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MEASUREMENT AND ESTIMATED HEALTH RISKS OF VOLATILE ORGANIC COMPOUNDS AND POLYCHLORINATED BIPHENYLS IN AIR AT THE HANFORD SITE

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SUMMARY

A variety of radioactive and nonradioactive chemicals have been released in effluent streams and discharged to waste disposal facilities during the nuclear materials production period at the Hanford Site. Extensive environmental surveillance for radioactive materials has occurred at Hanford; however, only limited information is available on the types and concentrations of organic pollutants potentially present. This report describes work performed to provide the Hanford Site Surface Environmental Surveillance Project with representative air concentration data for volatile organic compounds and polychlorinated biphenyls (PCBs). U.S. Environmental Protection Agency (USEPA) volatile organic compound sampling methods evaluated for Hanford Site use were carbon-based adsorbent traps (TO-2) and Summa air canisters (TO-14). Polychlorinated biphenyls were sampled using USEPA method (TO-4), which uses glass fiber filters and polyurethane foam adsorbent beds to collect the PCBs.

This report also presents results for environmental surveillance samples collected for volatile organic compound and PCB analyses from 1990 to 1993. All measured air concentrations of volatile organic compounds and PCBs were well below applicable maximum allowable concentration standards (occupational) for air contaminants. Because of the lack of ambient (non-occupational) air concentration standards, a conservative estimate is provided of the potential human health impacts from exposure to the ambient air concentrations measured on the Hanford Site.

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ABBREVIATED TERMS

AALG	ambient air level goals
ACGIH	American Conference of Government and Industrial Hygienists
Aroclor	a technical mixture of PCB isomers
AT	averaging time [period over which exposure is averaged (day)]
B	breakthrough
BW	body weight (kg)
CA	contaminant concentration (ng/m^3)
CFC	chlorofluorocarbon
CMS	carbon molecular sieve (TO-2 adsorbent)
DBC	dibutyl-chlorendate
DCFM	dichlorodifluoromethane
DCM	dichloromethane
EDE	effective dose equivalent (mrem)
ED	exposure duration (yr)
EF	exposure frequency (day/yr)
ET	exposure time (h/day)
GFF	glass fiber filter
HEAST	Health Effects Assessment Summary Tables (database, USEPA 1992)
IRIS	Information Risk Information System (database, USEPA 1993)
HSBRAM	Hanford Site Baseline Risk Assessment Methodology
ICR	incremental cancer risk
IR	inhalation rate (m^3/day)
mrem	radiation dose unit (0.01 msievert)
PCB	polychlorinated biphenyls (see Aroclor)
PUF	polyurethane foam plug
Qf (Qb)	quantity on front (back) trap
SESP	Surface Environmental Surveillance Project
TCFM	trichlorofluoromethane
TCMX	2,4,5,6- tetrachloro-meta-xylene
TLV	threshold limit value
TO-X	USEPA Methods for the Determination of Toxic Organics in Ambient Air
USEPA	U.S. Environmental Protection Agency
VOC	volatile organic compound

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1.0 INTRODUCTION

A variety of both radioactive and nonradioactive chemicals were released in effluent streams and discharged to waste disposal facilities during the past 40 years on the Hanford Site. Volatile organic compounds have been detected by Hanford Site subsurface chemical surveillance programs at some locations in the groundwater; however, only limited data exist to demonstrate whether or not elevated concentrations of organic chemicals exist in surface environmental media (Woodruff et al. 1993). Some potential mechanisms leading to surface exposure from airborne contaminants may be direct releases to the atmosphere from facilities, fugitive dust sources, and remediation activities. This report describes a field evaluation of selected U.S. Environmental Protection Agency (USEPA) ambient air sampling methods for use in the Hanford Site Surface Environmental Surveillance Project (SESP) and provides some initial data concerning the types and concentrations of airborne volatile organic compounds at the Hanford Site.

Based on the above considerations, the SESP conducted a scoping study to evaluate the need for surveillance of nonradiological contaminants in Hanford surface environmental media. This study used available source term information to provide an assessment of toxic species that may be approaching concentrations offsite that have a carcinogenic risk level of 1 E-7 excess cancer incidence. This value is 10% of the 1 E-6 risk level at which the USEPA usually evaluates contaminants in the environment (i.e., one excess cancer for a population of 1,000,000). For reference, the 1992 calculated dose to the hypothetical maximally exposed individual from radionuclides released from Hanford operations was 0.02 mrem [effective dose equivalent (EDE)], which equates to a risk of approximately 1 E-8 excess cancer incidence (Woodruff et al. 1993). The radiological risk level is based on a risk factor of 0.5 E-6 excess cancers/mrem EDE. For noncarcinogens the approach was to identify contaminants that may be approaching 10% of a Hazard Level (i.e., a

0.1 Hazard Index). The scoping study's assessment was fairly limited, but identified target species for initial sampling and quantitation.

For airborne releases the scoping study found little information on nonradiological contaminants at Hanford, with most of the available information related to coal and oil combustion. The release of carbon tetrachloride from the Plutonium Finishing Plant was an important exception, with a reported average release for 1984 to 1987 of 11,200 kg/yr. The reported cancer risk to an offsite hypothetical maximally exposed individual from carbon tetrachloride was 2 E-8 cancer/person, which is less than the 1 E-6 cancer/person generally considered acceptable.

An additional area of significance reported by the scoping study involved elevated levels of polychlorinated biphenyls (PCBs) present in sediments of the 300 Area process ponds. If resuspension of these sediments could occur, then the potential cancer risk to an offsite hypothetical maximally exposed individual was calculated to be in the range of 1 E-4 cancer/person, which is considerably more than the 1 E-6 risk level. Surveillance of airborne concentrations of PCBs near the 300 Area was recommended.

Riley et al. (1986) conducted a preliminary survey of PCBs in aquatic habitats and birds located on or near the Hanford Site. Concentrations of PCBs ranging from "over 1 ng/L and below 20 ng/L" were reported for the Hanford Site impoundments. These water concentrations are of the same magnitude as the 14 ng/L-water quality criteria (chronic) reported by the USEPA (1986a) for the protection of aquatic life. Riley et al. (1986) also reported PCB concentrations in fat from fish collected from the impoundments (0.04 to 4.72 μg/g wet weight) and in fat from juvenile great blue herons nesting on the Hanford Site (3.6 to 11 μg/g wet weight). The chromatographic profiles of PCBs in Hanford sediments, fish, and nesting birds closely matched the profile of Aroclor 1260 (a technical mixture of PCBs), while fat from non-Hanford birds (2.7 to 15.6 μg/g wet weight) contained PCB profiles that

indicated a mixture of Aroclors. The differences in Aroclor profiles between Hanford and non-Hanford birds suggest that the Hanford birds may have obtained PCBs from a diet local to the Hanford Site (Riley et al. 1986).

The general lack of data on the concentrations of volatile organic compounds in ambient air coupled with the presence of carbon tetrachloride and other chlorinated organics in ground water, and known inventories of toxic compounds in waste burial sites at the Hanford Site indicate the need for further investigation of the ambient air concentrations of these chemicals. This report describes work performed to identify suitable methods to provide the Hanford SESP with representative air concentration data for potentially toxic organic contaminants. The objective of this work was to characterize sampling and analytical schemes for both volatile organic compounds and PCBs and to evaluate the concentrations of the predominant organic pollutants at selected locations.

2.0 ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

Volatile organic compounds are members of a group of compounds with saturation vapor pressures above 0.1 torr (13 Pa) that exist in the atmosphere primarily as vapor phase material (i.e., not associated with airborne particulate). These compounds are used worldwide and are ubiquitous environmental contaminants. At elevated concentrations these compounds have the potential to impact human health, and some of the compounds are carcinogens or suspect carcinogens. This study investigated air sampling methods for volatile organic compounds potentially present in Hanford Site ambient air.

Volatile organic compounds can be collected from ambient air in a variety of ways including whole air collection (canister sampling), preconcentration onto adsorbent media, and cryogenic trapping. Most volatile organic compound sampling involves the collection of relatively low volumes of air on the order of tens to hundreds of liters. The sampling scheme must be shown to quantitatively collect the analyte and have good analytical recovery and low background contamination.

