEL for 2,5-dimethylfuran (2015 SWIHD HS), <21% of the OEL for 2-propylfuran (2015 SWIHD HS), <17% of the OEL for 2-pentylfuran (2015 SWIHD HS), and <14% of the OEL for 2-heptylfuran (2015 SWIHD HS).

The cartridge inlet maximum for 2,5-dimethylfuran, which was 25.2% of the OEL for the PAPR cartridges, was higher than the RL of the below-report historical maximum (<25% of the OEL), suggesting higher concentration during the cartridge test. However, there are no above-report historical data for these chemicals, so no firm conclusion can be drawn about where their cartridge inlet concentrations lie with respect to historical data. In addition, one blank and one baseline concentration of 2,5-dimethylfuran were above the DL and the blank was also above the RL. These data call the elevated inlet measurements for this COPC into question.

C.2.7 Acetonitrile

The maximum cartridge inlet concentration was 2.61% of the OEL for the PAPR cartridges, measured by the Carbotrap 300 TDU method. This value is low compared to the historical maximum concentration of 2.82 ppm (14% of the OEL using the acetonitrile method), or 0.803 ppm (4.02% of the OEL using the Carbotrap 300 TDU method). These two historical measurements were from the same sampling event, but different analytical methods were used. They came from the SWIHD HS database and were measured on July 10, 2015. The single measurement in the TWINS IH database, made in 2006 at the breather filter,

was less than the RL of 0.0028 ppm (<0.014% of the OEL). Although the difference in measurement methods might account for some of the differences between cartridge inlet and historical maxima concentrations, the maximum cartridge testing inlet concentration was less than 20% of the recent historical maximum and is considered significantly different.

C.2.8 N-nitrosodimethylamine (NDMA)

The maximum cartridge inlet concentration was 6935% of the OEL for the PAPR cartridges. The historical maximum concentration was 27.9 ppb (9300% of the OEL). The historical value came from the SWIHD HS database; it was measured on July 10, 2015. The cartridge testing inlet maximum was greater than 50% of the historical maximum and therefore is considered comparable.

C.2.9 N-nitrosodiethylamine (NDEA), N-nitrosomethylethylamine (NMEA), N-nitrosomorpholine

The PAPR cartridge inlet maxima were 79.4%, 100%, and 29.2% of the OEL, respectively, for NDEA, NMEA, and N-nitrosomorpholine. The TWINS IH and SWIHD HS databases contained only below-report data for these three nitrosamines. The maximum historical RLs, which were all from 2015 SWIHD HS data, were <37% of the OEL for NDEA, <14% of the OEL for NMEA, and <5.7% of the OEL for N-nitrosomorpholine. Although all the historical maxima are below-report measurements, their RLs are so much lower than the concentrations measured during cartridge testing that it is clear the cartridge-testing concentrations were higher.

C.2.10 Summary of Historical Data Comparisons

Some cartridge inlet maxima for the chemicals of interest in the SX-104 headspace were substantially higher than the historical maxima. These included NDEA, NMEA, and N-nitrosomorpholine. Other chemicals—ammonia, mercury, furan, and NDMA—had cartridge inlet maxima that were within a factor of 2 of historical maxima and were considered comparable.

The cartridge inlet concentrations that were lower than historical data can be described as follows:

- Differences could not be resolved because of the scarcity of above-report data: 2,3-dihydrofuran, 2,5-dihydrofuran, 2-methylfuran, 2,5-dimethylfuran, 2-propylfuran, 2-pentylfuran, 2-heptylfuran.
- Cartridge inlet concentrations were determined to be significantly lower than above-report historical concentrations: 1,3-butadiene, acetonitrile.
- In the case of acetonitrile, one possible reason for concentration differences between the cartridge-inlet maxima and the historical maxima was that the former were measured using the Carbotrap 300 TDU method and the latter using the acetonitrile method.

C.3 AX Exhauster Comparison to Historical Data

The maximum and average COPC concentrations measured during cartridge testing, which was performed after active ventilation was added to the AX Farm, were compared to the maximum and average historical concentrations that were present after the ventilation change. Where differences were found, the historical data were examined for explanations in the type or circumstances of sampling.

The AX Farm exhauster was installed in late February 2017. The only activity in the AX Farm during 2017 was an addition of 1 kgal of raw water during the July 18–19, 2017 timeframe. This low-volume activity is unlikely to have had any effect in October 2017 when vapor data were measured. Hence, none of the available data for the AX Farm, after exhauster installation, were taken during waste-disturbing conditions.

The larger discrepancies, or apparent discrepancies, between cartridge inlet and historical concentrations are discussed in the following sections.

C.3.1 Ammonia

The maximum cartridge inlet concentration was 19.2% for the PAPR cartridges. The historical maximum was 3.22 ppm (12.9% of the OEL). The cartridge-inlet maximum is comparable to the historical maximum.⁵³

C.3.2 Nitrous Oxide

Nitrous oxide was not measured in cartridge testing or in the relevant historical data.

C.3.3 Mercury

The maximum cartridge inlet concentration was 90.0% for the PAPR cartridges, which was high compared to the historical maximum of 0.005 mg/m³ (20.0% of the OEL). For this chemical, the cartridge test data and the historical data are in agreement in that there is no sign that the cartridge testing missed capturing high concentrations.

C.3.4 Formaldehyde

The maximum cartridge inlet concentration was 16.8% for the PAPR cartridges, a maximum that was higher than the historical maximum concentration of 11.3% of the OEL. For this chemical, the cartridge test data and historical data are in agreement.

C.3.5 N-nitrosodimethylamine (NDMA)

The maximum cartridge inlet concentration was 71.6% for the PAPR cartridges, higher than the historical maximum concentration of 45.7% of the OEL. For this chemical, the cartridge test data and historical data are commensurate.

C.3.6 N-nitrosodiethylamine (NDEA)

The maximum cartridge inlet concentration was 20.4% for the PAPR cartridges, higher than the historical concentrations, below-reports with a maximum RL of 3% of the OEL. This chemical had a cartridge test maximum concentration that exceeded the historical maximum concentration by more than a factor of 5; thus, there is no indication that the cartridge-testing missed capturing high concentrations.

⁵³ At the time when cartridge data were first reported [4], ammonia data from the AX exhauster surveys were not yet available either in SWIHD Source or in TWINS IH. The data have since been added to TWINS IH and are presented here.

C.3.7 N-nitrosomethylethylamine (NMEA)

The maximum cartridge inlet concentration was 40.3% for the PAPR cartridge test, higher than the historical maximum of 1.67% of the OEL. This was an unusually high concentration in the inlet data, but there were no quality flags or baseline or blank concentrations that would put the cartridge-inlet maximum under suspicion. In any case, the second-highest inlet concentration was 5.42%, also higher than the historical maximum. The cartridge test maximum concentration for NMEA exceeded historical maximum concentrations by more than a factor of 20. Thus, there is no indication that cartridge testing missed capturing high concentrations.

C.3.8 N-nitrosomorpholine

The maximum cartridge inlet concentration was 51.5% for the PAPR cartridges, lower than the historical maximum of 151% of the OEL. For this chemical, the cartridge test and historical data are considered to be commensurate because the cartridge test maximum concentration, although moderately lower than the historical measurement, is within a factor of 5.

C.3.9 Summary of Historical Data Comparisons

A number of cartridge inlet maximum concentrations for COPCs in the AX exhauster were higher than historical maximum concentrations. These COPCs included ammonia, mercury, formaldehyde, NDMA, NDEA, and NMEA.

Cartridge inlet concentrations that were substantially lower than historical data can be described as follows:

- Differences could not be resolved, and cartridge inlet data were between 20% and 50% of historical maximum: N-nitrosomorpholine.

C.4 BY-108 Headspace (2018 Tests) Comparison to Historical Data

The maximum and average COPC concentrations measured during cartridge testing were compared to the maximum and average historical concentrations, and where differences were found, the historical data were examined for explanations in the type or circumstances of sampling.

BY-108 has been inactive throughout the period of record for which historical vapor concentration data have been collected. Regarding waste disturbances, it must be noted that BY Farm tanks are arranged in six-tank cascades that tie three tanks in BX Farm to three tanks in BY Farm. Tanks BX-107, BX-108, BX-109, BY-107, BY-108, and BY-109 are connected by overflow lines through which vapors may move from one tank headspace to another (Huckaby et al. 2004). Thus, it would have been physically possible for waste disturbances in any of five other tanks to have affected vapor concentrations in BY-108. However, there were no waste-disturbing operations in any of the tanks of the BY-108-related cascades in the period during which vapor data were recorded. Hence none of the available data for BY-108 were taken during waste-disturbing conditions.

The larger discrepancies, or apparent discrepancies, between cartridge inlet and historical concentrations are discussed in the following sections.

C.4.1 Ammonia

The maximum PAPR cartridge inlet concentration was 767% of the OEL. This cartridge inlet maximum is low compared to the historical maximum concentration of 644 ppm (2576% of the OEL). This historical data point comes from the TWINS IH database, which contains only one ammonia datum that was a breather-filter measurement made on July 14, 2009. For comparison, five October 2016 samples in SWIHD HS contained 367 to 441 ppm ammonia. The cartridge inlet maximum falls between 20% and 50% of the historical maximum, but not below the 20% level that is considered significantly below historical.

