

Hanford Chemical Vapors: Worker Concerns and Exposure Evaluation

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-99RL14047

CH2MHILL
Hanford Group, Inc.

P.O. Box 1500
Richland, Washington

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Thomas J. Anderson, Ph.D., CIH
Director of Safety & Health
CH2M HILL Hanford Group, Inc.

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T. J. Anderson, PhD, CIH
CH2M HILL Hanford Group, Inc. / Environmental Health
P.O. Box 1000, S7-70, Richland, WA 99352
U.S.A

ABSTRACT

Chemical vapor emissions from underground hazardous waste storage tanks on the Hanford site in eastern Washington State are a potential concern because workers enter the tank farms on a regular basis for waste retrievals, equipment maintenance, and surveillance. Tank farm contractors are in the process of retrieving all remaining waste from aging single-shell tanks, some of which date to World War II, and transferring it to newer double-shell tanks. During the waste retrieval process, tank farm workers are potentially exposed to fugitive chemical vapors that can escape from tank headspaces and other emission points. The tanks are known to hold more than 1,500 different species of chemicals, in addition to radionuclides. Exposure assessments have fully characterized the hazards from chemical vapors in half of the tank farms.

Extensive sampling and analysis has been done to characterize the chemical properties of hazardous waste and to evaluate potential health hazards of vapors at the ground surface, where workers perform maintenance and waste transfer activities. Worker concerns, risk communication, and exposure assessment are discussed, including evaluation of the potential hazards of complex mixtures of chemical vapors. Concentrations of vapors above occupational exposure limits (OEL) were detected only at exhaust stacks and passive breather filter outlets. Beyond five feet from the sources, vapors disperse rapidly. No vapors have been measured above 50% of their OELs more than five feet from the source. Vapor controls are focused on limited hazard zones around sources. Further evaluations of vapors include analysis of routes of exposure and thorough analysis of nuisance odors.

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 the remaining waste from the older single-shell tanks and transferring it to the newer double-shell tanks, where it will await future processing, such as vitrification and long-term storage. During the waste retrieval process, tank farms workers are potentially exposed to fugitive chemical vapors that can escape from tank headspaces. The tanks are known to hold more than 1,500 different species of chemicals, in addition to radionuclides.

The Hanford tank farm vapor issue received national media attention in 2004 when workers raised concerns about possible health effects from work in the tank farms. The U.S. Department of Energy, which oversees the Hanford Site, had just announced a plan to accelerate retrieval of the tanks. This caused workers to question the safety of tank farms work due to the large volume of waste present in the tanks and the complex mixtures of chemicals plus radiation. Chief among the workers' questions were: How well are vapors characterized, and are health hazards known? The Hanford tank farm is an uncontrolled-hazardous waste site, at least to the extent that vapors can be emitted from the tanks at irregular times. Workers sometimes report exposure symptoms, such as eye and throat irritation, breathing difficulties, headaches, and nausea. Although these exposure events are uncommon, and the workforce is generally very healthy, isolated incidents cause considerable concern among the workforce. Workers also occasionally smell odors. The question had been, do odors represent harmful exposures to vapors?

Some industrial hygiene data was available in 2004, but it was realized that due to the highly complex nature of the chemical mixtures in the tanks, more information was needed to make a definitive decision on safety of the work environment. As an immediate precaution until more data could be collected, in April 2004 supplied air respiratory protection was mandated for all tank farms work. Management committed to an extensive re-evaluation of the tank farms environment, and a large, multi-year chemical hazard evaluation was inaugurated. In addition to the technical and scientific aspects of this endeavor, a key component was worker involvement. Teams of workers and managers met regularly to discuss problems, work out solutions, and chart a course toward resolution of the tank farms vapor issue. The major elements of the vapor resolution project consisted of the following:

- Commitment to identify all chemical vapors. Management embarked on a multi-year project to measure and quantify vapor concentrations in all areas of the tank farms, from the tank headspaces, to emission sources where vapors escape into the work areas, to exhaust stacks, and to work areas near and remote from the emission sources.
- Develop exposure limits for chemicals that did not have them. Nearly 1,000 of the chemicals known to be present in the tanks did not have published exposure limits, such as U.S. Occupational Safety and Health Administration (OSHA) Permissible Exposure limits (PEL), American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV), or National Institute for Safety and Health (NIOSH) Recommended Exposure Limits (REL). Teams of toxicologists, chemists, and occupational health professionals were engaged to develop exposure limits for all vapors, and to assess whether they were present at levels that could be significant to worker health.
- Develop analytical methods. Methods for sampling and analysis of the mixtures of chemical vapors had to be devised.
- Measure vapors in work areas. All vapors that were present or had potential to be present had to be quantitatively measured in all work areas.