There are several volatile organic compounds potentially present in Hanford air. Benzene, 1,1,1-trichloroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, carbon tetrachloride, and toluene are common organic solvents, with carbon tetrachloride being of special interest because of its presence in Hanford groundwater (Woodruff et al. 1993). Dichlorodifluoromethane (DCFM) and trichlorofluoromethane (TCFM) are chlorofluorocarbon (CFC) refrigerant gases and have been widely used as aerosol propellants and blowing agents for foams. The CFCs are being removed from the market because of their stratospheric ozone depletion potential. The 1,3-dichloropropenes are agricultural pesticides that have been used as soil fumigants and nematocides (Merck, Inc. 1989).

2.1 METHOD EVALUATION FOR VOLATILE ORGANIC COMPOUNDS (ANALYSIS BY BATTELLE-COLUMBUS)

For this study two techniques were evaluated for use in surveillance of ambient air at the Hanford Site: USEPA Method TO-2, which uses adsorbent traps to collect the samples, and USEPA Method TO-14, which uses canister samplers (Winberry et al. 1988). The USEPA methods for toxic organic compounds (TO-X) are designed to provide specific guidance on the determination of toxic volatile organic compounds; however, these methods are still somewhat developmental. Users of the TO-X Methods need to carefully evaluate and document their ability to perform the fairly complex sample collection and analytical procedures. Most of these methods have been tested for only a limited number of compounds and additional verification by the user is required to expand these techniques to other volatile organic compounds.

Ambient air samples were collected at the Hanford Site using both the TO-2 and TO-14 methods and analyzed for 42 target compounds including selected halogenated alkanes, alkenes, and benzenes; benzene and alkylbenzenes. A complete list of the 42 volatile organic compounds and their corresponding threshold limit values for occupational air concentrations (ACGIH 1989-90) are given in Table 2.1. This work was conducted in two parts with the first tier being a methods evaluation and screening study for contaminants of interest with the samples analyzed by Battelle-Columbus; the second tier of environmental surveillance followed where the major compounds (on a concentration basis) identified in the earlier work were collected using Method TO-2 and were analyzed by a commercial analytical laboratory (Air Toxics, Inc., Rancho Cordova, California).

TABLE 2.1. Threshold Limit Values and Site Average Concentrations for Target Volatile Organic Compounds[a] (ng/L).

Compound	TLV	Site[b] Average	Site[c] Average
dichlorodifluoromethane	4,950,000	0.65	2.4
methyl chloride	103,000	<0.12	-
1,2-dichloro-1,1,2,2-tetrafluoroethane	4,170,000	<0.1	-
vinyl chloride	13,000	<0.05	-
methyl bromide	19,000	<0.05	-
ethyl chloride	2,640,000	<0.05	-
trichlorofluoromethane	5,620,000	7.82	0.29
1,1-dichloroethene	20,000	<0.15	-
dichloromethane	174,000	<0.17	0.03
3-chloropropane	NA[d]	<0.1	-
1,1,2-trichloro-1,2,2-trifluoroethane	7,670,000	0.78	0.26
1,1-dichloroethane	810,000	<0.05	-
cis-1,2-dichloroethene	793,000	<0.05	-
trichloromethane	49,000	<0.13	0.05
1,2-dichloroethane	40,000	<0.11	-
1,1,1-trichloroethane	1,910,000	1.04	0.59
benzene	32,000	0.79	0.36
carbon tetrachloride	31,000	0.89	0.51
1,2-dichloropropane	347,000	<0.05	-
trichloroethene	269,000	<0.11	-
cis-1,3-dichloropropene	4,500	1.54[e]	0.01[f]
trans-1,3-dichloropropene	4,500	1.03[e]	0.01[g]
1,1,2-trichloroethane	55,000	<0.05	-
toluene	377,000	1.85	0.38
1,2-dibromoethane	NA	<0.05	-
tetrachloroethene	339,000	<0.1	-
chlorobenzene	345,000	<0.1	-
ethylbenzene	434,000	<0.18	-
m + p-xylene	434,000	<0.42	0.14
styrene	213,000	<0.15	-
1,1,2,2-tetrachloroethane	6,900	<0.05	-
o-xylene	434,000	<0.22	0.07
4-ethyltoluene	NA	<0.12	-
1,3,5-trimethylbenzene	123,000	<0.11	-
1,2,4-trimethylbenzene	123,000	<0.19	-
benzyl chloride	5,200	<0.1	-
m-dichlorobenzene	NA	<0.12	-
p-dichlorobenzene	451,000	<0.1	-
o-dichlorobenzene	301,000	<0.1	-
1,2,4-trichlorobenzene	37,000	<0.1	-
hexachlorobutadiene	210	<0.05	-

(a) ACGIH 1989-1990.
(b) Table 2.5 (Method TO-2, Analysis by Battelle-Columbus).
(c) Table 2.8 (Method TO-2, Analysis by Air Toxics, Inc.).
(d) NA = Not available.
(e) Detected in only 4 of 12 samples.
(f) Detected in only 5 of 26 samples.
(g) Detected in only 8 of 26 samples.

2.1.1 USEPA Sample Collection Method TO-2 (Carbon Molecular Sieve Traps)

In this technique ambient air is pulled through a mixed bed of carbon molecular sieve (Carbosieve; CMS) and graphitized carbon (Carbotrap). Stainless steel Carbotrap 300 adsorbent tubes packed with Carbotrap C, Carbotrap, and Carbosieve S-III (Supelco, Inc.) were used to preconcentrate the volatile organic compounds. The compounds were removed from the adsorbent traps by thermal desorption and analyzed by gas chromatography/mass spectrometry. Considerable testing of this method was required because it has been used extensively by only a single laboratory and its general applicability has not been thoroughly documented (Winberry et al. 1988). In addition, Method TO-2 documented the performance of only 9 of the 42 target volatile organic compounds; however, the method could be extended to other volatile organic compounds with additional validation by the user.

2.1.1.1 General Procedure

Adsorbent tubes were installed on a gas manifold using 0.635-cm Swagelock fittings with Vespal ferrules (Supelco Inc., M-2A) and precleaned by outgassing for 24 h in a gas chromatography oven at 390° C with at least 100 mL/min of prepurified nitrogen gas (Westinghouse Store Order #21-3440-220) passing through each tube. Clean tubes were removed from the oven, placed in screw- capped glass sleeves, and packed into a metal tin containing a thin layer of activated charcoal on the bottom. Air samples were usually collected within 48 h of cleaning.

A simple gas manifold constructed by coupling sets of four 0.635-cm stainless steel Swagelock "T" fittings was used for the December 1989, February 1990, and March 1990 air samples. However, this simple manifold gave inconsistent flow rates and may not have provided uniform temperature control; thus, an improved manifold was constructed and used for the other samples. In the improved manifold the nitrogen gas stream was passed through a 1-m preheated coil before entering the manifold (a 10.2-cm inside diameter by

33-cm length stainless steel pipe). Beginning in August 1990, the nitrogen gas stream was further cleaned by passing it through a molecular sieve trap (0.22 kg Molecular Sieve A, Supelco Inc.) and a charcoal trap (400 mL, #2-2451M, Supelco, Inc.) before entering the preheated coil.

Samples were collected using either a DC-powered pump (Spectrex Model PAS-3000 Personal Air Sampler) or an AC-powered diaphragm vacuum/pressure pump (Cole-Palmer, #DOA-P104B-AA). The pumps and sampling equipment were housed in free-standing aluminum shelters (General Metals Works, PS-1 type) with the sample inlets approximately 1.2 m above the ground. Tygon tubing was used to couple the adsorbent tubes to the DC pumps. Collection tubes were connected to the AC pumps with 0.635-cm Swagelock fittings with Teflon ferrules. Air flows were measured using either a soap bubble flow meter or a calibrated rotameter. Flow rates were 43 to 261 mL/min for the DC pump (final volumes, 61 to 348 L) and 27 to 86 mL/min for the AC pump (final volumes, 39 to 130 L).

For most samples one adsorbent tube was used; however, for some samples two collection tubes were placed in series with the second tube providing information on analyte breakthrough. A 5-cm piece of Tygon tubing was used to couple the CMS tubes in series for the DC powered samples (December 1989) and 0.635-cm Swagelock fittings with Teflon ferrules were used to couple the CMS tubes for the AC samples (August 1990).