C.4.2 Nitrous Oxide

Nitrous oxide was not measured in cartridge testing. The relatively recent historical maximum in TWINS IH, 1.80 ppm (3.60% of the OEL) was measured at the breather filter in 2009. However, this concentration of 1.8 ppm (3.6% of the OEL) was measured via a nitrous oxide badge, which probably did not describe the nitrous oxide concentration in the tank headspace. The maximum above-report concentration in the TWINS HS database was 831 ppm (1662% of the OEL); it was measured in September 1996.

C.4.3 Mercury

The maximum PAPR cartridge inlet concentration was 27.3% of the OEL. The value is low compared to the historical maximum, 0.0170 mg/m³ (68.0% of the OEL). This measurement came from SWIHD HS and was taken in October 2016. The cartridge inlet maximum falls between 20% and 50% of the historical maximum, but not below the 20% level that is considered significantly below historical.

C.4.4 1,3-Butadiene

The maximum PAPR cartridge inlet concentration was a below-report with an RL of 3.82% of the OEL. This is low compared to the historical maximum concentration, which comes from TWINS IH and was taken on April 8, 2008. It had a concentration of 3.38 ppm (338% of the OEL). For comparison, six October 2016 samples in SWIHD HS contained 1.79 to 2.64 ppm of butadiene. The 10 above-reports in TWINS HS were taken between 1994 and 1997 and ranged from 0.0430 ppm to 0.174 ppm (4.30 to 17.4% of the OEL). The maximum cartridge inlet concentration was much less than 20% of the maximum historical measurement, and therefore was significantly below the historical record.

C.4.5 Benzene

The maximum PAPR cartridge inlet concentration of 0.48% of the OEL is low compared to the historical maximum concentration, a below-report datum that had an RL of 0.0529 ppm (10.6% of the OEL). This RL was for a September 17, 2009, sample in TWINS IH whose volume was small (0.15 L), producing an unusually high RL. The maximum relatively recent above-report concentration, excluding TWINS HS data, was 0.0100 ppm (2.00% OEL), found in the SWIHD HS database and measured in October 2016. The numerous above-report historical data in TWINS HS, which were collected between 1994 and 1997, ranged from 0.0160 ppm to 0.189 ppm (up to 37.9% of the OEL). The maximum cartridge inlet concentration is a little more than 20% of the recent historical maximum in SWIHD HS, and <20% of the older historical maximum in TWINS HS. The cartridge inlet maximum is considered to be significantly less than the historical maxima.

C.4.6 1-Butanol

The maximum PAPR cartridge inlet concentration of 2.76% of the OEL is less than 20% of the TWINS IH maximum of 4.32 ppm (21.6% OEL) found from 2009 breather-filter data. It is also much lower than the 63.5 ppm (318% of the OEL) measured in the headspace on October 27, 1994. The above-report TWINS HS headspace data collected on other dates between 1994 and 1997 were between 4.40 and 22.1 ppm (22.0 to 110% of the OEL). The cartridge inlet concentration is less than 20% of historical high concentrations and therefore is considered to be significantly less than the historical maxima.

All of the above-report PAPR cartridge inlet data have multiple data-quality flags, “ELQYa” or “ELQYac,” indicating measurements made above the calibration range with spike recovery outside its specified range. The “EY” portion of the set of flags means that concentrations are probably in the range where the instrument response is no longer linear and may be underestimates. The “Q” indicates data are qualitative only. However, it is unlikely that the flags mean that actual concentrations were high enough to change the conclusion that cartridge inlet maxima were significantly less than historical maxima.

C.4.7 Acetaldehyde

The maximum PAPR cartridge inlet concentration of 0.52% of the OEL is lower than the maximum of 2.8 ppm (11.3% of the OEL) that was measured on April 8, 2008. This was the only measurement in TWINS IH. No data were found in TWINS HS, and the October 2016 SWIHD HS maximum was 0.302 ppm (1.21% of the OEL). The cartridge inlet concentration is less than 20% of the historical maximum and is considered significantly less than historical, with the caveat that several recent headspace concentrations were close to the cartridge inlet maximum.

C.4.8 Furan

The maximum PAPR cartridge inlet concentration of 576% of the OEL is much lower than the maximum in the TWINS IH database, which is a below-report with an RL of 58.3 ppb (<5830% of the OEL). This high RL came from a 0.15-L sample taken on September 17, 2009. The cartridge inlet concentration also was much lower than the only above-report concentration in the TWINS HS database, 547 ppb (54,700% of the OEL), which was measured in the headspace in 1994 using a method similar to the Carbotrap 300 TDU. The only above-report concentration in the TWINS IH database was 10.4 ppb (1036% of the OEL), which was measured in a 1-L sample taken at a breather filter on September 17, 2009. In the SWIHD HS database, the maximum concentration was 18.4 ppb (1840% of the OEL) in October 2016. The cartridge inlet concentration is less than 20% of the oldest historical maximum but is within the range of 20 to 50% of the more recent above-report maximum. The cartridge inlet concentration is considered significantly less than historical, with the caveat that several recent headspace concentrations were close to the cartridge inlet maximum.

C.4.9 2,3-Dihydrofuran, 2,5-Dihydrofuran, 2-Methylfuran, 2,5-Dimethylfuran, 2-Pentylfuran, 2-Propylfuran

For both 2,5-dihydrofuran and 2-methylfuran, the PAPR cartridge inlet concentrations are much less than the below-report historical maxima that had RLs of ~5000% of the OEL. These high historical RLs came from the same 0.15-L TWINS IH sample discussed for furan. The cartridge inlet maximum was less than the DL of 23.5% OEL for 2,5-dihydrofuran, while the cartridge inlet maximum was 16.6% of the OEL for 2-methylfuran. Both of these cartridge inlet maxima were measured by the Carbotrap 300 TDU method.

For 2,3-dihydrofuran, 2,5-dimethylfuran, 2-pentylfuran, and 2-propylfuran, the PAPR cartridge inlet concentrations were measured by the furans method and are less than the DL of ~3% of the OEL (or 1.79% of the OEL, for 2-propylfuran). All of the historical maxima were below-reports with RLs in the range of ~20 to 50% OEL.

There were no above-report historical data, so no conclusion can be drawn about where the cartridge inlet concentrations lie with respect to historical data.

C.4.10 2-Heptylfuran

The maximum PAPR cartridge inlet concentration is a below-detect for which the DL was 2.84% of the OEL. This may or may not be consistent with the historical maximum from recent data, a below-report with an RL of 0.196 ppb (<19.6% of the OEL in SWIHD HS). In addition, the cartridge inlet maximum is much lower than the TWINS HS maximum of 61.2 ppb (6120% of the OEL) measured in the headspace in 1994 using a method similar to the Carbotrap 300 TDU. The maximum cartridge inlet concentration is less than 20% of the maximum (TWINS HS) historical data and is considered to be significantly lower than the historical maximum. However, it is worth noting that both of the BY-108 2-heptylfuran measurements that are present in TWINS HS were considered to be misidentifications [7].

C.4.11 Acetonitrile

The maximum PAPR cartridge inlet concentration of 0.87% of the OEL, measured by the Carbotrap 300 TDU method, is much lower than the historical maximum of 18.8 ppm (94.0% of the OEL) that was measured in October 2016. This historical maximum comes from SWIHD HS and was made using the acetonitrile method. Other measurements made in the same period, by the same method, ranged from 2.23 ppm to 9.76 ppm. The cartridge inlet concentration is less than 20% of the historical maximum and is considered significantly less than historical.

C.4.12 N-nitrosodimethylamine (NDMA)

The maximum PAPR cartridge inlet concentration was 721% of the OEL, about one-third of the historical maximum of 6.19 ppb (2063% of the OEL). The historical maximum came from the SWIHD HS database, a headspace measurement made in October 2016. There are no TWINS HS data for nitrosamines in this tank. The cartridge inlet maximum falls between 20% and 50% of the historical maximum, but not below the 20% level that is considered significantly below historical.

All the NDMA inlet concentrations for the TL2 PAPR cartridge had multiple data-quality flags, “BLYa” or “LY.” The “BLYa” notation indicates measurable concentration in the blank, calibration-standard measurement outside its specified range at the low end of the calibration range, and spike recovery outside its specified range. However, the maximum PAPR cartridge inlet concentration did not come from this data set and had no flags.

C.4.13 N-nitrosodiethylamine (NDEA), N-nitrosomethylethylamine (NMEA), and N-nitrosomorpholine

For these three nitrosamines, the PAPR cartridge inlet maxima were 13.1% of the OEL for NDEA, 188% of the OEL for NMEA, and below the DL of 1.68% of the OEL for N-nitrosomorpholine. The historical maxima were October 2016 SWIHD HS below-reports that had RLs of 1030% of the OEL for NDEA, 413% for NMEA, and 153% for N-nitrosomorpholine. The only above-report data come from a single breather-filter sample in TWINS IH, taken on July 15, 2009. The concentrations were 0.00809 ppb NDEA (8.09% of the OEL), 0.0239 ppb NMEA (7.97% of the OEL), and 0.0482 ppb N-nitrosomorpholine (8.03% of the OEL). There are no TWINS HS data for nitrosamines in this tank. The cartridge inlet maxima are broadly equivalent to the above-report historical maximum for NDEA, much higher than historical above-reports for NMEA, and nearly equal to 20% of the above-report historical maximum for N-nitrosomorpholine. Of these three nitrosamines, only N-nitrosomorpholine can be demonstrated to be significantly less than historical maxima.