- **Hazard evaluation.** From the large body of data that was generated in the vapor characterization phase of the project, a hazard analysis was done to determine potential health impacts of the vapors.
- **Risk communication.** Key to success was effective communication of complex technical issues to workers and other constituents so that all questions were addressed to the satisfaction of the inquirer, and the deeply emotional state of the workers was eased.
- **Engineering solutions.** Appropriate engineered controls had to be developed and implemented to eliminate as much as possible the exposure of workers to chemicals.

This paper focuses on the chemical vapor hazard evaluation process. The process began with characterization of work areas to identify and quantify all chemicals that are present. Because of the strong concerns of workers for their own safety, it was also important to provide assurance that no other chemicals are present. That is, in addition to documenting and evaluating positive results of chemical monitoring, the project team also had to engage in the far more onerous task of proving that no other unidentified chemicals were present. Workplace air concentrations were measured in exhaustive monitoring campaigns (described below) and results were compared to exposure standards to determine whether over-exposures were occurring. Due to the large number of chemicals that could be present, the analysis also had to account for mixture effects. Finally, routes of exposure had to be evaluated. It could not be assumed that all possible exposures could be explained by inhalation of vapors. Evaluations were done of possible exposures to vapors, aerosols, and the (rare) contact with actual tank waste – any of which could have components of respiratory, dermal, ocular, or ingestion route of entry. Exposure through injection was determined not to be a factor, due to the rigorous radiological controls in place.

Due to the nature of the Hanford Site as one of the largest hazardous waste sites in the world, workers can be exposed to chemical vapors from tank waste at the tank farms. The responsibility of management is to determine where and how these exposures can occur, and to limit exposures to levels that are safe and as low as feasible. Vapor exposures vary according to type and location of work, meteorological factors (barometric pressure, thermal inversions, etc), type of controls in place, and other factors. All work is above ground, and workers never enter tanks. Some jobs require work operations to send monitoring or retrieval equipment into tanks through various risers and ports. Vapors are emitted from tanks through the risers when they are open to the atmosphere. The older single-shell tanks are designed to breathe passively to the atmosphere through HEPA filters. The double-shell tanks are equipped with elevated exhaust stacks through which vapors are actively exhausted to ventilate the tanks. Vapors can also escape as fugitive emissions through leaking valves and other sources. Vapor hazards can be high directly at vapor sources. Workers do not have to be directly working with waste to be exposed. For example, workers have reported exposures from standing or working near a vapor source. Evaluations from the enhanced characterization study have shown that beyond a limited distance (about 5 ft) from sources, vapor concentrations diminish rapidly, and there is no hazard in tank farm areas away from sources or outside tank farms. Vapors can disperse widely at very low concentrations, however. For some of these vapors (such as some aldehydes) the odor threshold is very low, much lower than exposure limits. Workers tend to have the perception that odors equate to hazards. For this reason, part of the vapor resolution project focused on evaluating and quantifying odors.

Background and Methods

The enhanced characterization project to evaluate workplace vapor exposures is being completed in stepwise fashion, evaluating the tank farms sector by sector. Each tank farm contains from 2 to 16 *underground storage tanks* with capacities up to one million-gallons of chemical and radiological waste. The surface area of each tank farm is generally in the vicinity of 10 to 20 acres, but since the farms are widely spread out, the entire tank farms site occupies approximately 50 square miles.

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. When analytical sampling was conducted, it was done at times when the tanks were know to be emitting vapors.

Area and personal sampling was done to measure all vapors that could be present in work areas. For each sector of the tank farms multiple replicates were taken at up to 65 different sampling sites both inside and outside the tank farms. Figure 1 shows the general sampling plan used for each sector of the tank farms. Preliminary computer modeling of vapor dispersion showed that vapor concentrations could be elevated at about 100 M from elevated exhaust stacks. Sample sites were located within 100 M (near) and greater than 100 M (far) to capture these effects. Since chemical analysis was done in the ppb range and lower, and many of the chemicals being evaluated are environmental contaminants generated by vehicle exhaust, smoking, cooking, and other human activities, sites outside the farms were located near and far from human and vehicle traffic areas to control for chemicals that many have sources other than the tanks. Inside the farms, sites were further distinguished by proximity to ground-level sources, such as fugitive emission points and single-shell tank passive breather filters.

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 source	5 ft from source
1	2	3	4	4
2	2	3	3	4
3	0	3	3	0
Total	4	9	10	8

Fig. 1. Generalized sampling plan.

At each sampling location, tripods were set up with industrial hygiene sampling pumps, evacuated sampling summa cylinders (with 8 hr restrictors for gradual filling), and continuous-reading data-logging monitors. Table 1 lists sampling media used at each location, along with representative target analytes (many more analytes were able to be detected). Media were analyzed at certified laboratories with appropriate analytical methods. In addition to target analytes, any traces that showed up as tentatively-identified compounds on mass spectroscopy read-outs (above 10% of reference peaks) were positively identified, so that the list of organic chemicals potential seen was very broad.