After sampling, the adsorbent tubes were placed in glass sleeves, capped, labeled, and returned to the metal tin for shipping. Unexposed sampling tubes (cleaned with the other sampling tubes) were carried to the field and shipped with the samples for use as blank samples. Samples were analyzed by Battelle-Columbus using gas chromatography-mass spectrometry with selected ion monitoring. The adsorbent tubes were returned for reuse

following analysis. Occasionally some of the adsorbent material escaped from the tubes during sampling, shipping, or analysis; thus, duplicate samples were taken at most locations.

2.1.1.2 Results and Discussion

Eleven blank adsorbent tubes (at least one per sample set) were analyzed with 10 of 43 of the compounds having detectable values in at least one sample (Table 2.2). The mean blank amount of volatile organic compounds and a comparison to the average amount typically collected in a 100-L ambient air sample at Hanford are also given in Table 2.2. Seven of the detected volatile organic compounds were found in only one or two samples and only four of these compounds (trichloromethane, tetrachloroethene, 1,3,5-, and 1,2,4-tri-methyl-benzene) were >10% of the amounts from the mean Hanford Site sample. Dichloro-difluoromethane, 1,1,1-trichloroethane, and benzene, were detected in three or more blank samples, with these compounds being 12%, 5%, and 11%, of the mean Hanford Site air sample, respectively. Because of the generally low levels of volatile organic compounds detected in the blank samples, the Battelle-Columbus sample results are reported without blank corrections.

The possibility of organic vapors penetrating through the adsorbent traps was checked by placing a second collection tube behind the front tube. Percent breakthrough (B%) was calculated as B% = 100(Qb/Qf), where Qb and Qf are the quantities found in the back and front traps. For this study breakthrough was operationally defined as having occurred when B% = 20. This value was selected because it allows for essentially quantitative collection on the front trap while allowing a sufficient amount of material to be collected on the back trap for accurate determination of breakthrough. Analyte breakthrough for selected volatile organic compounds from the August 1990 air samples are given in Table 2.3. Dichlorodifluoromethane (DCFM) showed breakthrough for the 72-L and 130-L samples but was retained for the 39-L sample; therefore, single tube experiments >39 L were not quantitative

TABLE 2.2 Ratio of Samples with Detectable Values to the Total Number of Samples for Volatile Organic Compound Air Samples, Average Blank Amount and Amounts of Volatile Organic Compounds Found in a Typical Air Sample

					(ng)	
Compound	200-West Area	300 Area	Rattlesnake Springs	Blanks	Mean[a] Blank	100 L[b] Sample
dichlorodifluoromethane	11/11	7/8	2/2	3/11	7.6	65
methyl chloride	7/11	2/8	1/2	0/11		
1,2-dichloro-1,1,2,2-tetrafluoroethane	7/11	2/8	1/2	0/11		
vinyl chloride	0/11	0/8	0/2	0/11		
methyl bromide	0/11	0/8	0/2	0/11		
ethyl chloride	0/11	0/8	0/2	0/11		
trichlorofluoromethane	11/11	8/8	2/2	1/11	60	780
1,1-dichloroethene	4/11	3/8	2/2	0/11		
dichloromethane	11/11	7/8	2/2	0/11		
3-chloropropane	2/11	1/8	0/2	0/11		
1,1,2-trichloro-1,2,2-trifluoroethane	11/11	8/8	2/2	0/11		
1,1-dichloroethane	0/11	0/8	0/2	0/11		
cis-1,2-dichloroethene	0/11	0/8	0/2	0/11		
trichloromethane	11/11	6/8	1/2	1/11	4.1	13
1,2-dichloroethane	10/11	6/8	1/2	0/11		
1,1,1-trichloroethane	11/11	8/8	2/2	7/11	5.0	104
benzene	11/11	8/8	2/2	4/11	8.5	79
carbon tetrachloride	11/11	8/8	2/2	0/11		
1,2-dichloropropane	0/11	0/8	0/2	0/11		
trichloroethene	5/11	6/8	0/2	0/11		
cis-1,3-dichloropropene	4/11	4/8	0/2	0/11		
trans-1,3-dichloropropene	4/11	4/8	0/2	0/11		
1,1,2-trichloroethane	0/11	0/8	0/2	0/11		
toluene	11/11	8/8	2/2	2/11	5.3	185
1,2-dibromoethane	0/11	0/8	0/2	0/11		
tetrachloroethene	9/11	8/8	2/2	1/11	5.3	15
chlorobenzene	4/11	4/8	0/2	0/11		
ethylbenzene	10/11	8/8	0/2	1/11	1.5	18
m+p-xylene	10/11	8/8	1/2	0/11		
styrene	1/11	1/8	0/2	0/11		
1,1,2,2-tetrachloroethane	0/11	0/8	0/2	0/11		
o-xylene	10/11	8/8	0/2	0/11		
4-ethyltoluene	5/11	8/8	0/2	0/11		
1,3,5-trimethylbenzene	5/11	7/8	0/2	1/11	2.1	11
1,2,4-trimethylbenzene	8/11	6/8	0/2	2/11	7.8	19
benzyl chloride	1/11	1/8	0/2	0/11		
m-dichlorobenzene	4/11	5/8	0/2	0/11		
p-dichlorobenzene	3/11	1/8	0/2	0/11		
o-dichlorobenzene	1/11	0/8	0/2	0/11		
1,2,4-trichlorobenzene	2/11	0/8	0/2	0/11		
hexachlorobutadiene	0/11	0/8	0/2	0/11		

(a) Average of detectable amounts only.
(b) 100 (L) times the mean site average concentration (ng/L, Table 2.5).

TABLE 2.3. Breakthrough of Selected Volatile Organic Compounds from Front to Back Traps (Analysis by Battelle-Columbus)

Compound	100 (Qb/Qf)[a]		
	39-L[b]	72-L[c]	130-L[d]
dichlorodifluoromethane	0	124	52
trichlorofluoromethane	0	0	0
1,1,2-trichloro-1,2,2-trifluoroethane	0	0	0
1,1,1-trichloroethane	0	0	6.4
benzene	0	16	0
carbon tetrachloride	0	0	0
toluene	0	12	3.6

(a) QB = amount on back trap, QF = amount on front trap.
(b) August 1990 air sample at the 200-West Area.
(c) August 1990 air sample at the 200-West Area.
(d) August 1990 air sample at the 300 Area.

TABLE 2.4. Volatile Organic Compound Sample Collection Dates and Sample Types

Analysis by Battelle Columbus							
Date	200-West Area	300 Area	Rattlesnake Springs			Field Blank	DL[a]
12/21/89	F[b], B[c]	F, B	-[d]			2	1
2/1/90	F	F	-			2	1
3/23/90	3F	3F	-			2	1
6/14/90	3F	2F	-			3	1
8/16/90	3F, 2B	2F, 2B	3F			3	1
Analysis by Air Toxics, Inc.							
Date	200-West Area	300 Area	Rattlesnake Springs	200-East Area	100-N Area	Field/ Lab Blank	DL
07/31/92	F, B	2F, 2B	2F	-	-	3/3	1
09/03/92	2F, 2B	2F, 2B	3F	-	-	3/2	1
02/05/93	2F, 2B	2F, 2B	3F	-	-	3/2	1
07/01/93	2F, 2B	F, B	2F	F	F	1/2	5

(a) DL = Detection Limit (ng/sample).
(b) F = Front Trap.
(c) B = Back Trap.
(d) - = No sample.

for DCFM. No other detected compounds showed breakthrough for the August 1990 samples. As more information on vapor breakthrough becomes available, it will be possible to maximize the sample volume (increase sensitivity) while preventing analyte loss.

