

**Occupational Exposure Evaluation of Complex Vapor Mixtures
at the Hanford Nuclear Waste Site, Washington
Worksite Vapor Characterization**

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ABSTRACT

Extensive sampling and analysis has been done over the years to characterize the radioactive and chemical properties of hazardous waste stored in 177 underground tanks at the Hanford site in eastern Washington State. The purpose of these analyses was to evaluate safety and environmental concerns related to tank stability. More recently, characterization studies have broadened to evaluate potential health hazards of chemical vapors at the ground surface, where workers perform maintenance and waste transfer activities.

Chemical vapor emissions from underground hazardous waste storage tanks on the Hanford site are a potential concern because workers enter the tank farms on a regular basis for waste retrievals, equipment maintenance, and surveillance. The extensive sampling done during this campaign evaluated vapor concentrations of more than 100 different chemical at 70 sites in and around one section of the tank farms. Sampling identified only four vapors (ammonia, nitrous oxide, nitrosodimethylamine, and nitrosomethylethylamine) that were present above occupational exposure limits. These elevated concentrations were detected only at exhaust stacks and passive breather filter outlets. Beyond five feet from the sources, vapors disperse rapidly. No vapors were measured above 10% of their OELs more than five feet from the source. This suggests that vapor controls can be focused on limited hazard zones around sources.

INTRODUCTION

The Hanford Site in eastern Washington State produced plutonium for the United States' nuclear weapons program from the 1940s to the 1980s. Nuclear and chemical waste from plutonium production was initially transferred to 149 single-shell underground storage tanks, each holding up to one million gallons of waste. In later years, waste was transferred to 28 newer double-shell tanks. The double-shell tanks were constructed by the U.S. Department of Energy in the 1970s and 1980s to provide more secure interim storage until the waste could be treated for stable long-term disposal. Tank farm contractors are in the process of retrieving all remaining waste from the older single-shell tanks and transferring it into the newer double-shell tanks. During the waste retrieval process, tank farms workers are potentially exposed to fugitive chemical vapors that can escape from tank headspaces. Preliminary investigations have shown that the tanks hold more than 1,500 different species of chemicals, in addition to radionuclides.

Exposure assessments were undertaken to fully characterize the hazards from chemical vapors. This paper describes the extensive work that was done to characterize tank wastes, tank headspace vapors, and workplace vapor concentrations. Assessment of potential worker exposure to vapors is described in separate papers.

Background and Sampling Methods

Extensive sampling and analysis has been done over the years to characterize the radioactive and chemical properties of waste stored in the underground Hanford tanks. The main purpose of these analyses was to evaluate safety and environmental concerns. More recently, characterization studies have broadened to evaluate potential health hazards of chemical vapors at the ground surface, where workers perform maintenance and waste transfer activities.

Vapors are released from the underground tanks into the ambient air from several sources. The double-shell tanks have active exhaust systems which continuously vent tank headspace vapors, after high-efficiency particular air (HEPA) filtration to remove radioactive particles. Vapors are released on a more random basis from the HEPA-filtered passive exhaust ports (breather filters) of single-shell tanks. Breather filter emissions often come in bursts linked to meteorological conditions, and are not always predictable. The tanks also have various risers and access ports, some of which are open to the atmosphere and can release vapors.

For certain operations, such as waste retrieval from single-shell tanks for transfer to newer double-shell tanks, tank risers are deliberately opened. These waste-disturbing activities naturally release larger volumes of vapors. The assessment described in this paper deals solely with routine, non-waste-disturbing activities. Work done to evaluate waste-disturbing activities will be presented separately.

The fundamental question to begin evaluating 1,500 chemical vapors is whether they are present in the tank headspaces at potentially dangerous concentrations. A robust, comprehensive process was designed to evaluate the potential health hazards of the vapors. This process, referred to as the Industrial Hygiene Technical Basis, incorporated the following elements:

- Using information from tank headspace characterization, chemical interaction products, and historical process information, a list was generated of all known and probable headspace vapor constituents. This list included more than 1,800 chemicals.
- Headspace concentrations of 1,500 vapors were retrieved from characterization analyses.
- Approximately 1,100 of the 1,500 chemicals did not have published occupational exposure limits (OEL) – either OSHA permissible exposure limits (PEL), or the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit values (TLV). Standard toxicological methods were used to develop working OELs for these 1,100 chemicals.
- The headspace concentrations of the chemicals were compared to the OELs. If any chemical was present in any of the 177 tanks at a concentration above 10% of its OEL, it was put on a list of “chemicals of potential concern” (COPC). In addition, any of the chemicals which are known or probable carcinogens were added to the list regardless of headspace concentration. The final COPC list contained about 80 chemicals.