Table 1. 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
Thermosorb N sorbent tube				Carbon disulfide	75-15-0
	4-Nitrosomorpholine	59-89-2		Carbon Tetrachloride	56-23-5
	Nitrosomethane	865-40-7		Chloroform	67-66-3
	N-Nitrosodimethylamine	62-75-9		Ethylene dibromide	106-93-4
	N-Nitrosomethylethylamine	10595-95-6		Hexanenitrile	628-73-9
				Methanol	67-56-1
Summa canister				Methylene chloride (dichloromethane)	75-09-2
	1,4-Dioxane	123-91-1		Pentanenitrile	110-59-8
	2-Hexanone (Methyl butyl ketone)	591-78-6		Propanenitrile	107-12-0
	2-Nitropropane	79-46-9		Pyridine	110-86-1
	3-Hexanone	589-38-8		Tetrachloroethylene	127-18-4
	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			Carbotrap sorbent tube		
	Mercury	7439-97-6		Dimethyl mercury	593-74-8
XAD 7 sorbent trap					
	Methyl isocyanate	624-83-9			

Results

Figure 2 shows a summary of the sampling results. This pattern has been consistent throughout the three sectors of the tank farms evaluated to date. No elevated vapor concentrations were seen at expected touch-down points from elevated exhaust stacks. Human activities (other than the tanks) did not contribute differentially, comparing low-traffic and high-traffic areas. The one significant trend was that vapor concentrations were elevated, sometimes extremely high relative to exposure limits, directly at emission sources. Because the volume and flow rate out of the passive breather filters is low, concentrations fall to safe levels within five feet from the sources. Figure 3 shows all vapors detected, along with the percent of their respective occupational exposure limit. All of these maxima were detected directly at a vapor source (exhaust stack or breather filter. Note that nitrosodimethylamine was present in one sample at a breather filter at

138 times its exposure limit. In no instances were elevated vapor concentrations detected beyond five feet from an emission source.

Outside Tank Farms			
Low-traffic area		High-traffic area	
Far from stack	Near stack	Far from stack	Near stack
No vapors above 10% of OEL			
Inside Tank Farms			
Far from stack	Near stack	At source	5 ft from source
No vapors above 10% of OEL	No vapors above 10% of OEL	Vapors above 10% of OEL	No vapors above 10% of OEL

Fig. 2. Summary of results with respect to sample plan (OEL – occupational exposure limit).

Agent	Max Concentration	%OEL
N-Nitrosodimethylamine	0.04 ppm	13,866.25
Ammonia	104.08 ppm	416.31
N-Nitrosomethylethylamine	0.00073 ppm	243.77
Nitrous Oxide	120.00 ppm	240.00
Mercury	0.02 mg/m ³	65.99
n-Nitrosomorpholine	0.00039 ppm	65.43
Ethylamine	0.83 ppm	16.57
Formaldehyde	0.03 ppm	9.96
Methylamine	0.44 ppm	8.75
Acetonitrile	0.54 ppm	2.69
1-Butanol	500.00 ppb	2.50
bis(2-ethylhexyl)phthalate	0.00348 ppm	1.16
n-Nitrosodipropylamine	0.00001 ppm	0.92
n-Nitrosopyrrolidine	0.00003 ppm	0.77
Benzene	3.00 ppb	0.60
Carbon Disulfide	0.03 ppm	0.31
Methanol	0.60 ppm	0.30
n-Nitrosodibutylamine	0.00001 ppm	0.27
n-Nitrosopiperdine	0.00001 ppm	0.18
2-Hexanone	9.00 ppb	0.18
Acetaldehyde	44.00 ppb	0.18
Tetrahydrofuran	71.00 ppb	0.14
Acetone	0.05 ppm	0.10
Dimethylmercury	0.00001 mg/m ³	0.10
Butanal	22.00 ppb	0.09
Sulfur Dioxide	0.002 ppm	0.08
Tetrachloroethylene	0.01 ppm	0.05
Cyclohexanone	6.00 ppb	0.03
Toluene	12.00 ppb	0.02
1-Propanol	26.00 ppb	0.01
meta-xylene	0.01 ppm	0.01
Ethanol	100.00 ppm	0.01
2-Butoxy ethanol	0.002 ppm	0.01
ortho-xylene	4.00 ppb	0.004

Fig. 3. Maximum concentrations of all vapors detected, sorted from greatest to least percent of their respective occupational exposure limit (OEL).