Volatile organic compounds in air were determined in 23 samples (Table 2.4) from three sites at Hanford (Figure 2.1). Two sites were located at operating areas (200-West Area and 300 Area), and one at a background location at Rattlesnake Springs. Rattlesnake Springs is a remote location on the Fitzner/Eberhardt Arid Lands Ecology Reserve and was chosen as the background site because it is upwind of Hanford production areas as indicated by annual wind roses (Figure 2.2) established by the Hanford Meteorology Monitoring Network (Woodruff et al. 1991). The Rattlesnake Springs location should represent regional background air because of its distance from the organic pollutants associated with automobile traffic and population centers; however, air concentrations at this location may be influenced by nearby agricultural emission sources. Average concentrations of the detected compounds for each sampling location are given in Table 2.5. A comparison of concentrations of volatile organic compounds at Hanford to concentrations at other locations (as reported in the literature) is presented in Table 2.6. Only 9 of the 42 compounds (DCFM, TCFM, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,1,1-trichloroethane, benzene, carbon tetrachloride, cis- and trans-1,3-chloropropene, and toluene) were found at average site concentrations exceeding 0.5 ng/L, with TCFM having the highest average concentration (7.8 ng/L). The mean concentration for DCFM should be taken as a lower limit because of breakthrough. The volatile organic compound concentrations reported here are of the same general magnitude as those reported for CMS tube samples taken for an air quality surveillance program during the remedial investigation of the 1100-EM-1 Site at Hanford (Glantz and Laws 1990).

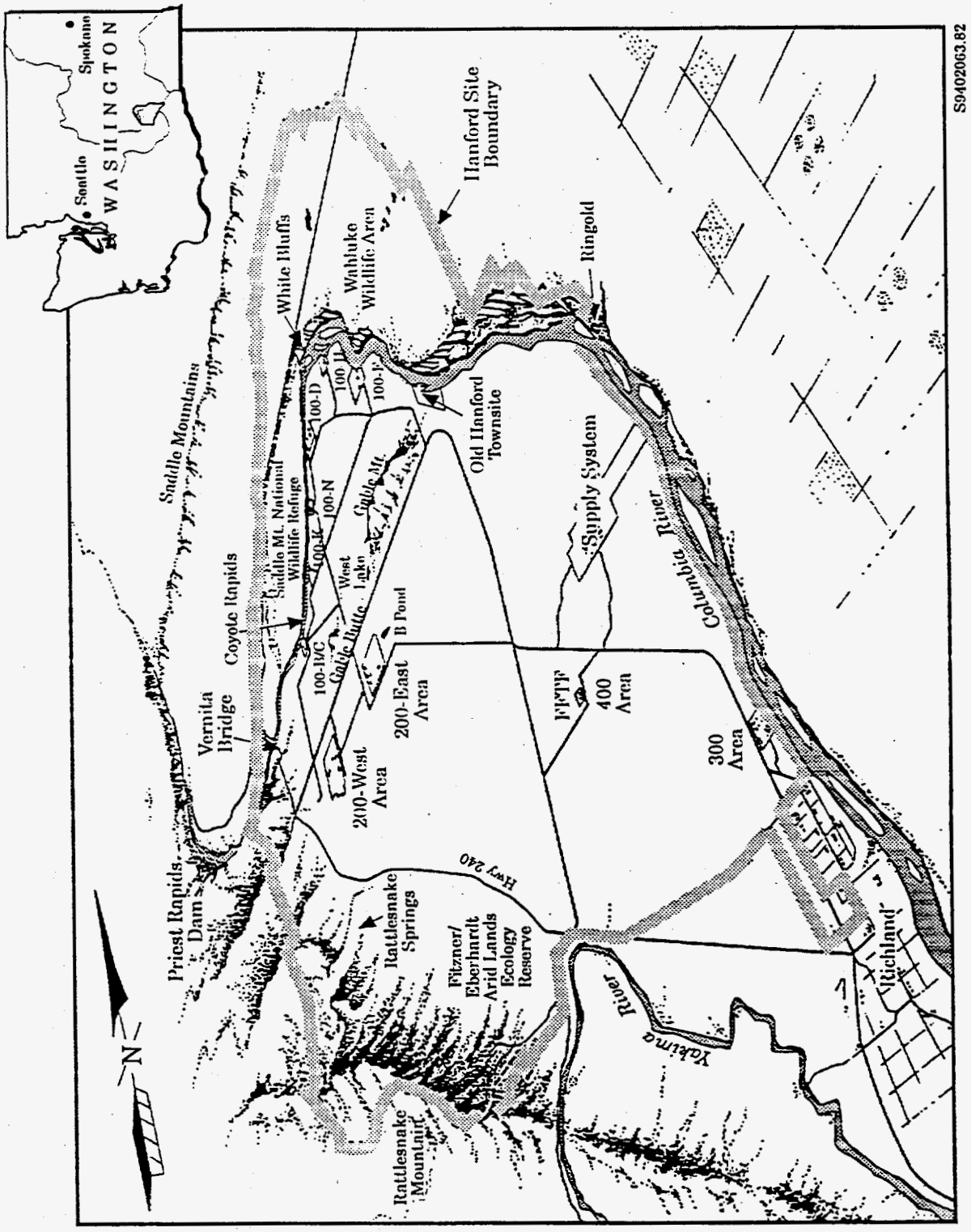

FIGURE 2.1. U.S. Department of Energy's Hanford Site and Surrounding Areas

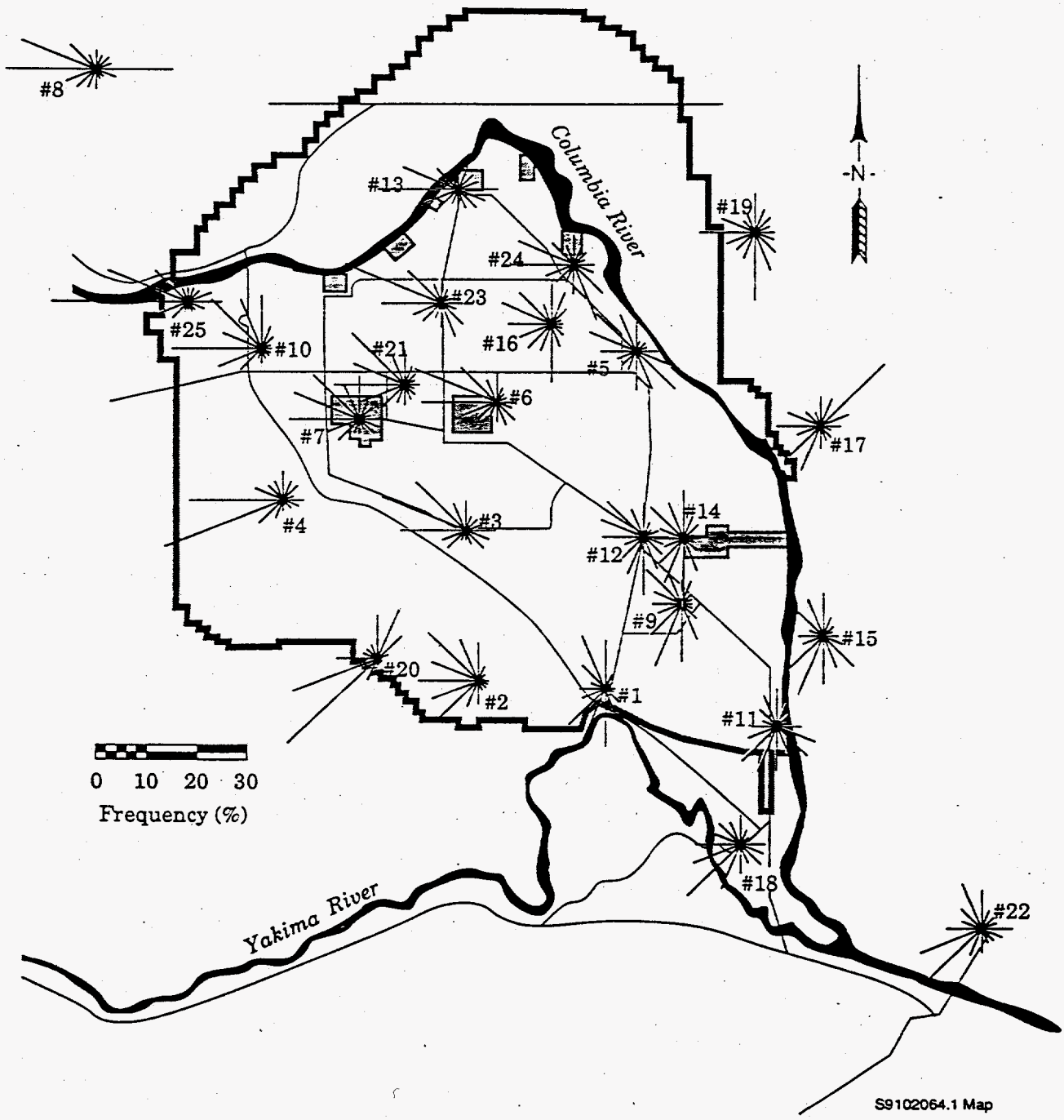

FIGURE 2.2. Hanford Meteorology Monitoring Network Wind Roses for 1990 (Station #4 is at Rattlesnake Springs, Station #7 is in the 200-West Area, and Station #6 is in the 200-East Area. Wind roses indicate the frequency distribution of wind directions at each station; the length of each line in the wind rose is proportional to the amount of time the wind blows from the indicated direction toward the station.)