C.4.14 Dibutyl Butylphosphonate (DBBP)

The maximum PAPR cartridge inlet concentration is below its DL of 0.36% of the OEL. The historical maximum concentration was a below-report datum with an RL of 0.00636 ppm (<90.9% of the OEL). This RL was for a September 17, 2009, sample in TWINS IH that had a small volume, 0.15 L. All the historical data in TWINS HS, dating from 1994, were also below-reports. There were no above-report historical data, so no conclusion can be drawn about where the cartridge inlet concentrations lie with respect to historical data.

C.4.15 2-Fluoropropene

2-fluoropropene was a tentatively identified compound in the PAPR cartridge inlet—it was not positively identified as being present—while the historical maximum concentration was 0.53 ppm (530% of the OEL). The historical data were present only in the TWINS HS database, a single data point taken in 1994. The cartridge inlet concentration is probably less than 20% of historical data, but because it is a tentatively identified compound, no conclusion can be drawn.

C.4.16 Summary of Historical Data Comparisons

In summary, in 2018 the PAPR cartridge inlet concentrations for the BY-108 headspace that were substantially lower than historical data can be described as follows:

- Differences arose from using historical data taken during disturbance as the historical maximum: none.
- Differences arose from using the RLs of below-report data for the historical maximum: none.
- Differences arose from using data for vapor produced by a no-longer-existing inventory for the historical maximum: none.
- Differences could not be resolved because of the scarcity of non-disturbance above-report data: 2,3-dihydrofuran, 2,5-dihydrofuran, 2-methylfuran, 2,5-dimethylfuran, 2-propylfuran, 2-pentylfuran, dibutyl butylphosphonate, 2-fluoropropene.
- Cartridge inlet concentrations were determined to be significantly lower than above-report historical concentrations: 1,3-butadiene, benzene, 1-butanol, acetaldehyde, furan, 2-heptylfuran, acetonitrile, N-nitrosomorpholine.

C.5 AP Exhauster (2018) Comparison to Historical Data

The maximum and average COPC concentrations measured during cartridge testing were compared to the maximum and average historical concentrations, and where differences were found, the historical data were examined for explanations in the type or circumstances of sampling.

The AP Farm contains six actively ventilated double-shell tanks, all of which are exhausted through the AP stack. Waste transfers involving these tanks are frequent, potentially leading to changes in the concentrations of COPCs in the wastes in the tanks and in the exhaust from the headspaces. However, there were no waste transfers or water additions in any AP tank during March 23–24, 2018, the date of the FY 2018 cartridge-testing campaign.⁵⁴

As of September 8, 2016, after the AP cartridge-testing campaign that had been conducted June 24–26, 2016, the AP exhauster was upgraded, thus changing the active ventilation rate. Consequently it was necessary to compare the FY 2018 cartridge-testing inlet concentrations to data taken after the exhauster upgrade, omitting earlier stack samples. In addition, because of the exhauster change it is not appropriate to compare the FY 2018 AP cartridge-inlet concentrations to those measured during the FY 2016 cartridge-testing campaign.

The larger discrepancies, or apparent discrepancies, between cartridge inlet and historical concentrations are discussed in the following sections.

C.5.1 Ammonia

The maximum PAPER cartridge inlet concentration was 102% of the OEL. The cartridge inlet maximum is low compared to the historical maximum concentration of 103 ppm (412% of the OEL). This historical measurement was made on January 26, 2017, about a month after the last preceding transfer of 6 kgal from AP-102 to AY-102 on December 31, 2016. The cartridge-inlet maximum falls between 20% and 50% of the historical maximum but is not below the 20% level that is considered to be significantly below historical.

C.5.2 Nitrous Oxide

Nitrous oxide was not measured in cartridge testing, nor was it measured at the AP exhauster after September 8, 2016.

C.5.3 Mercury

The PAPER maximum cartridge inlet concentration was 12.4% of the OEL. The historical maximum was a below-report TWINS IH measurement with a reporting limit (RL) of 0.0125 mg/m³ (50.0% OEL). The highest historical above-report measurement was 0.00791 mg/m³ (31.6% OEL). The cartridge-inlet maximum was between 20% and 50% of the historical maximum but is not below the 20% level that is considered significantly below historical.

⁵⁴ Although there were no waste-disturbing operations during cartridge-test sampling, a transfer of 17 kgal of supernatant liquid from AP-103 to AN-101 (March 17-18, 2018) occurred the previous week. Some residual elevation in headspace concentration might have remained; on the other hand, the transfer was relatively small.

C.5.4 Furan

The maximum PAPR cartridge inlet concentration of 57.3% OEL which was measured by the Carbotrap 300 TDU method, is much lower than the maximum in the TWINS IH database, which is 7.15 ppb (715% of the OEL). This above-report concentration was measured by the Carbotrap 300 TDU method on March 22, 2017, more than a month after the last preceding tank activity. The PAPR maximum concentration is less than 20% of the more recent historical maximum. The cartridge inlet concentration is considered significantly less than historical.

C.5.5 2,3-Dihydrofuran, 2,5-Dihydrofuran, 2-Methylfuran, 2,5-Dimethylfuran, 2-Pentylfuran, 2-Propylfuran, 2-Heptylfuran

For all of the substituted furans, the cartridge-inlet maxima were below detection limits and the historical maxima were below the detection limits, with details as follow:

- 2,3-dihydrofuran: PAPR <8.19%, historical < 3.2% (furans method)
- 2,5-dihydrofuran: PAPR <25.2%, historical <290% (Carbotrap 300 TDU method)
- 2-methylfuran: PAPR 6.93%,⁵⁵ historical <247% (Carbotrap 300 TDU method)
- 2,5-dimethylfuran: PAPR <4.09%, historical <53.4% (furans method)
- 2-pentylfuran: PAPR <2.95%, historical <37.1% (furans method)
- 2-heptylfuran: PAPR <2.78%, historical <30.9% (furans method)
- 2-propylfuran: PAPR <2.98%, historical <46.6% (furans method).

The methods listed are for the historical data. There were no above-report historical data, so no conclusion can be drawn about where the cartridge inlet concentrations lie with respect to historical data.

C.5.6 N-nitrosodimethylamine (NDMA)

The maximum PAPR cartridge inlet concentration of NDMA was 3130% of the OEL. The historical maximum was 15.8 ppb (5267% OEL). It was measured on August 8, 2017, less than a month after a transfer of 273 kgal from the 242-A evaporator to AP-104 (July 1–13, 2017). This historical maximum might have included residual elevated headspace concentration in AP-104 because of the large transfer. However, the second-highest historical NDMA concentration was almost the same, 15.7 ppb, and there had been no activity for about 5 months preceding that sample. The cartridge-inlet maximum is >50% of the historical maximum and is not considered significantly below historical.

All the NDMA inlet concentrations for the TL1 PAPR cartridge had multiple data-quality flags, “DLa”, and all of the TL2 cartridge data had the single flag “D”. The “DLa” notation indicates dilution of sample to put concentration in the instrument range (“D”), calibration-standard measurement outside its specified range at the low end of the calibration range (“L”), and spike recovery outside its specified range (“a”). The maximum PAPR cartridge inlet concentration, 3130% of the OEL, came from the suspect TL1 data set. The maximum inlet concentration for the PAPR TL2 cartridge data alone was 2127% of the OEL.

⁵⁵ This measurement, for the TL2 cartridge, was the only above-detect of the TL2 inlet samples. The other samples had higher DLs.

The PAPR cartridge maxima is suspect because of multiple data-quality flags in the PAPR TL1 cartridge inlet data. However, the PAPR TL2 maxima is greater than 20% of the historical maximum. The PAPR cartridge maxima for NDMA can be considered consistent with the historical maximum.

C.5.7 N-nitrosodiethylamine (NDEA)

All PAPR cartridge-inlet concentrations of NDEA were less than the detection limit, which was 13.2% OEL for the TL cartridge and 9.0% OEL for the FR-57 cartridge. The historical maximum was a below-report with a reporting limit of 0.0478 ppb (47.8% of the OEL). The maximum of the above-report measurements was 0.0169 ppb (16.9% of the OEL), measured on December 13, 2016, with no tank activity during sampling or in the preceding 7 months. It is possible that the cartridge-inlet maxima are consistent with the historical above-report maximum, since the cartridge-inlet DL is close to the historical datum. However, in the absence of above-report cartridge-inlet data for NDEA, no conclusion about consistency can be drawn.

C.5.8 N-nitrosomethylethylamine (NMEA)

The maximum PAPR cartridge inlet concentration of NMEA was 21.7% of the OEL. The historical maximum was 0.148 ppb (49.3% of the OEL). It was measured on August 8, 2017, less than a month after a large transfer of 273 kgal from the 242-A evaporator to AP-104 (July 1–13, 2017). This historical maximum might have included residual elevated headspace concentration because of the large transfer. However, the second-highest historical NMEA concentration was almost the same, 0.137 ppb, and there had been no activity in the 5 months preceding that sample. The cartridge-inlet maximum was between 20% and 50% of the historical maximum but is not below the 20% level that is considered significantly below historical.

All the NMEA inlet concentrations for the TL1 PAPR cartridge had the single flag “a”, denoting spike recovery outside its specified range. The maximum PAPR cartridge inlet concentrations came from the TL1 data sets. There were low recoveries of nitrosamines for the TL1 samples because of a change in extraction procedure, but the 222-S laboratory considers the data usable.⁵⁶ For comparison, the maximum for the TL2 cartridge was 17.0% and was not flagged.