Vapors on the COPC list were the targets of workspace characterization assessments. Key questions to be answered were:

- What are the concentrations of COPCs at sources of tank farms vapor emissions (double-shell tank stacks and single-shell tank breather filters)?
- How far from the sources are vapors present at levels of concern?
- Do tank vapors migrate beyond tank farm boundaries at levels of concern?

Results presented in this paper are for sampling done at one complex of tanks in the southeastern portion of the Hanford tank farms. The tank farms evaluated are the double-shell tank farms AN, AP, AW, AY, and AZ; and the single-shell tank farms A and AX. This area was collectively referred to as “A-prefix farms.”

A combination of sampling strategies was used to ensure that results captured near-maximum vapor concentrations. Stack vapor emissions occur continuously, but those from breather filters occur at irregular intervals. To ensure that sampling coincided with vapor emissions, continuous monitors (ppb RAE or Area RAE) were placed in breather filters, so that ammonia and volatile organic compound (VOC) emissions could be recorded continuously. Evaluation of these indicator vapors for weeks in advance of sampling revealed trends for timing the sampling. Fig. 1 shows VOC monitoring results at 6 breather filters, and their relation to one of the sampling events.

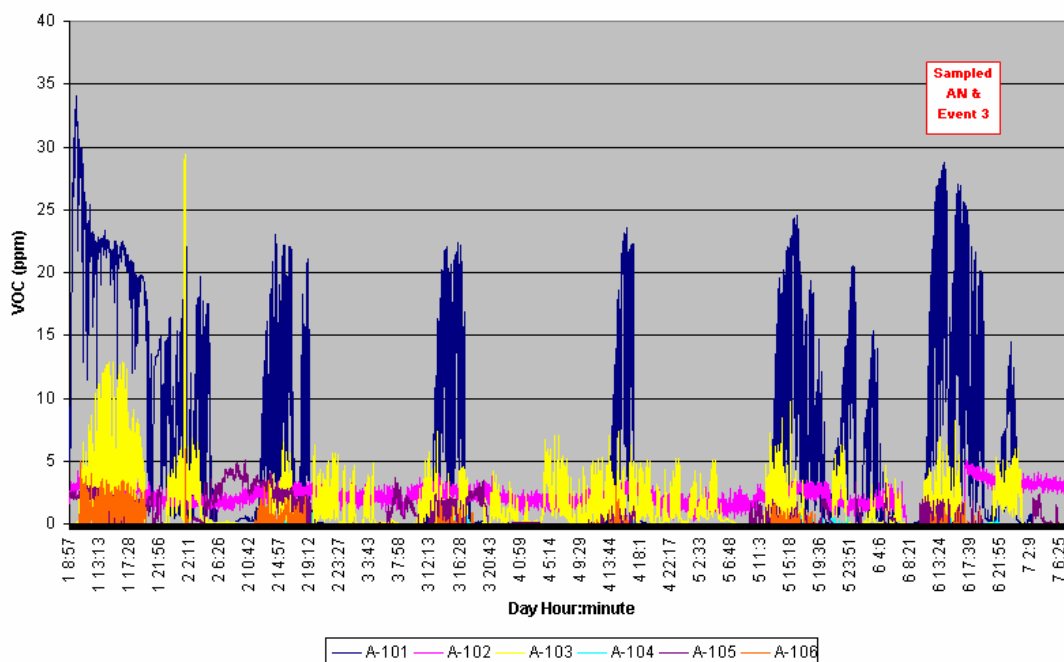


Fig. 1. Continuous monitoring results for volatile organic compound (VOC) emissions from six breather filters for the period of September 1 to 7, 2005. One sampling event is noted on September 6 from about 12:00 to 18:00.

The overall sampling plan for the 65 sampling sites is shown in Table I. In addition to these, samples were collected at five elevated stacks, for a total of 70 sampling sites. To control for possible effects of environmental factors such as vehicle exhaust, smoking, and other sources not directly associated with the tanks, sites outside the tank farms were selected in low- and high-traffic areas. Sites inside and outside the tank farms were also selected based on distance (greater or less than 100 meters) from the elevated stacks. Finally, sites were located directly at the 10 breather filters; in addition, at two of the breather filters, simultaneous samples were taken 5 feet away at the four points of the compass. A layout of the sample area showing the relative locations of the sampling sites is given in Figure 2.

Sampling was done from May through September, 2005. Multiple samples were taken during each sampling event, situated at various points across the tank farms, to test for wind dispersion effects. All sampling was done when wind was less than 25 mph.