TABLE 2.5. Average Concentrations (ng/L) of Volatile Organic Compounds Detected at the Hanford Site by Method TO-2 (Analysis by Battelle-Columbus); Standard Deviation Given in Parenthesis.

	Dec. 1989[a]		Feb. 1990[b]		March 1990[b]		June 1990[b]		August 1990[c]				
Compound	n=1[e] 200-West Area	n=1 300 Area	n=1 200-West Area	n=1 300 Area	n=3 200-West Area	n=3 300 Area	n=3 200-West Area	n=1 300 Area	n=1[f] 200-West Area	n=2 200-West Area	n=2 300 Area	n=2 Rattle-snake Springs	Average of the Means[d]
dichlorodifluoromethane[g]	0.29	0.14	0.19	0.10	0.30 (0.45)	0.12 (0.19)	0.33 (0.08)	0.20	0.81	1.74 (0.36)	1.98 (0.12)	1.61 (0.5)	0.65 (0.71)
methyl chloride	0.20	ND[h]	0.15	<0.1	<0.1	ND	ND	ND	ND	<0.1	<0.1	<0.1	<0.12
1,2-dichloro-1,1,2,2-tetrafluoroethane	0.10	ND	<0.1	ND	ND	ND	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
trichlorofluoromethane	54.3	8.97	13.7	9.91	1.67 (0.55)	0.92 (0.84)	0.87 (0.08)	0.97	1.16	1.27 (0.04)	1.08 (0.37)	1.10 (0.11)	7.82
1,1-dichloroethene	ND	ND	ND	ND	<0.1	0.45 (n=1)	<0.1	0.12	ND	<0.1	0.11 (n=1)	0.10 (0.01)	<0.15
dichloromethane	0.80	0.22	0.10	<0.1	0.18 (0.04)	0.11 (0.10)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.17
3-chloropropene	ND	ND	ND	ND	<0.1	<0.1	ND	ND	ND	ND	ND	ND	<0.1
1,1,2-trichloro-1,2,2-trifluoroethane	2.81	0.63	0.83	0.96	0.62 (0.16	0.65 (0.27)	0.35 (0.07)	0.34	0.63	0.55 (0.03)	0.57 (0.24)	0.40 (0.10)	0.78 (0.66)
trichloromethane	0.41	0.14	0.14	0.10	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.13
1,2-dichloroethane	0.18	<0.1	0.10	0.10	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	ND	<0.1	<0.11
1,1,1-trichloroethane	3.43	1.14	1.27	1.24	0.91 (0.13)	0.79 (0.56)	0.63 (0.08)	0.42	0.73	0.66	0.76	0.47	1.04 (0.08)
benzene	3.59	1.38	0.88	0.93	0.66 (0.08)	1.05 (0.27)	0.14 (0.03)	0.14	0.12	0.12 (0.01)	0.34 (0.04)	0.10 (.02)	0.79 (0.99)
carbon tetrachloride	3.01	0.61	1.00	1.00	0.83 (0.15)	0.78 (0.42)	0.61 (0.08)	0.49	0.65	0.57 (0.04)	0.60 (0.25)	0.53 (0.05)	0.89 (0.69)
trichloroethene	<0.1	0.10	<0.1	<0.1	<0.1	<0.1	ND	ND	ND	ND	<0.1	ND	<0.11
cis-1,3-dichloropropene	2.62	1.50	ND	ND	0.81 (0.20)	1.21 (1.02)	ND	ND	ND	ND	ND	ND	1.54 (0.78)
trans-1,3-dichloropropene	1.81	1.06	ND	ND	0.53 (0.13)	0.73 (0.64)	ND	ND	ND	ND	ND	ND	1.03 (0.56)
toluene	4.12	14.1	0.57	0.91	0.52 (0.07)	0.64 (0.35)	0.14 (0.02)	0.18	0.19	0.18 (0.10)	0.55 (0.05)	0.12 (0.02)	1.85 (4.01)

TABLE 2.5. (contd)

Compound	Dec. 1989[a]		Feb. 1990[b]		March 1990[b]		June 1990[b]		August 1990[c]				Average of the Means[d]
	n=1[e] 200-West Area	n=1 300 Area	n=1 200-West Area	n=1 300 Area	n=3 200-West Area	n=3 300 Area	n=3 200-West Area	n=1 300 Area	n=1[f] 200-West Area	n=2 200-West Area	n=2 300 Area	n=2 Rattle-snake Springs	
tetrachloroethene	0.49	0.15	0.15	0.12	0.13 (0.02)	0.15 (0.03)	<0.1	<0.1	<0.1	ND	<0.1	<0.1	<0.15
chlorobenzene	ND	ND	ND	ND	<0.1	<0.1	<0.1	<0.1	ND	ND	ND	ND	<0.1
ethylbenzene	0.74	0.38	0.10	0.11	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	0.11	ND	<0.18
m + p-xylene	2.18	1.23	0.16	0.33	<0.1	<0.1	<0.1	<0.11	<0.1	<0.1	0.40 (0.00)	<0.1	<0.42
styrene	0.12	0.17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.15 (0.04)
o-xylene	0.91	0.50	<0.1	0.13	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.19 (0.02)	ND	<0.22
4-ethyltoluene	0.21	0.13	<0.1	<0.1	<0.1	<0.1	ND	<0.1	ND	ND	<0.1	ND	<0.12
1,3,5-trimethylbenzene	0.18	0.12	<0.1	<0.1	<0.1	<0.1	ND	<0.1	ND	ND	<0.1	ND	<0.11
1,2,4-trimethylbenzene	0.69	0.36	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	ND	ND	<0.1	ND	<0.19
benzyl chloride	ND	ND	ND	ND	<0.1	<0.1	ND	ND	ND	ND	ND	ND	<0.1
m-dichlorobenzene	0.19	<0.1	ND	<0.1	<0.1	<0.1	ND	ND	ND	ND	ND	ND	<0.12
p-dichlorobenzene	ND	ND	ND	ND	<0.1	ND	<0.1	<0.1	ND	ND	ND	ND	<0.1
o-dichlorobenzene	ND	ND	ND	ND	<0.1	ND	ND	ND	ND	ND	ND	ND	<0.1
1,2,4-trichlorobenzene	ND	ND	ND	ND	<0.1	ND	ND	ND	ND	ND	ND	ND	<0.1

(a) DC pump, front and back tubes.
(b) DC pump, front tube only.
(c) AC pump, front tube only.
(d) Average of detected concentration, less than values included.
(e) n = the number of air samples averaged.
(f) AC pump, front and back tubes.
(g) Lower limit only because of breakthrough.
(h) ND = Not detected, value <0.05 mg/L).

TABLE 2.6. Comparison of the Range of Volatile Organic Compound Concentrations (ng/L) at the Hanford Site to Other Locations

	Hanford[a]		Illinois State Water Survey[b]		Colorado Dept. of Health[c]	
Compound	Battelle	Air Toxics[d]	Urban	Rural	Summer	Winter
dichlorodifluoromethane[e]	0.10 - 2	0.26-7.0	NA[f]	NA	ND[g]-70	ND-59
trichlorofluoromethane	0.97 - 54	0.01-1.1	NA	NA	18 - 104	ND - 18
1,1,1-trichloroethane	0.42 - 3.4	0.12-1.2	ND - 34	ND - 9.5	3 - 238	ND - 12
benzene	0.10 - 3.6	0.04-0.99	ND - 80	ND - 2.6	7 - 290	ND - 91
carbon tetrachloride	0.49 - 3.0	0.10-1.3	0.14 - 11	0.5 - 6.2	0.7 - 14	ND
toluene	0.12 - 4.1	0.02-1.2	0.8 - 234	0.4 - 5	12 - 385	ND - 320

(a) Table 2.5, Analysis by Battelle-Columbus
(b) Summa canister values (Sweet and Willett 1989).
(c) Summa canister values (Rogers and Pierce 1988).
(d) Maximum value from results from Air Toxics, Inc.
(e) Values are lower limits because of breakthrough.
(f) NA = Compound was not analyzed in this study.
(g) ND = Compound was not detected.