The NMEA cartridge maxima can be considered consistent with the historical maximum.

C.5.9 N-nitrosomorpholine

The maximum PAPR cartridge inlet concentration of N-nitrosomorpholine was 3.31% of the OEL. The historical maximum was 0.0944 ppb (15.7% of the OEL). It was measured on August 22, 2017, more than a month after the last preceding transfer. The cartridge-inlet maxima are a little more than 20% of the historical maximum. The range from 20% to 50% is not considered significantly discrepant from historical, although this nitrosamine is on the borderline of discrepancy.

All the N-nitrosomorpholine inlet concentrations for the TL1 PAPR cartridges had the single flag “a”, and the maximum PAPR cartridge inlet concentrations came from the TL1 data sets. There were low recoveries of nitrosamines for the TL1 samples because of a change in extraction procedure, but the 222-S laboratory considers the data usable.⁵⁶ The presence of low recoveries suggests that the actual cartridge-inlet concentrations for TL1 may have been higher than the measured values.

⁵⁶ Email from DR Hansen (222-S Laboratory) to LA Mahoney, “RE: Two residual questions (both AP)”, March 27, 2019 12:39 PM.

The N-nitrosomorpholine cartridge maxima can be considered consistent with the historical maxima.

C.5.10 Dibutyl Butylphosphonate (DBBP)

The maximum cartridge inlet concentration of DBBP is below its DL of 0.36% of the OEL. The historical maximum concentration was a below-report datum with an RL of 0.0007 ppm (<10.2% of the OEL). There were no above-report historical data, so no conclusion can be drawn about where the cartridge inlet DBBP concentrations lie with respect to historical data.

C.5.11 Summary of Historical Data Comparisons

In summary, at the AP exhauster, after its September 8, 2016 upgrade, the maximum cartridge inlet concentrations that were substantially lower than historical data can be described as follows:

- Differences arose from using historical data taken during disturbance as the historical maximum: none.
- Differences arose from using the RLs of below-report data for the historical maximum: none.
- Differences arose from using data for vapor produced by a no-longer-existing inventory for the historical maximum: none.
- Differences could not be resolved because of the scarcity of non-disturbance above-report data: 2,3-dihydrofuran, 2,5-dihydrofuran, 2-methylfuran, 2,5-dimethylfuran, 2-pentylfuran, 2-heptylfuran, 2-propylfuran, N-nitrosodiethylamine, dibutyl butylphosphonate.
- Cartridge inlet concentrations were determined to be significantly lower than above-report historical concentrations: furan.

C.6 References

1. Mahoney, LA, and EW Hoppe. 2018. *Hanford Tank Vapor FY 2017 Chemicals of Potential Concern Update*. PNNL-26820, Pacific Northwest National Laboratory, Richland, Washington
2. Hoppe EW, LA Mahoney, and D Daly. 2016. *Hanford Tank Vapors COPCs Update*. PNNL-25880, Pacific Northwest National Laboratory, Richland, Washington.
3. Nune, SK, CK Clayton, J Liu, CJ Freeman, TM Brouns, and LA Mahoney. 2020. *Analysis of Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on Hanford Tanks SX-101 and SX-104*. PNNL-27558 Vol. 1, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.
4. Nune, SK, CK Clayton, J Liu, CJ Freeman, TM Brouns, and LA Mahoney. 2020. *Analysis of Air-Purifying Respirator (APR) and Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on a Hanford AX Tank Farm Exhauster Slipstream*. PNNL-27860 Vol. 1, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.
5. Nune, SK, CL Bottenus, J Liu, LA Mahoney, CJ Freeman, and TM Brouns. 2020. *Analysis of Air-Purifying Respirator (APR) and Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on Hanford Tanks BY-108 and BY-110*. PNNL-28334 Vol. 1, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

6. Nune, SK, CL Bottenus, J Liu, LA Mahoney, CJ Freeman, and TM Brouns. 2020. *Analysis of Air-Purifying Respirator (APR) and Powered Air-Purifying Respirator (PAPR) Cartridge Performance Testing on Hanford AP Tank Farm Exhauster*. PNNL-28680 Vol. 1, Rev. 0, Pacific Northwest National Laboratories, Richland, Washington.
7. Sklarew DL and AV Mitroshkov. 2006. *Review of Mass Spectrometry Data from Waste Tank Headspace Analyses*. PNNL-15673, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington. http://www.pnl.gov/main/publications/external/technical_reports/PNNL-15673.pdf.

Appendix D

Detection Limits Versus Reporting Limits for Furans

Appendix D

Detection Limits Versus Reporting Limits for Furans

A total of 14 furan or substituted furans are on the current list of Chemicals of Potential Concern (COPC). Six of these furans are tentatively identified compounds that were not detected in any respirator cartridge test samples. Eight remaining furans were quantified in respirator cartridge testing: 1) furan, 2) 2,3-dihydrofuran, 3) 2,5-dihydrofuran, 4) 2-methylfuran, 5) 2,5-dimethylfuran, 6) 2-pentylfuran, 7) 2-heptylfuran, and 8) 2-propylfuran. The Occupational Exposure Limit (OEL) for each of these furans is 1 ppb, which is among the lowest OELs of all COPCs.

COPC analysis results for tank farm vapors are typically reported in relation to a reporting limit (RL), which represents a quantitation limit referring to the minimum mass of an analyte that can be measured within specified limits of precision and accuracy. RL is a measured value representing the low point of the calibration curve. The analytical method or instrument detection limit (DL) represents a minimum mass of an analyte that can be measured above the instrument background noise. DL is a statistically calculated value. When an RL is used for reporting, it generally means that the analyte is not present in a sufficient amount to be reliably quantified below the RL value. The DL is always lower than the RL. When a DL is used for reporting, it generally means that the analyte is not present at or above the DL value. Historical tank vapor source data reported in the Tank Waste Information Network System (TWINS) and Site-Wide Industrial Hygiene Database (SWIHD) data sets primarily have been quantified and reported as RLs. Depending on the sample volume collected for analysis, an RL reported on a concentration basis may vary widely. For furans, historical RL concentrations have ranged from as low as 0.1 ppb to more than 50 ppb, depending on the specific COPC and sample volume collected. On a percentage of the OEL basis, this equates to 10% to more than 5000% of the OEL.

For cartridge testing, the furan samples were collected over 2 hours with an approximate volume target of 4 L or more. The analytical laboratory was requested to report to a DL versus an RL to ensure that the COPCs could be detected down to 10% of the OEL or less. In practice, analytical DLs for the furans in cartridge testing were typically 5% of the OEL or lower. While use of the DL provides the opportunity for a lower level reported concentrations, it also introduces lower confidence in precision or accuracy of the analyte's quantitation. During review of cartridge-testing data from the furan analysis in the individual tank/exhauster test reports, concerns were raised because the cartridge inlet and outlet values were very close, and in some cases, the outlet values above detection were suspected of exhibiting potential "bleed through" in the cartridge. There was a greater level of variability than seen, for example, with nitrosamine analysis results that reported to an RL.

For these reasons, further assessments of furan analytical results, including comparison to baseline samples (i.e., background) and blank samples (i.e., pre-test sorbent tubes) were conducted. Baseline samples were measurements obtained for ambient air (fresh air vs. tank vapor) running through the test system from the inlet (IN) or effluent (EF) locations before initiation of tank vapor testing. Blank samples were obtained from sorbent tubes that were opened and immediately capped in the field but that had no vapor stream passed through them. Table D.1 shows the respirator cartridge maximum inlet furan data that were reported in the five tank/cartridge reports in the upper third of the table (labeled "Measured"). The two other sections of the table show the analytical results for the "Baseline" and "Blank" samples.

Table D.1. Maximum Measured Respirator Inlet Concentrations for the Eight Furan COPCs