Because several chemicals combine in most of the tank farms vapor emissions, it was important to evaluate not only the individual result but also the potential for combined effects from complex mixtures. The OSHA mixture rule was used to evaluate the impact of mixtures. All chemicals detected at any location were added into the mixture analysis for that location. The mean concentrations of all replicates were calculated for each agent. If an agent had some detectable results and also some non-detects, the non-detect results were included in the mean by dividing the detection limit by the square root of 2. Agents in each area were then grouped by target organ or effect (using the ACGIH designated health effect). The sum of the ratios of the mean concentrations divided by their exposure limit was then calculated. This sum of ratios is considered over-exposed if the total is greater than unity (1). The tank farms action level for all chemicals is one-half the exposure limit. Therefore, mixtures were considered potential overexposures if the mixture index was greater than 0.5. Figure 4 shows an example of this calculation at one source, a single-shell tank breather filter. Note that this is considered a potential over-exposure for carcinogens because the index exceeds 0.5.

The mixture analysis exactly paralleled the results for individual chemicals. That is, the only mixture indices above 0.5 were directly at emission sources. No mixtures above 0.5 were found greater than five feet from sources.

Agent	Average Concentration	Concl/ OEL	Effect	Mixture TWA
Benzene	0.0023 ppm	0.0046	cancer	
Nitrosodimethylamine	0.0002 ppm	0.7678	cancer	0.7724
Mercury	0.0018 mg/m ³	0.0602	CNS	
Toluene	0.0044 ppm	0.0001	CNS	0.0603
1-Butanol	0.0090 ppm	0.0005	irritation	
Ammonia	5.5367 ppm	0.2215	irritation	
Butanal	0.0110 ppm	0.0004	irritation	
Tetrachloroethylene	0.0012 ppm	0.00005	irritation	0.2224
Acetonitrile	0.1644 ppm	0.0082	lung	0.0082
Nitrous Oxide	14.0000 ppm	0.2800	reprod.	0.2800

Fig. 4. Example of a mixture application at one breather filter.

Odors were also evaluated because of worker sensitivities. Odor thresholds were determined for most of the vapors detected. In the areas away from sources, which had been determined by mixture analysis to have vapor concentrations well below occupational exposure limits, 3 vapors were noted to be present above their odor threshold, but well below their exposure limits (Figure 5). These vapors are suspected of causing the characteristic "musty tennis shoe" odor of some parts of the tank farms.

Vapor	Max. Conc.	Odor Threshold	OEL
Acetaldehyde	0.04	0.003	25 ppm
Ammonia	0.22	0.04	25 ppm
Butanal	0.026	0.005	25 ppm

Fig. 5. The three vapors found to be present above odor their thresholds but well below occupational exposure limits (OEL) in areas determined to be non-hazardous.

Routes of exposure were evaluated using standard toxicological methods. It was assumed that sources of body burden could come from vapors, aerosols generated by various disturbing mechanisms, and by the rare instances (such as removing probes from inside tanks) when workers can contact actual tank wastes. Actual measurements were made of the concentrations of chemicals present in each of these types of activity. The suspected routes of exposure are inhalation, dermal, ocular and ingestion (usually by oral or nasal uptake followed by coughing and swallowing phlegm). Systematic analysis was done of work activities to understand, in the worst case, the amount of contact a worker could have with each of the phases of a chemical through each of the exposure routes. Using toxicological uptake models, the amount of the chemical that actually entered the body was calculated for each of the work activities, using the chemical concentrations known to be present in that activity. The body burden from this exposure was compared to the body burden that would ensue from 8 hours of inhalational exposure at the exposure limit (the know safe level, as documented in the published exposure levels). Work activity controls and personal protective equipment were adjusted accordingly to reduce exposures below hazardous levels for each type of job. For example, if a particular job was shown to pose a risk through dermal exposure to a chemical or group of chemicals, appropriate skin protection was prescribed for that job through the work planning process.

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 chemicals at 65 sites in and around three sections of the tank farms. Elevated vapor 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 sources. Based on these results, vapor controls are focused on limited hazard zones around vapor sources.

Engineering controls are used to reduce worker exposure to vapors. These include active ventilation of double-shell tanks, stack exhaust extensions to raise stacks higher into the air, foaming of vapor sources to reduce fugitive emissions, re-sealing motor shafts on exhaust fans, replacing aging plastic tubing on installed sampling ports with stainless steel tubes, and others. Administrative controls include site access restriction, adapting work schedules to keep workers out of farms during vapor-generating activities, and establishing boundaries around known vapor sources. These "vapor control zones" are demarcated with physical boundaries and posted with warning signs. Inside the zones workers are required to wear supplied air respiratory protection. Outside the zones, no respiratory protection is required. The campaign of risk communication helped to ease worker concerns, and the previously high level of worker concern has dropped considerably. Nonetheless, a small percentage of workers still feel uncomfortable even in the zones that have been determined to be safe. Accordingly, a voluntary respiratory protection program is in place. Workers can request any type of respiratory protection, including self-contained breathing apparatus (SCBA) if they choose.