Threshold limit values (TLVs) represent airborne concentrations at which most workers may be exposed (8 h/day, 40 h/week) without adverse health effects. The TLVs are provided in this report as an estimate of the hazard index (non-cancer risk) for each volatile organic compound. When the ambient concentration exceeds the TLV, a potential exists for adverse health effects from prolonged exposure. All detected compounds were orders of magnitude less than the TLVs given in Table 2.1; cis- and trans-1,2-dichloropropene were the compounds closest to the TLV with their limits being 2,900 and 4,400 times their measured concentrations, respectively. The TLV values were developed as guidelines for use in the practice of industrial hygiene and are not intended as air quality measures. Comparisons of TLV limits to Hanford air concentrations were conducted because of the absence of regulatory standards for volatile organic compounds in ambient air; however, caution should be used in interpreting this information. A comparison of Hanford air concentrations to risk-based cancer standards is provided in Section 4.0 and provides a better estimate of air quality impacts for nonoccupational environments.

2.1.2 USEPA Sample Collection Method TO-14 (SUMMA CANISTERS)

2.1.2.1 General Procedure (Analysis by Battelle-Columbus)

Air samples to be analyzed for volatile organic compounds were collected using a Summa canister sampling system developed by Battelle-Columbus (Holdren and Smith 1989). The Summa systems pumped ambient air (at 7 mL/min) through 0.32-cm-diameter stainless steel tubing and into evacuated stainless steel canisters (6 L) over a 24-h period. The sample inlets were approximately 1.2 m above the ground. The air samples were analyzed by Battelle-Columbus using gas chromatography/mass spectrometry with selected ion monitoring (USEPA Method TO-14, Winberry et al. 1988).

2.1.2.2 Results and Discussion

Seven Summa samples were obtained concurrently with the December 1989 to March 1990 CMS tube samples, and the results for selected compounds are given in Table 2.7. Overall the Summa results are comparable to the adsorbent trap results (Figure 2.3). The concentrations of DCFM in Summa samples were higher than those in the adsorbent trap samples because of breakthrough losses for the adsorbent tubes.

Problems were experienced in the field obtaining adequate final pressures in the canisters with the Summa pumping systems. The flow rates measured before installing the canister and after sampling were appropriate; however, the cans consistently had low or no final pressure above ambient pressure. When the systems were tested at Pacific Northwest Laboratory at the same flow rates, the cans filled to a normal pressure of 70 to 90 kPa (10 to 13 $lb/inch^2$). Staff were unable to determine the cause of the problem for the field samples. Summa canisters can be used to collect air samples at either ambient or elevated pressures. It is assumed that the cans filled to ambient pressure, but the pumping systems were unable to fully pressurize the cans. The results for samples collected using the Summa cans may be more representative of short-term grab samples than the time-integrated samples collected with the adsorbent tubes.

2.2 COMPARISON OF SAMPLE COLLECTION METHODS TO-2 AND TO-14

The ultimate choice of an air sampling system depends on a number of factors including technical applicability to the measurement required, availability of analytical support, cost of sampling and analysis, ruggedness of sampling equipment, and convenience of sample collection.

TABLE 2.7. Concentrations of Volatile Organic Compounds at the Hanford Site by Method TO-14 (Summa Canisters)

Compound	Concentrations, ng/L						
	December 1989		February 1990		March 1990		
	n = 1 200-W Area	n = 1 300 Area	n = 1 200-W Area	n = 1 300 Area	n = 1 200-W Area	n = 2 300 Area	n = 6 Site Average ± S.D.
dichlorodifluoromethane	2.03	1.88	2.18	1.73	0.53	2.11	1.74 ± 0.62
trichlorofluoromethane	9.41	8.57	3.64	4.59	9.56	8.44	7.37 ± 2.6
dichloromethane	<0.35	<0.35	<0.35	<0.35	<0.35	<0.35	<0.35
trichlorotrifluoroethane[a]	<0.77	3.60	0.84	0.84	1.20	0.40	1.38 ± 1.28[b]
1,1,1-trichloroethane	0.87	1.03	1.20	1.20	2.78	1.20	1.38 ± 0.70
benzene	0.96	1.34	0.89	0.93	1.24	1.05	1.07 ± 0.18
carbon tetrachloride	0.63	0.69	0.88	0.76	0.82	0.77	0.76 ± 0.09
cis-1,3-dichloroproprene	<0.45	0.62	<0.45	<0.45	<0.45	0.50	0.56 ±0.08[c]
trans-1,3-dichloropropene	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45	<0.45
toluene	1.20	2.90	0.64	0.86	0.61	0.52	1.12 ± 0.90
tetrachloroethene	<0.68	<0.68	<0.68	<0.68	<0.68	<0.68	<0.68

(a) 1,1,2-trichloro-1,2,2-trifluoroethane.
(b) n = 5.
(c) n = 2.
S.D. = 1 standard deviation.