	COPC Number and Name	OEL	2018 BY-108 Max. % OEL	SX-101 Max. % OEL	SX-104 Max. % OEL	AP_2018 Max. % OEL	AX_2017 Max. %OEL	% OEL Approximate Reporting Limit*
Measured	19 Furan	1 ppb	575.7%	28.5%	100.0%	57.3%	39.8%	108%
	20 2,3-Dihydrofuran	1 ppb	3.2%	4.3%	6.5%	8.2%	2.2%	17.6%
	21 2,5-Dihydrofuran	1 ppb	24.1%	52.5%	52.5%	25.5%	17.5%	104%
	22 2-Methylfuran	1 ppb	16.6%	12.6%	21.1%	6.9%	9.4%	89.2%
	23 2,5-Dimethylfuran	1 ppb	3.0%	4.1%	34.0%	4.1%	4.2%	12.8%
	27 2-Pentylfuran	1 ppb	3.0%	6.9%	5.7%	3.1%	3.4%	8.9%
	28 2-Heptylfuran	1 ppb	2.8%	2.6%	2.5%	3.4%	2.6%	7.4%
	29 2-Propylfuran	1 ppb	1.8%	2.5%	2.5%	3.0%	2.6%	11.2%
Baseline	19 Furan	1 ppb	103.4%	27.0%	26.6%	20.7%	37.6%	108%
	20 2,3-Dihydrofuran	1 ppb	2.8%	2.0%	2.0%	7.5%	2.0%	17.6%
	21 2,5-Dihydrofuran	1 ppb	22.8%	49.9%	49.0%	11.7%	16.5%	104%
	22 2-Methylfuran	1 ppb	8.6%	12.0%	11.7%	9.3%	8.9%	89.2%
	23 2,5-Dimethylfuran	1 ppb	2.6%	3.8%	7.4%	3.8%	3.7%	12.8%
	27 2-Pentylfuran	1 ppb	2.6%	9.6%	4.0%	3.1%	3.1%	8.9%
	28 2-Heptylfuran	1 ppb	2.5%	2.3%	2.4%	2.9%	2.3%	7.4%
	29 2-Propylfuran	1 ppb	1.6%	2.3%	2.4%	2.7%	2.3%	11.2%
Blank derived	19 Furan	1 ppb	13.2%	27.0%	26.6%	20.7%	37.6%	108%
	20 2,3-Dihydrofuran	1 ppb	2.8%	2.0%	2.0%	10.2%	2.0%	17.6%
	21 2,5-Dihydrofuran	1 ppb	22.8%	49.9%	49.0%	11.7%	16.5%	104%
	22 2-Methylfuran	1 ppb	8.6%	12.0%	11.7%	9.3%	8.9%	89.2%
	23 2,5-Dimethylfuran	1 ppb	2.6%	3.8%	18.1%	3.8%	3.7%	12.8%
	27 2-Pentylfuran	1 ppb	2.6%	4.0%	3.2%	3.1%	3.1%	8.9%
	28 2-Heptylfuran	1 ppb	2.5%	2.3%	2.4%	2.9%	2.3%	7.4%
	29 2-Propylfuran	1 ppb	1.6%	2.3%	2.4%	2.7%	2.3%	11.2%

Notes:

- Two analytical methods were used for furans. Furan, 2,5-dihydrofuran, and 2-methylfuran were analyzed using the Carbotrap 300 TDU method while the other furans were analyzed using Tenax method.
- Measurement less than DLs are shown in red. Values larger than DLs have the qualifier "J" except for the values in green boxes. Qualifier "J" means that the values were estimated because they are in between the DL and the RL.
- The values in the yellow boxes are highlighted because they are larger than the maximum measured results or higher than RL, which indicate an incomplete media regeneration for blank samples or local air or system contamination.

* The approximate RL values were calculated based on a reference mass (3.1 NGS for Tenax and 12 NGS for Carbotrap 300 TDU) and overall average volume for all PAPR tanks.

The “Baseline” and “Blank” data in Table D.1 clearly show furan measurements that are significantly above the analytical DL, when there should have been no measurable furan on those samples. Measurable values on blanks could be residue from prior analysis because the analytical tubes are regenerated and reused.⁵⁷ Regardless, the background and blank level of furans above the DL complicate interpretation of variations in outlet concentrations at low levels. For this reason, the RL for the furans was adopted in this report to better assess the overall furan results and provide a more consistent comparison to historical furan data that was also quantified to an RL. The RL provided by the analytical laboratory for the furan measurements, corresponds to 3.1 ng/tube. This value was used to calculate an equivalent average percent of the OEL RL for each of the furans, which are shown in the right-most column of Table D.1. Two of the “Baseline” or “Blank” values (highlighted in yellow) are above the RL values. These correspond to one 2-

⁵⁷ One tube of each batch of 20 tubes that are regenerated is analyzed to certify cleanliness of the batch, which should minimize the opportunity for contamination of future samples.

pentylfuran value and one 2,5-dimethylfuran value. Because of the identified variation between the “Baseline” and “Blank” values, the use of RLs versus DLs is recommended for furans going forward. It also is important to note that none of the respirator cartridge outlet measurement for any of the furans were greater than the corresponding RLs. There is still a need to improve the RL and DL for furans so analysis results can reliably attain low percentage of OEL values (e.g., $\leq 10\%$ of the OEL).

Appendix E

Meteorological Data Comparisons to Respirator Testing Conditions

Appendix E

Meteorological Data Comparisons to the 2016 Respirator Testing Conditions

Meteorological data from the Hanford Meteorological Station (Station 21, or HMS) was accessed for comparisons to the respirator cartridge-testing data. The HMS is located between the 200-East and 200-West areas at Hanford. Two other meteorological stations also were evaluated—Station 6 located in the 200-East area, and Station 19 located in the 200-West area. All three towers are in relatively close proximity, so the values were similar. Data from the HMS were used because it was available on an hourly basis. A full set of 2016 data was pulled for the cartridge testing comparisons. Figure E.1 shows plots of the hourly relative humidity and temperature data for 2016 through 2018.

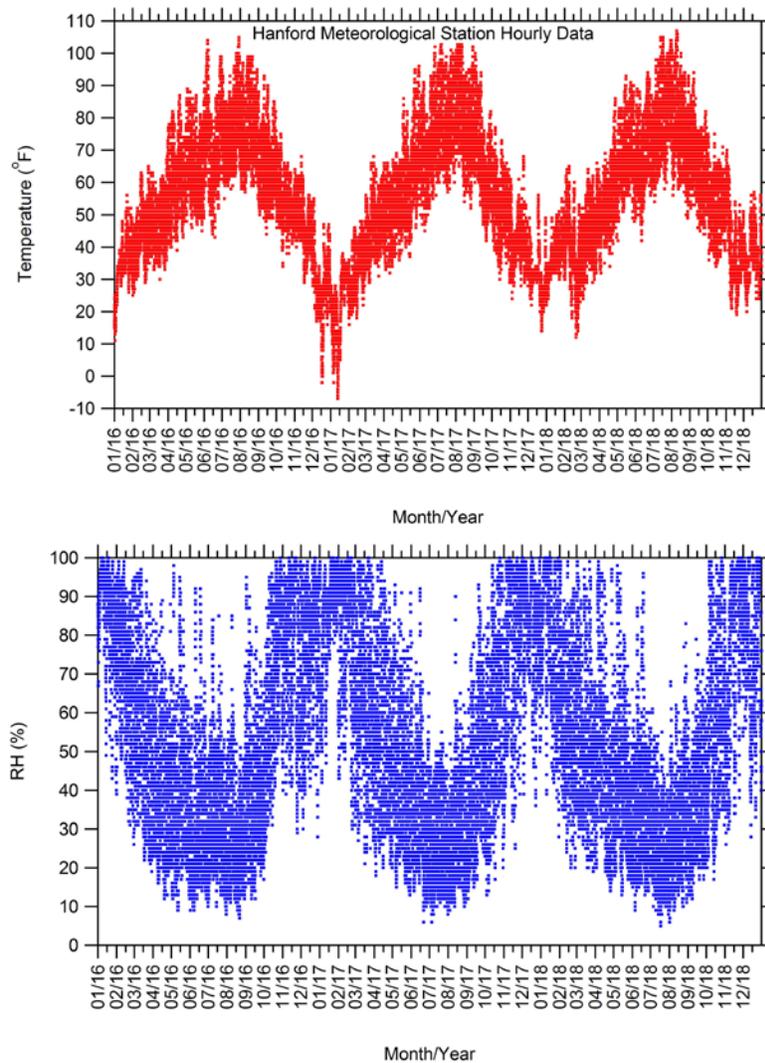


Figure E.1. Hourly Temperature (upper panel – red markers) and Relative Humidity (lower panel – blue markers) Measurements for January 1, 2016, through December 31, 2018, as Recorded at the HMS.

Figure E.2 shows a comparison plot of the same relative humidity and temperature data as in Figure E.1. Here, additional points were included from January 1, 2017, through December 31, 2018. HMS data are represented as black markers in the figure. The colored markers represent times when cartridge testing was being performed, with each color representing a unique tank or exhauster test. Figure E.2 helps to represent and highlight the maximum relative humidity and temperature conditions that occur in the Hanford 200 area throughout the year. Based on the cluster of the colored markers, it can be interpreted that the cartridge tests were performed in the middle to upper range of the annual outside temperatures, spanning approximately 50 to 90°F, and approximately 15 to 85% relative humidity. Correspondingly, the cartridge testing did not occur during the lowest and highest annual outside temperatures.