At each site, multiple sampling media were used to capture more than 100 different chemical vapors. Table II shows the list of sampling media used, along with representative analytes. Not all chemicals actually analyzed are listed.

Table I. Overall Sampling Plan For the 65 Sampling Sites.

Outside Tank Farms					
		Low-traffic area		High-traffic area	
Sampling Event	Far from stack	Near stack	Far from stack	Near stack	
1	3	3	3	3	
2	3	3	2	3	
3	3	3	2	3	
Total	9	9	7	9	

Inside Tank Farms				
Sampling Event	Far from stack	Near stack	At low-level source	5 ft from low source
1	2	3	4	4
2	2	3	3	4
3	0	3	3	0
Total	4	9	10	8

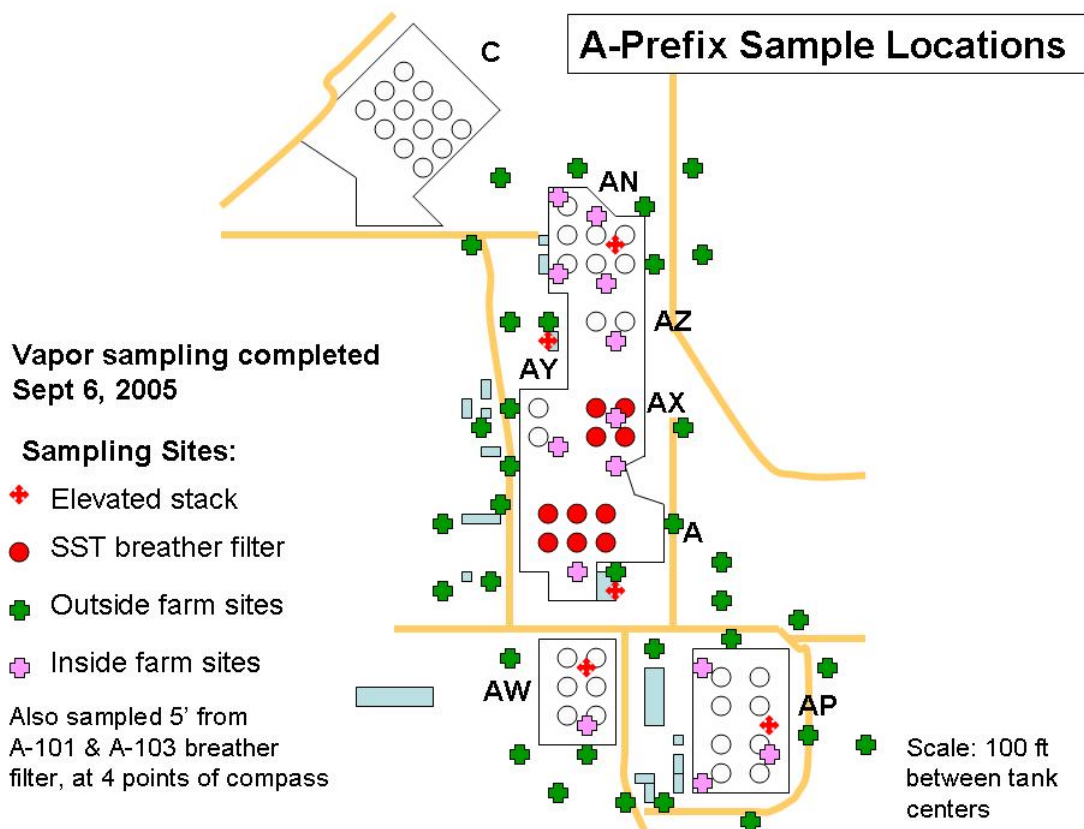


Fig. 2. Locations of the 70 sample sites.

Table II. List of Sampling Media Used, Along with Representative Analytes.

Chemicals of Potential Concern (COPC) Sample Media

Media	Analyte List	CAS #	Media	Analyte List	CAS #
Carbotrap 300 semi-volatile			Carbotrap 300 volatile		
	1,1'-Biphenyl	92-52-4		1,2-Dichloroethane	107-06-2
	alpha-Naphthylamine	134-32-7		1-Butanol	71-36-3
	bis(2-ethylhexyl)phthalate	117-81-7		2-Ethyl-1-hexanol	104-76-7
	Dichlorodiphenyldichloroethylene	72-55-9		3-Buten-2-one	78-94-4
	Tributylphosphate (TBP)	126-73-8		Acetonitrile	75-05-8
				Benzene	71-43-2
				Carbon disulfide	75-15-0
				Carbon Tetrachloride	56-23-5
				Chloroform	67-66-3
				Ethylene dibromide	106-93-4
				Hexanenitrile	628-73-9
				Methanol	67-56-1
				Methylene chloride (dichloromethane)	75-09-2
				Pentanenitrile	110-59-8
				Propanenitrile	107-12-0
				Pyridine	110-86-1
				Tetrachloroethylene	127-18-4
Thermosorb N sorbent tube					
	4-Nitrosomorpholine	59-89-2			
	Nitrosomethane	865-40-7			
	N-Nitrosodimethylamine	62-75-9			
	N-Nitrosomethylethylamine	10595-95-6			
Summa canister					
	1,4-Dioxane	123-91-1			
	2-Hexanone (Methyl butyl ketone)	591-78-6			
	2-Nitropropane	79-46-9			
	3-Hexanone	589-38-8			