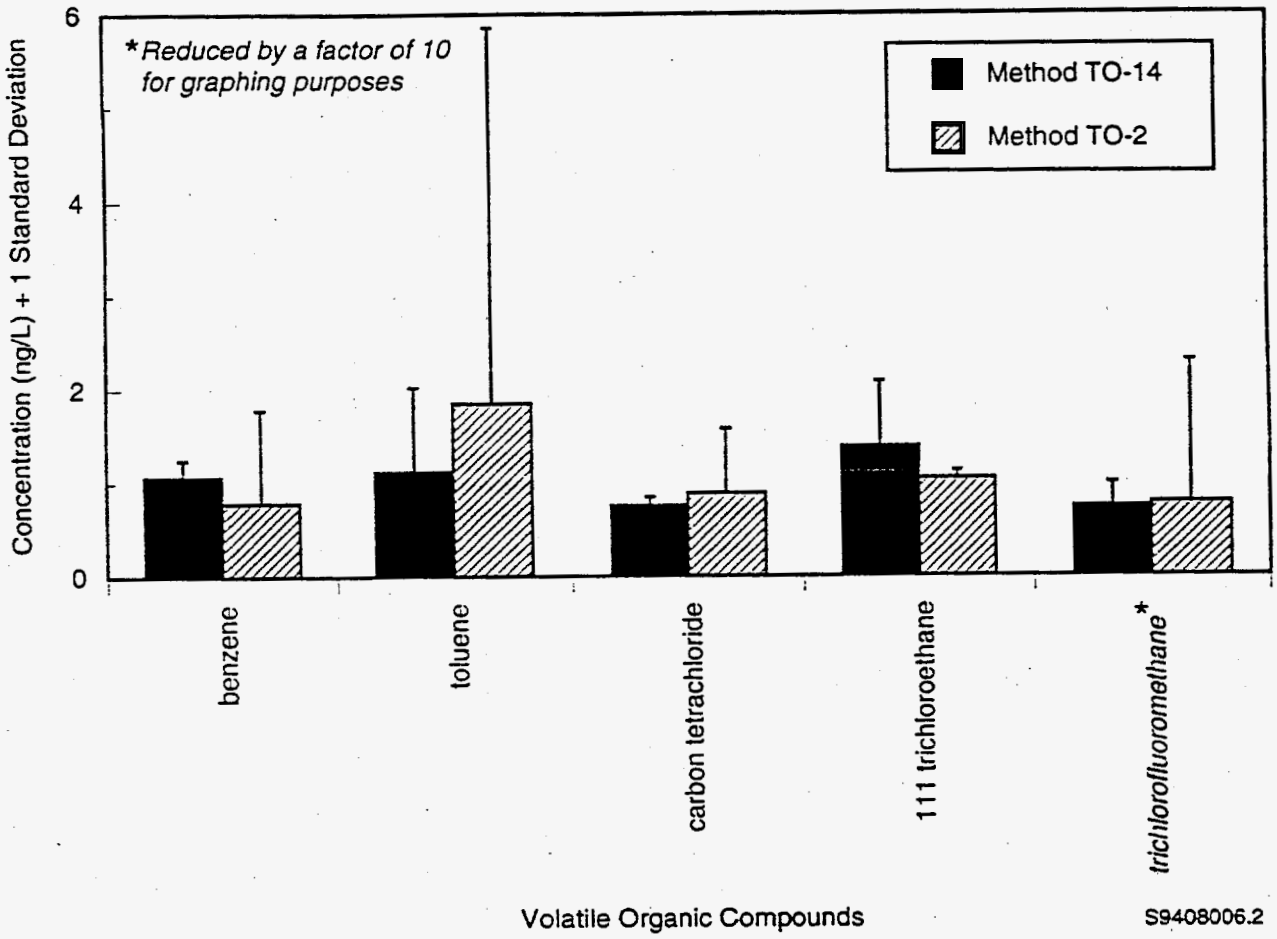

FIGURE 2.3. Comparison of Average Concentrations for Samples Collected by Methods TO-2 and TO-14 for Selected Volatile Organic Compounds in Hanford Site Air (Analysis by Battelle-Columbus)

Both sample collection methods TO-2 and TO-14 meet the technical requirements of the Hanford Site surveillance program, have analytical support available from several sources, and were of comparable overall cost.

Summa canisters have such advantages over adsorbent tubes as 1) breakthrough is not possible because it is a whole-air collection technique, and 2) the long shelf life for clean Summa cans makes grab sampling more convenient. Possible problems with the Summa cans are

analyte degradation after sampling, irreversible adsorption to active sites within the can (may be more of a problem with low humidity samples), lower sensitivity (Summa cans collect less than 10 L compared to 50 to 100 L for adsorbent trap samples), and difficulty in obtaining a time-integrated sample for more than a few hours. Method TO-2 requires sampling personnel that have considerable experience working with absorbent-based sampling schemes because analytical blanks, recoveries, and breakthrough must be carefully monitored. Method TO-14 would be recommended for air sampling programs using relatively inexperienced sampling personnel because of ease of operation, particularly if short-term grab samples need to be collected.

Method TO-2 (adsorbent traps) was selected over TO-14 (Summa cans) as the method of choice for environmental surveillance at the Hanford Site because of the method's higher sensitivity, portability, easier ability to collect a time-integrated sample over several days, and the availability of experienced field collection personnel. The possibility of poor analytical recovery for Summa canisters under the low humidity conditions at the Hanford Site was also a factor in the decision.

2.3 ENVIRONMENTAL SURVEILLANCE FOR VOLATILE ORGANIC COMPOUNDS (ANALYSIS BY AIR TOXICS, INC.)

2.3.1 General Procedure

Method TO-2 was selected as the best available choice for Hanford Site surveillance, as discussed in Section 2.2. Fourteen contaminants of concern were chosen from the list of volatile organic compounds detected in the initial study (Section 2.1) and are listed in Table 2.8. The target compounds were selected based upon the ratio of detected to non-detected results for previous samples, highest air concentrations, potential risk relative to the threshold limit values, and past use of the chemicals in Hanford Site operations. Air samples from the Hanford Site were analyzed

TABLE 2.8. Concentrations (ng/L) of Volatile Organic Compounds in Ambient Air at the Hanford Site by Method TO-2 (Analysis by Air Toxics, Inc.)

Compound	200-West Area				300 Area				Rattlesnake Springs				200-East Area		100-N Area		All Areas			
	D/S[a]	Max	Mean	1SD	D/S	Max	Mean	1SD	D/S	Max	Mean	1SD	D/S		D/S		D/S	Max	Mean	1SD
dichlorodifluoromethane	7/7	7.00	3.41	2.63	7/7	6.39	3.31	2.39	9/10	4.85	1.39	1.46	1/1	0.52	1/1	0.48	25/26	7.00	2.38	2.24
trichlorofluoromethane	6/7	0.83	0.36	0.30	7/7	1.08	0.43	0.31	8/10	0.35	0.16	0.11	1/1	0.13	1/1	0.12	23/26	1.08	0.29	0.25
1,1,1 - trichloroethane	7/7	1.17	0.55	0.39	7/7	1.07	0.74	0.30	9/10	1.01	0.49	0.29	1/1	0.42	1/1	0.26	25/26	1.17	0.56	0.32
benzene	7/7	0.99	0.30	0.36	7/7	0.97	0.52	0.33	9/10	0.75	0.31	0.30	1/1	0.21	1/1	0.26	25/26	0.99	0.36	0.32
dichloromethane	4/7	0.11	0.03	0.04	5/7	0.17	0.05	0.06	5/10	0.02	0.01	0.01	0/1	0.00	0/1	0.00	14/26	0.17	0.03	0.04
trichloromethane	3/7	0.27	0.05	0.10	3/7	0.26	0.08	0.12	6/10	0.14	0.04	0.06	0/1	0.00	0/1	0.00	12/26	0.27	0.05	0.09
carbon tetrachloride	7/7	1.27	0.56	0.45	7/7	0.90	0.56	0.24	9/10	0.87	0.48	0.27	1/1	0.40	1/1	0.31	25/26	1.27	0.51	0.30
toluene	7/7	0.92	0.28	0.31	7/7	1.18	0.72	0.44	9/10	0.59	0.27	0.23	1/1	0.15	1/1	0.18	25/26	1.18	0.38	0.36
cis - 1,3 - dichloropropene	2/7	0.01	0.00	0.00	3/7	0.06	0.02	0.03	0/10	0.00	0.00	0.00	0/1	0.00	0/1	0.00	5/26	0.06	0.01	0.01
trans - 1,3 - dichloropropene	1/7	0.01	0.00	0.00	4/7	0.03	0.01	0.01	3/10	0.01	0.00	0.01	0/1	0.00	0/1	0.00	8/26	0.03	0.01	0.01
trichlorotrifluoroethane	6/7	0.87	0.25	0.30	7/7	0.59	0.38	0.14	9/10	0.36	0.20	0.11	1/1	0.26	1/1	0.18	24/26	0.87	0.26	0.19
m-xylene + p-xylene	5/7	0.26	0.09	0.11	7/7	0.66	0.34	0.23	7/10	0.16	0.06	0.07	1/1	0.05	1/1	0.02	21/26	0.66	0.14	0.18
o - xylene	4/7	0.19	0.06	0.08	6/7	0.24	0.14	0.10	6/10	0.12	0.04	0.05	0/1	0.00	0/1	0.00	16/26	0.24	0.07	0.08

(a) The number of detectable concentrations/total number of samples.

by Air Toxics, Inc., Rancho Cordova, California using USEPA Method TO-2. The sample collection methods are described in Section 2.1.1.1. Adsorbent tubes were precleaned by Pacific Northwest Laboratory staff before sampling. Field blanks (cleaned but unused tubes) were carried to the field with the samples and handled in the same manner as actual samples. Following collection in the field, samples were placed in a cooler with dry ice and sent to the analytical laboratory. Air samples were collected using both the DC- and AC-powered sampling pumps described in Section 2.1.1.1.

2.3.2 Results and Discussion

2.3.2.1 Spike Recovery and Blanks

Spike recovery tests were performed by Air Toxics, Inc., for all batches of samples processed, and these results are given in Table 2.9 and shown in Figure 2.4. Average percent recoveries ranged from 83% ± 18% to 106% ± 10%. Field blanks were submitted with all sample batches, and the analytical laboratory also analyzed additional laboratory blanks with each sample batch. The analytical blank value for each sample batch was determined to be the highest value of either the field or the laboratory blank. The analytical blank value was then subtracted from each sample in the processing batch. Analytical blanks for individual batches are given in Table 2.10. Dichloromethane (DCM) consistently had a high analytical blank value that was as large as the amount typically collected in a 100-L sample. Dichloromethane is a widely used extraction solvent in analytical laboratories, and cross contamination with solvent vapors may explain the high blank value. Trichlorofluoromethane had high analytical blank values for three out of four samples with values ranging from 12% to 51% of the amount typically collected in a 100-L sample. Toluene was also elevated in three out of four analytical blanks, with values ranging from 6% to 28% of the amount typically found in a 100-L sample. The analytical blanks for all other compounds were small relative to the amount typically collected in an actual sample.