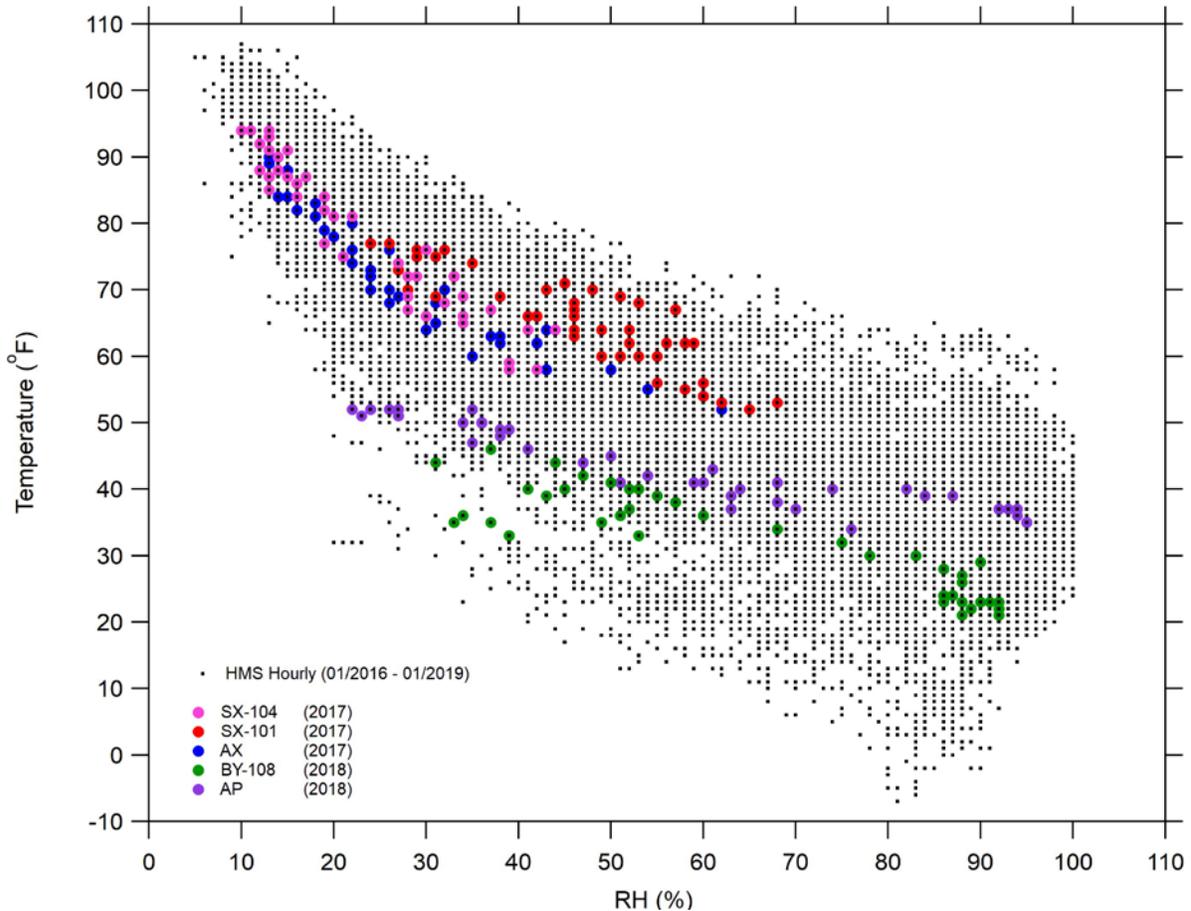


Figure E.2. Scatter Plot of the Ambient Temperature versus Relative Humidity Ambient Data Measured at HMS between January 1, 2016, and January, 2019. Colored markers indicate times corresponding to specific tank or exhauster cartridge-testing activities.

Next, the meteorological relative humidity and temperature data were compared to the corresponding relative humidity and temperature data taken during the cartridge testing for the three tanks tested (SX-101, SX-104, and BY-108) and the two exhausters tested (AX and AP). These comparisons are shown in Figure E.3.

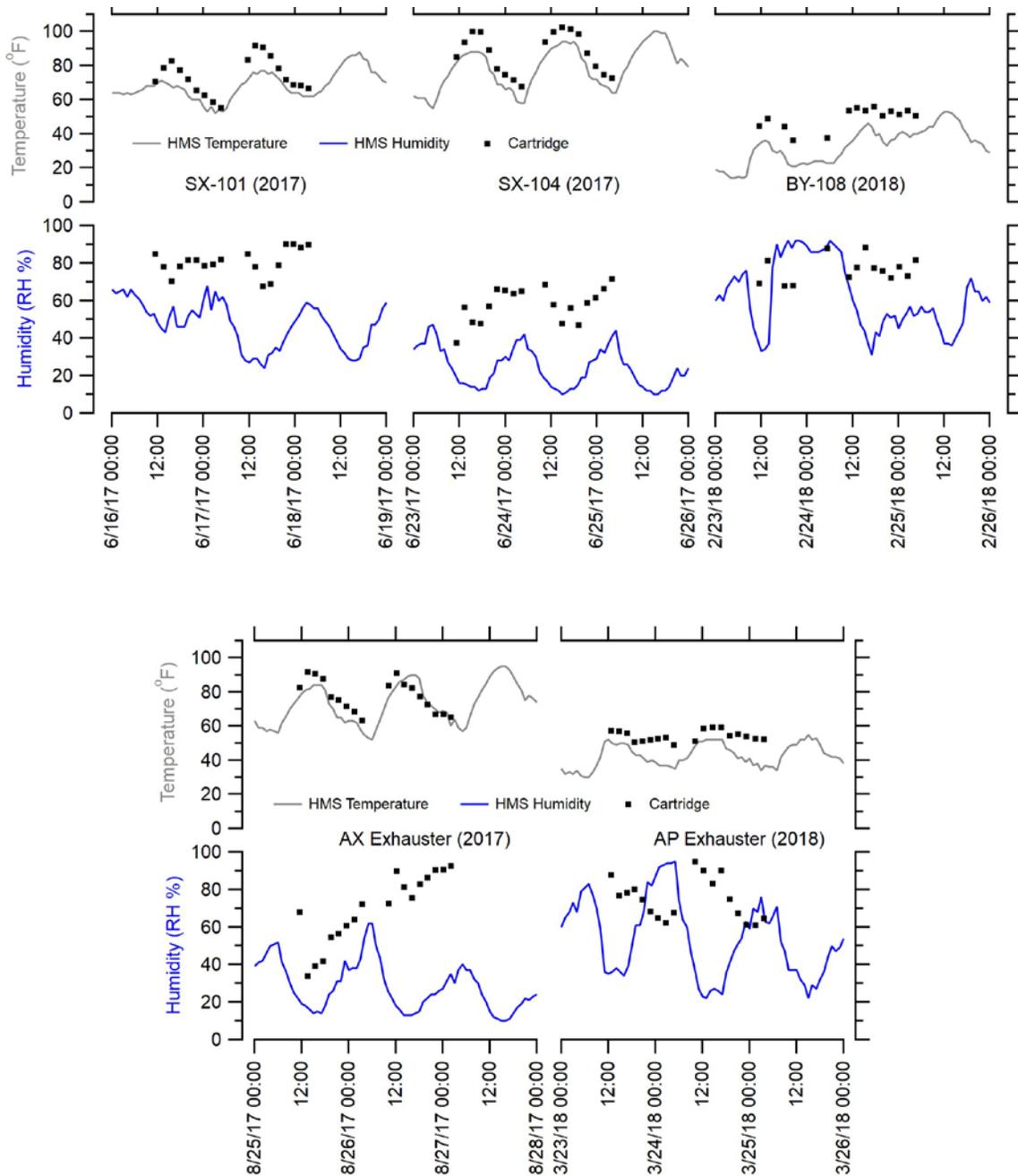


Figure E.3. Overlay of Cartridge Relative Humidity and Temperature Measurements Collected at 2-Hour Intervals during Cartridge Testing with 200 Area Meteorological Data from HMS. The upper panel summarizes data for the three tanks tested (SX-101, SX-104, and BY-108) and the lower panel summarizes the data for the two exhausters tested (AX and AP).

The data in Figure E.3 show a strong relationship between the meteorological and cartridge temperature data for all eight tank testing periods. This relationship pertains to both exhausters and tank headspaces. However, the comparison of relative humidity levels was much less consistent. For the majority of tests (exhauster and tank headspaces), the cartridge testing relative humidity levels were significantly higher than meteorological relative humidity levels. The likely reason is that humidity from tank-based water was being generated.

Appendix F

Manufacturer's Service-Life Estimation

Appendix F

Manufacturer's Service-Life Estimation

F.1 Background

The experimental breakthrough times for ammonia from each of the PAPR cartridge tests were compared to predicted service life of the cartridges using the online calculators or algorithms provided by the cartridge manufacturers. Although the experimental breakthrough times were obtained from a mixture composed of potentially over a thousand of chemicals, the predicted service life of the cartridge are based on single component ammonia concentrations.

The breakthrough signature of ammonia was further assessed to infer a higher resolution than the 2-hour collection times obtained from cartridge tests. An interpolation was used to determine the time when 10% of the OEL concentration at the outlet would have occurred. Based on theoretical adsorption information, a semi-logarithmic relationship was found between the cumulative ammonia mass introduced to the cartridge and the cartridge outlet concentration. Therefore, the approximate cumulative mass of ammonia introduced at 10% of the OEL can be interpolated based on this relationship. Then, the breakthrough time at 10% of the OEL can be linearly interpolated based on the cumulative ammonia mass and the recorded breakthrough time. Once the interpolated breakthrough time was determined, the average inlet concentrations and measured gas stream properties (relative humidity, temperature, and pressure) were determined up until that point for use in subsequent statistical analyses. The interpolated breakthrough times and gas stream properties for each of the PAPR cartridge tests are provided in Appendix B.

The MSA-TL (TL1) cartridge is a type TL (AM/CL/CD/FM/HC/MA/SD/HE) PAPR cartridge from MSA (order #10080456). The TL2 cartridge is a type FR-57 (OV/SD/HC/CL/CD/HF/AM/MA/FM/HE) PAPR cartridge from 3M. There are three cartridges in the selected 3M PAPR respirator and there are two cartridges in the selected MSA PAPR respirator. However, in the cartridge tests, only one cartridge was used so the flow rate in the manufacturer's calculator or suggested method are normalized to the flow rate per cartridge for comparisons of service life estimates and experimental breakthrough times.