Table II. List of Sampling Media Used, Along with Representative Analytes (continued).

Chemicals of Potential Concern (COPC) Sample Media

Media	Analyte List	CAS #	Media	Analyte List	CAS #
	Acetaldehyde	75-07-0			
	Butanal	123-72-8	Silica gel sorbent tube		
	Butanenitrile	109-74-0		Formaldehyde	50-00-0
	Trichloroethylene	79-01-6			
	Vinyl chloride (chloroethene)	75-01-4	CISA sorbent tube		
				Ammonia	7664-41-7
Frontier Geosciences sorbent tube					
	Mercury	7439-97-6	Carbotrap sorbent tube		
				Dimethyl mercury	593-74-8
XAD 7 sorbent trap					
	Methyl isocyanate	624-83-9			

Results

Table III through VII give the results of area sampling at the 70 sites. COPCs were measured above their occupational exposure limits only at the sources (breather filters and stacks). More than five feet from the sources, vapor concentrations decreased to levels below 10% of their OELs. Of more than 100 vapors analyzed, ammonia, nitrosodimethylamine, and nitroso-methylethylamine were the only ones measured above their OEL anywhere in the study area.

As stated above, these results represent a subset of tank farm activities: routine operations. Higher vapor concentrations are expected to occur in some areas during waste-disturbing activities. Those results are currently being evaluated and will be presented separately

Table III. Mean Air Concentrations, Plus Minimum and Maximum Values, for Samples Taken Directly at Breather Filters.

Directly at Breather Filters

Agent	CAS	n	Concentration	OEL	min	max
Acetonitrile	75-05-8	6	0.05 ppm	20	0.01	0.16
Ammonia	7664-41-7	5	13.41 ppm	25	0.18	52.26
Formaldehyde	50-00-0	1	0.03 ppm	0.3		
Mercury	7439-97-6	3	0.25 µg/m ³	30	0.002	0.74
Nitrosodimethylamine	62-75-9	4	0.26 ppb	0.3	0.02	0.76
Nitrosodipropylamine	621-64-7	5	0.01 ppb		0.004	0.01
Tetrachloroethylene	127-18-4	1	8.60 ppb	25		

[Bold type in the body of the table indicates agents present above their OEL (occupational exposure limit)].

Table IV. Mean Air Concentrations, Plus Minimum and Maximum Values, for Samples Taken 5 Feet from Breather Filters.

5 Feet from Breather Filters

Agent	CAS	n	Concentration	OEL	min	max
Acetonitrile	75-05-8	12	0.11 ppm	20	0.004	0.55
Ammonia	7664-41-7	1	0.13 ppm	25		
Formaldehyde	50-00-0	1	0.02 ppm	0.3		
Nitrosodipropylamine (OEL – occupational exposure limit)	621-64-7	4	0.005 ppb		0.004	0.006

Table V. Mean Air Concentrations, Plus Minimum and Maximum Values, for Samples Taken Inside the Tank Farms, More Than 5 Feet from Breather Filters.

Inside Farms, More Than Five Feet from Vapor Sources

Agent	CAS	n	Concentration	OEL	min	max
Acetonitrile	75-05-8	10	0.04 ppm	20	0.004	0.12
Ammonia	7664-41-7	2	0.13 ppm	25	0.13	0.13
Formaldehyde	50-00-0	13	6.68 ppb	300	4.96	10.22

(OEL – occupational exposure limit)

Table VI. Mean Air Concentrations, Plus Minimum and Maximum Values, for Samples Taken Outside the Tank Farms.