The estimated service lives for TL1 cartridges were obtained with the average inlet concentrations, temperatures, flowrates, and relative humidities (up to the breakthrough point determined in each cartridge field test) using the online calculator provided by MSA. Table F.1 provides the estimated service lives compared to experimental breakthrough times for each MSA PAPR cartridge test.⁵⁸ These estimated service-life times are slightly lower than the breakthrough times obtained in the field test. This indicates that the MSA calculator is conservative in these cases. For ammonia, the impact of relative humidity on the service life was not included in the MSA calculator. MSA technical support believes that the estimated service life obtained using the MSA calculator is conservative when the relative humidity (RH) is higher than 50%. No response was obtained from MSA on the estimated service life using the MSA calculator when the RH is lower than 50%. The correspondence between PNNL and MSA regarding this matter is shown in Figure F.1.

Table F.1. Comparison of Interpolated Experimental Breakthrough Times to Manufacturer Service Life Estimates for the MSA TL Cartridge

COPCs	Cartridge	Tank	T (°F)	RH (%)	OEL (ppm)	Breakthrough Criterion (%OEL)	Avg. Inlet Conc.(ppm)	Exptl. Flow Rate (L/min)	Exptl. Pressure (Torr)	Exptl. Breakthrough Time (h)	Calculation Flow Rate (L/min)*	Estimated Service Life (h)
NH ₃	TL1	SX-101	77.4	77.8	25	10	141	95	670	4.7	102.5	2.9
	TL1	SX-104	92.7	49.5	25	10	272	95	669	2.0	102.5	1.6
	TL1	BY-108 ('18)	45.8	75.6	25	10	158	95	681	5.6	102.5	2.1
	TL1	AP ('18)	52.8	73.0	25	10	22	95	700	> 16	102.5	16
	TL1	AX ('17)	79.8	52.7	25	10	4.3	95	693	> 16	102.5	16

*This is a per cartridge-based flowrate obtained by dividing the original 205 L/min flowrate in the MSA service life calculator by the number (two) of TL cartridges in each PAPR respirator.

⁵⁸ Estimated service lives were also estimated and documented in Appendix B of each individual PAPR cartridge test report. Results documented here are updated from the original analysis to assure consistent basis for each test.

From: cstechsupport@msasafety.com [<mailto:cstechsupport@msasafety.com>]
Sent: Tuesday, September 24, 2019 9:07 AM
To: Liu, Jian (LSL2) <Jian.Liu@pnnl.gov>
Subject: Re: RE: MSA Response Guide Calculator

Jian:
This is the information from the PLM.

The cartridge calculation for ammonia that was in question would not likely have any variance based on increments of temperature and humidity. For ammonia, specifically, the calculated service time would not be impacted by changes in temperature.

The service life of ammonia which is based on chemisorption, typically increases with increasing relative humidity. Because most service life data is generated at 50% RH. Therefore, the service life will be longer than expected and the humidity factor would offset the effects of temperature and flow rate.

Therefore the formula used for ammonia specifically on the cartridge calculator does not incorporate the effects of temperature, humidity or breathing rate.

I hope this helps.
Rhonda
MSA Sr. Technical Support
[Visit our website for more information](#)

From: cstechsupport@msasafety.com [<mailto:cstechsupport@msasafety.com>]
Sent: Thursday, September 12, 2019 4:29 AM
To: Liu, Jian (LSL2) <Jian.Liu@pnnl.gov>
Subject: Re: MSA Response Guide calculator

Jian:
Your information has been submitted to MSA Product Support. Please allow at least 24 hours to get a response. It could take a little more time based on availability to answer your study questions.

8000062297

The above number is the reference number for your case.

Rhonda
MSA Sr. Technical Support
[Visit our website for more information](#)

From: Jian.Liu@pnnl.gov
To: us.cs@msasafety.com
Sent: Tue, Sep 10, 2019, 12:33 PM EDT
Subject: MSA Response Guide Calculator

Hi MSA support,

I am a chemical engineering working at the Pacific Northwest National Laboratory. I was using the MSA calculator to study the effects of relative humidity, temperature and concentration on the service life for NH₃ adsorption in the TL PAPR cartridge (Hood). I observed that the service life did not change when I changed the relative humidity (or temperature) and fixed the other parameters. For example, when I first fixed NH₃ at 125 ppm @ 77F and 760 mm Hg with a flow rate of 205 LPM, 10% OEL breakthrough concentration and 0% safety factor, then changed the relative humidity from 10% to 90% with a 10% interval, I found that the service life for the TL PAPR (hood) is always 193 min as shown in the Table below. The same thing also occurred when I fixed all other parameters but varied the temperature. I would like to know the reason behind this. Thank you.

Chemical	Concentration (ppm)	Temperature (F)	Pressure (mm Hg)	Relative humidity (%)	Flow rate (LPM)	Breakthrough cocentration (% OEL)	Safety factor (%)	Service life (min)
NH3	125	77	760	10	205	10	0	193
NH3	125	77	760	20	205	10	0	193
NH3	125	77	760	30	205	10	0	193
NH3	125	77	760	40	205	10	0	193
NH3	125	77	760	50	205	10	0	193
NH3	125	77	760	60	205	10	0	193
NH3	125	77	760	70	205	10	0	193
NH3	125	77	760	80	205	10	0	193
NH3	125	77	760	90	205	10	0	193

Best regards,

Jian

Figure F.1. Email Correspondence between PNNL and MSA Regarding the Impact of Relative Humidity

For the FR-57 (TL2) cartridge a manufacturer's (3M) service life-estimator is available for organic vapors. However, 3M does not have a model to describe the adsorption performance of ammonia in the FR-57 cartridge as stated in a correspondence from a 3M specialist (Figure F.2). A rough estimation was done mainly based on a reciprocal relationship assumption between the service life and the challenged mass (Figure F.2) using data from the FR-57 National Institute of Occupational Safety and Health (NIOSH) test results. The adsorbed mass is linearly related to the inlet concentration and flow rate (per cartridge). A 0.5 adjusting coefficient also is included in the estimation method based on the manufacturer's recommendation to account for the difference in the permissible concentration between the NIOSH test procedure (50 ppm, 200% of the OEL) and Washington River Protection Solutions (WRPS) cartridge field test (2.5 ppm, 10% of OEL). The possible temperature and RH effects were not included in this estimation method. An email from the 3M specialist describing the calculation procedure is provided as Figure F.2. The estimated service-life times were obtained with the average inlet concentrations and flowrates (up to the breakthrough point determined in field test) using this procedure. Table F.2 provides the estimated service lives compared to the experimental breakthrough times for each 3M PAPR cartridge test. Although the 3M method is a conservative estimation based on a minimum service life NIOSH requirement (25 minutes), the resulting service life estimates are not as comprehensive as manufacturers' service life calculators that relate experimental and model-derived performance data to important variables. Therefore, there is greater uncertainty in results obtained from this estimation algorithm for the 3M FR-57 cartridge.

Table F.2 Comparison of Interpolated Experimental Breakthrough Times to Manufacturer Service Life Estimates for the 3M FR57 Cartridge

COPCs	Cartridge	Tank	T (°F)	RH (%)	OEL (ppm)	Breakthrough Criterion (%OEL)	Avg. Inlet Conc.(ppm)	Exptl. Flow Rate (L/min)	Exptl. Pressure (Torr)	Exptl. Breakthrough Time (h)	Calculation Flow Rate (L/min)*	Estimated Service Life (h)
NH ₃	TL2	SX-101	84.6	80.5	25	10	174	95	667	1.7	57	0.7
	TL2	SX-104	96.1	60.8	25	10	254	95	709	1.6	57	0.5
	TL2	BY-108 ('18)	54.3	76.6	25	10	128	95	698	1.7	57	0.7
	TL2	AP ('18)	57.4	87.6	25	10	23	95	693	5.5	57	5.5
	TL2	AX ('17)	87.3	44.7	25	10	3.8	95	670	> 16	57	> 16

*This is a per cartridge-based flowrate which was obtained by dividing the original 170 L/min flowrate in the NIOSH test for the 3M PAPR cartridge by the number (three) of FR57 cartridges in each PAPR respirator.

From: Erik Johnson
To: [Liu, Jian \(LSL2\)](#)
Subject: RE: PAPR cartridge service life estimation
Date: Friday, October 27, 2017 11:03:41 AM
Attachments: [image003.png](#)
[image002.png](#)

Jian,

The FR-57 is in the 3M Service Life Software for organic vapors. Unfortunately there are fewer math models for non-organic vapors. For other gases/vapors, please see the following technical data bulletins.

<https://www.dqeready.com/Documents/Products/3M-FR-57-Technical-Data.aspx>

<https://multimedia.3m.com/mws/media/4716630/determination-of-service-life-for-niosh-cbrn-cartridges.pdf>

For example, the NIOSH test criteria for ammonia is 1000 ppm challenge, and at least 25 minutes before 50 ppm breakthrough. Temperature and humidity ranges you mentioned are less of a concern for ammonia as opposed to organic vapor service life. The Breathe Easy PAPR flow rate is about 220 L/min for the system (73 L/min per cartridge); as opposed to the NIOSH testing at 170 L/min (57 L/min per cartridge).

It is best to have service life data at multiple exposure levels in order to estimate service life. As a very rough estimate, one could use an inverse linear relationship (e.g. decrease exposure in half and double service life). However, it is more often an exponential relationship (longer service life). The effect of breakthrough concentration is difficult to include because once breakthrough starts, it increases rapidly. Therefore, based on the graph below, a correction factor of 2 seems more than adequate for differing breakthrough quantities.

Typical Gas-Vapor Breakthrough Curve

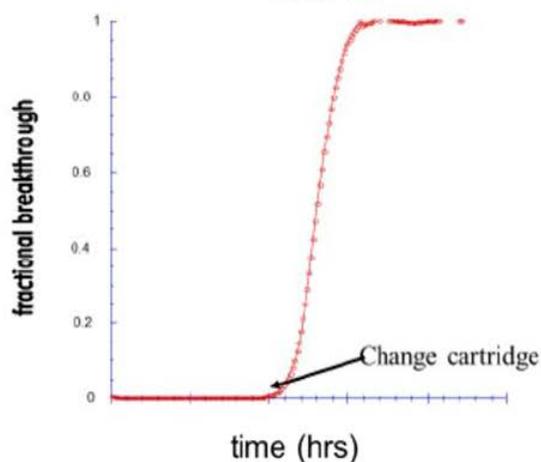


Figure F2. Email Correspondence between PNNL and 3M Regarding the Breakthrough Calculation Procedure

Putting this all together, a rough estimate of service life at 193 ppm would be:
 $25 \text{ minutes} * (1000 \text{ ppm} / 193 \text{ ppm}) * (170 \text{ L/min} / 220 \text{ L/min}) * (1/2) = 50 \text{ minutes}$

Likewise at 311 ppm would be = 31 minutes.

Mind you these are based on the minimum NIOSH service life requirements and some conservative assumptions. Actual service life may be longer. However, cartridges must be changes sooner if contaminant odor/irritation is detected.

-Erik



Erik W. Johnson, CIH, CSP | Technical Service Specialist
 3M Personal Safety Division
 3M Center, Bldg. 235-2E-91 | St. Paul, MN 55144
 Office: 651 737 2713 | Mobile: 651 263 8752 | Fax: 651 736 7344
erikwjohnson@mmm.com | www.3M.com/ppesafety

From: Liu, Jian (LSL2) [mailto:Jian.Liu@pnnl.gov]
Sent: Friday, October 27, 2017 11:31 AM
To: Erik Johnson <erikwjohnson@mmm.com>
Subject: [EXTERNAL] PAPR cartridge service life estimation

Hi Erik,

It was nice talking to you. I would like to ask you to estimate the service life of the FR57 (OV/SD/HC/CL/CD/HF/AM/MA/FM/HE) for some chemicals using your online calculator.

Scenario 1. Temperature: 26.5 C, RH: 81%, flowrate 95 L/min (for one cartridge)

Ammonia inlet concentration 193 ppm/breakthrough limit 2.5 ppm

Scenario 2. Temperature: 33.3 C, RH: 58%, flowrate 95 L/min (for one cartridge)

Ammonia inlet concentration 311 (or 300 if 311 is not possible) ppm/breakthrough limit 2.5 ppm

Thank you.

Best regards,

Jian

3M Note: This message is from an [EXTERNAL] sender. If you suspect this message is malicious or spam, please click on the "Report Phishing - PhishMe" icon within the Outlook Ribbon to report it for evaluation, and do NOT open any attachments or click on any links. If you are using OWA, a handheld device, or do not see the icon, please follow the

Figure F.2. (continued)

An example application of the 3M calculation procedure to estimate the service life of the FR57 cartridge for ammonia adsorption is provided below for the AP Tank (2018) cartridge tests. The parameters in both the NIOSH test procedure and the WRPS test procedure are listed and compared in Table F.3.

Table F.3. Example of Calculating Breakthrough Time for PAPR Cartridge FR57 in AP Tank (2018) using the 3M Estimation Method

NIOSH test procedure	WRPS test procedure
Ammonia concentration: 1000 ppm	Average inlet ammonia concentration: 23 ppm
RH: 50±5% ¹	Average RH: 87.6%
Temperature: 77±9°F ¹	Average inlet temperature: 57.4°F
Flowrate per cartridge: 57 L/hour	Average flowrate per cartridge: 95 L/hour
Permissible ammonia concentration: 50 ppm	Permissible ammonia concentration: 2.5 ppm
Minimum breakthrough time: 25 minutes or 0.42 hour	Minimum breakthrough time: ~326 minutes or ~5.4 hour

¹ Found in Technical Data Bulletin #180–Determination of Service Life for NIOSH CBRN approved 3M™ Cartridges and Canisters. The temperature and humidity are not specified in the communication email and their effects were not considered in the calculation suggested by 3M.

The ammonia breakthrough time t_b for the 3M PAPR cartridge FR-57 tested in AP (2018) tank can be calculated using the following equation:

$$t_b \text{ (min)} = 25 \text{ min} \times \frac{1000 \text{ ppm}}{23 \text{ ppm}} \times \frac{57 \text{ L/h}}{95 \text{ L/h}} \times 0.5 = 326 \text{ min} = 5.4 \text{ hours}$$

F.2 Comparison of MSA Service Life Estimates for PAPR and APR Cartridges.

WRPS cartridge testing between 2016 and 2018 focused on both APR and PAPR cartridges, including two SCOTT Safety 7422-SD1 and 7422-SC1 APR cartridges, one MSA (TL) PAPR cartridge, and one 3M (FR-57) PAPR cartridge. The MSA APR cartridge (GME Comfo) is also commonly used at the Hanford Site but was not subjected to APR cartridge testing. However, results from both APR and PAPR cartridge testing performed to date have shown that the manufacturer's ammonia service life estimates provided valuable and generally conservative results (with the APR recommended adjustment⁵⁹) that an Industrial Hygiene professional can use to assist in selecting appropriate cartridges and establishing appropriate cartridge change schedules. The estimated ammonia service lives of the MSA APR cartridge (GME Comfo) using the MSA service life calculator also is provided here and compared with those of the MSA PAPR cartridge (TL) as shown in Figure F.3 below. The results of the SCOTT 7420 cartridge (7420-SD1) also are included for comparison. The parameters of the calculation for all cartridges are 25°C, 760 torr, and 50% RH. There is no safety factor for MSA APR and PAPR cartridges, but there is a built-in safety factor for the SCOTT APR as pointed out in the Multi-tank APR summary report [15]. The only difference is that the flowrate in the APR (MSA GME Comfo and SCOTT 7420) cases is 60 L/minute for two cartridges and the flowrate for the MSA PAPR (TL) case is 205 L/minute for two cartridges. The estimated results for the MSA cartridges do not include the possible impacts from RH. The estimated service life of the MSA PAPR cartridge is generally greater than that of the MSA APR cartridge. The SCOTT SureLife calculator does include the impact of RH, and the estimated service life would change if a different RH other than 50% RH was selected. The estimated service life for the MSA APR (MSA GME Comfo) is generally longer than that of the SCOTT APR (7420-SD1) at the same inlet ammonia concentration.

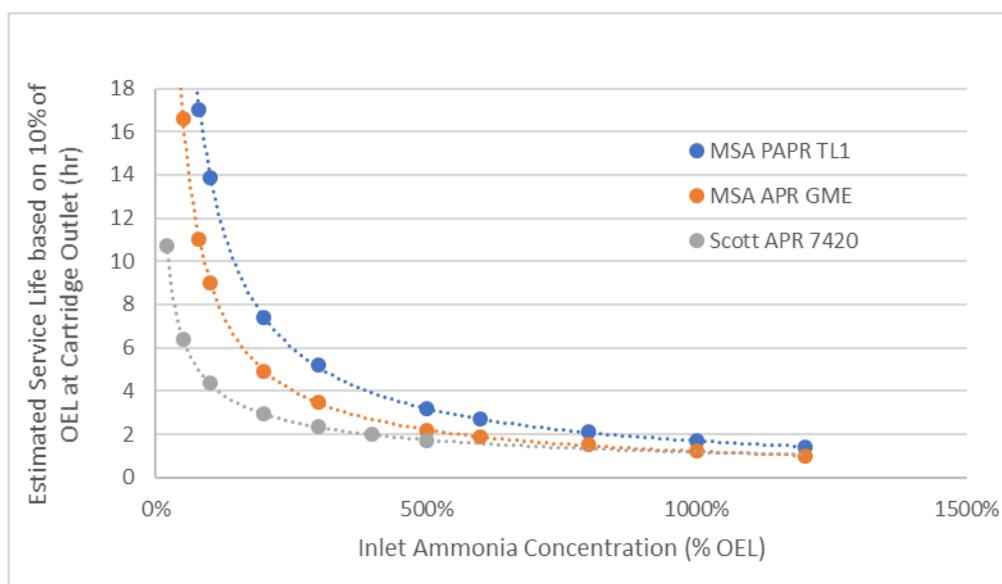


Figure F.3 Comparison of Estimated Service Life at Different Inlet Concentrations of Ammonia for the MSA APR and PAPR cartridges. The results of the SCOTT APR cartridge also are included. Breakthrough times were obtained using the MSA service life calculator and SCOTT SureLife calculator.

⁵⁹ The recommended APR adjustment from Freeman et.al. [15] - In general, most estimations obtained from the SCOTT SureLife^{®59} Cartridge Calculator were near or below the measured breakthrough values for each of the cartridge tests, thereby validating the use of that tool by Industrial Hygiene in future ammonia service life estimations. However, a number of service life estimations were greater than measured breakthrough times. If an additional 2-hour safety factor were applied to the SureLife[®] estimates, all observed ammonia breakthrough times would be greater than corresponding service life estimations, and ammonia would be a leading candidate for defining the minimum breakthrough times for the cartridges.



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