Outside Farms

Agent	CAS	n	Concentration	OEL	min	max
1-Butanol	71-36-3	1	0.05 ppm	20		
Acetaldehyde	75-07-0	6	0.02 ppm	25	0.01	0.03
Acetonitrile	75-05-8	8	0.04 ppm	20	0.003	0.17
Ammonia	7664-41-8	14	0.05 ppm	25	0.03	0.22
Formaldehyde	50-00-0	27	4.62 ppb	300	2.60	7.99
Methanol	67-56-1	4	0.012 ppm	200	0.011	0.014

(OEL – occupational exposure limit)

Table VII. Mean Air Concentrations, Plus Minimum and Maximum Values, for Samples Taken At the Double-Shell Tank Exhaust Stacks.

Inside Double-Shell Tank Exhaust Stacks

Agent	CAS	n	Concentration	OEL	min	max
1-Butanol	71-36-3	2	0.30 ppm	20	0.10	0.50
1-Propanol	71-23-8	1	0.03 ppm	200		
Acetaldehyde	75-07-0	1	0.02 ppm	25		
Acetaldehyde	75-07-0	1	0.03 ppm	25		
Acetone	67-64-1	3	0.04 ppm	500	0.02	0.05
Acetonitrile	75-05-8	1	0.08 ppm	20		
Ammonia	7664-41-7	4	63.30 ppm	25	10.53	104.08
Butanal	123-72-8	1	0.02 ppm			
Butane	106-97-8	1	0.02 ppm	1000		
Carbon disulfide	75-15-0	1	0.03 ppm	10		
Dimethyl mercury	593-74-8	2	0.005 $\mu\text{g}/\text{m}^3$	10	0.001	0.010
Ethanol	64-17-5	2	0.07 ppm	1000	0.04	0.10
Formaldehyde	50-00-0	2	13.45 ppb	300	13.31	13.58
Mercury	7439-97-6	3	1.58 $\mu\text{g}/\text{m}^3$	30	0.08	4.40
Methanol	67-56-1	3	0.31 ppm	200	0.09	0.60
Nitrosodibutylamine	924-16-3	1	0.01 ppb			
Nitrosodimethylamine	62-75-9	3	14.02 ppb	0.3	0.15	41.60
Nitrosomethylethylamine	10595-95-6	3	0.25 ppb	0.02	0.005	0.73
Nitrosomorpholine	59-89-2	2	0.21 ppb		0.03	0.39
Nitrosopiperidine	100-75-4	1	0.01 ppb			
Nitrosopyrrolidine	930-55-2	1	0.03 ppb			
Nitrous Oxide	10024-97-2	2	5.71 ppm	50	4.70	6.73

Table VII. Mean Air Concentrations, Plus Minimum and Maximum Values, for Samples Taken At the Double-Shell Tank Exhaust Stacks (continued).

Inside Double-Shell Tank Exhaust Stacks							
Agent	CAS	n	Concentration		OEL	min	max
Propane	74-98-6	1	0.02	ppm	1000		
Tetradecane	629-59-4	1	1.95	ppb			
Tetrahydrofuran	109-99-9	2	0.05	ppm	50	0.02	0.07
Trichlorofluoromethane	75-69-4	1	0.01	ppm	1000		
Undecane	1120-21-4	1	2.09	ppb			

[Bold type in the body of the table indicates agents present above their OEL (occupational exposure limit)].

Discussion and Conclusions

Chemical vapor emissions from underground hazardous waste storage tanks on the Hanford site are a potential concern because workers enter the tank farms on a regular basis for waste retrievals, equipment maintenance, and surveillance. The extensive sampling done during this campaign evaluated vapor concentrations of more than 100 different chemical at 70 sites in and around one section of the tank farms. Sampling identified only four vapors (ammonia, nitrous oxide, nitrosodimethylamine, and nitrosomethylethylamine) that were present above occupational exposure limits. These elevated concentrations were detected only at exhaust stacks and passive breather filter outlets. Beyond five feet from the sources, vapors disperse rapidly. No vapors were measured above 10% of their OELs more than five feet from the source. This suggests that vapor controls can be focused on limited hazard zones around sources.

Evaluation of tank headspace data shows that there is variability in vapor concentration between tanks. For this reason, these results for the A-prefix farms cannot reliably be applied to other tank farms. The robust sampling and analytical campaign piloted in this study should be applied to the other Hanford tank farms to characterize workplace vapor concentrations there.

Additionally, this study was done under routine conditions when tank waste was not being disturbed. Preliminary evaluations have shown that workplace vapor concentrations can be higher, at least in localized areas, during waste-disturbing activities. Further sampling and analysis is required to characterize non-routine operations, for which vapor controls will likely be different (more conservative).

Further work is underway to characterize the toxicology of the vapors and the worker exposure potential during routine operations, as well as to identify proper controls for the vapor hazard zones. Results of this work, as well as characterization of other farms and of non-routine operations will be presented separately.