TABLE 2.9. Analytical Recovery of Volatile Organic Compounds from TO-2 Adsorbent Traps (Analysis by Air Toxics, Inc.)

Compound	Recovery of Spiked Analytes (%)					
	Jun-88	Aug-88	Jan-89	Jun-89	Mean	1 SD
dichlorodifluoromethane	83	100	57	92	83	19
trichlorofluoromethane	94	101	96	106	99	5
1,1,1 - trichloroethane	97	103	107	88	99	8
benzene	96	103	99	106	101	4
dichloromethane	92	100	96	100	97	4
trichloromethane	95	101	98	109	101	6
carbon tetrachloride	98	99	103	107	102	4
toluene	97	106	98	107	102	5
cis - 1,3 - dichloropropene	95	94	101	115	101	10
trans - 1,3 - dichloropropene	93	88	101	112	99	10
trichlorotrifluoroethane	75	102	NA[a]	107	95	17
m-xylene + p-xylene	95	120	101	107	106	11
o - xylene	102	104	101	106	103	2

(a) NA = compound was not analyzed in this study.

2.3.2.2 Breakthrough

For some samples collected during each sampling period, a second adsorbent trap was placed behind the primary trap to monitor for vapor penetration (breakthrough). Breakthrough was defined as the amount on the back trap relative to the amount on the front trap (Section 2.1.1.2), and the breakthrough results for detected volatile organic compounds are given in Table 2.11. For a given adsorbent type and bed geometry, breakthrough is

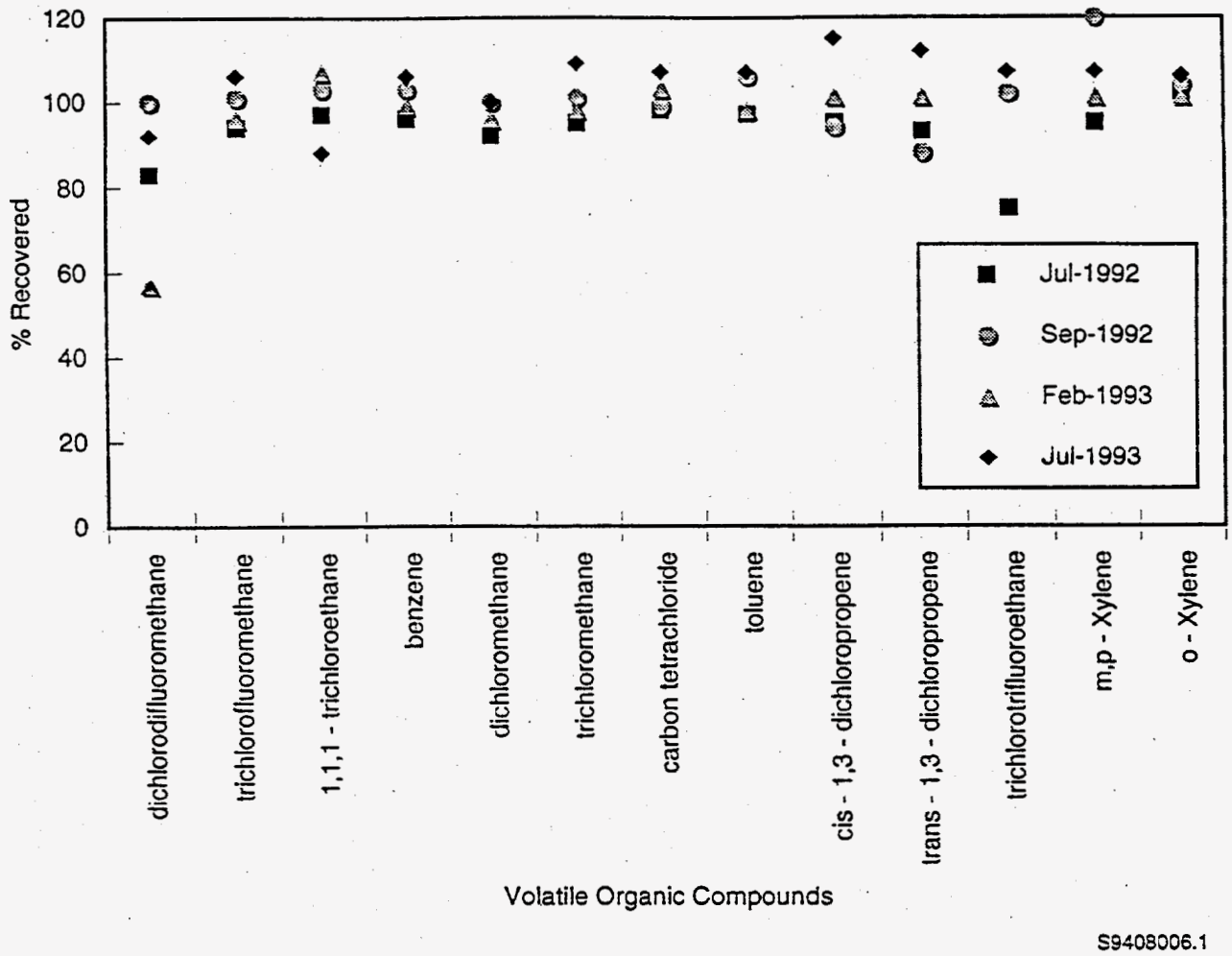

FIGURE 2.4. Analytical Recovery of Volatile Organic Compounds From TO-2 Adsorbent Traps (Analysis by Air Toxics, Inc.)

primarily a function of vapor pressure, temperature, and total air volume sampled. The most volatile compound tested was DCFM, and it experienced breakthrough for most samples. Excluding DCFM, the target compounds were well retained on the adsorbent tubes with average breakthrough of 0 to 36%. Other possible causes of high back trap to front trap results (apparent breakthrough) are loss of adsorbent material or poor packing of the front trap,

TABLE 2.10. Analytical Blank Values[a] (ng) for Individual Method TO-2 Sample Batches (Analysis by Air Toxics, Inc.)

Compound	July 92 Blank	Sept. 92 Blank	Feb. 93 Blank	July 93 Blank	Typical 100-L[b] Sample
dichlorodifluoromethane	5.34	0.00	6.66	0.00	238
trichlorofluoromethane	0.00	7.72	3.50	14.80	29
1,1,1 - trichloroethane	0.00	0.00	0.00	0.00	56
benzene	1.31	1.77	0.00	0.00	36
dichloromethane	4.78	7.92	8.17	5.77	3
trichloromethane	0.00	6.38	1.87	0.00	5
carbon tetrachloride	0.00	0.00	0.00	0.00	51
toluene	0.00	2.10	10.80	5.85	38
cis - 1,3 - dichloropropene	0.00	0.00	0.00	0.00	1
trans - 1,3 - dichloropropene	0.00	0.00	0.00	0.00	1
trichlorotrifluoroethane	0.00	1.70	0.00	0.00	26
m-xylene + p-xylene	0.00	2.60	0.00	0.00	14
o - xylene	0.00	0.00	0.00	0.00	7

(a) Highest individual value for all field and laboratory blanks in processing batch.
(b) Amount of volatile organic compounds found in a typical 100-L sample (Table 2.8).

TABLE 2.11. Breakthrough of Selected Volatile Organic Compounds for TO-2 Adsorbent Traps (Analysis by Air Toxics, Inc.)

Compound	Breakthrough Percentage														
Sample Volume (L)	67	70	74	74	78	78	87	180	205	211	211	224	232	319	Mean
trichlorofluoromethane	0	0	25	0	0	0	40	2	17	2	0	0	39	0	9
dichloromethane	0	0	0	83	0	0	34	0	0	0	6	0	0	0	9
trichloromethane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
trichlorotrifluoroethane	3	0	0	0	0	0	0	0	8	5	0	0	86	0	7
o-Xylene	40	0	0	0	0	0	7	0	2	0	0	0	0	0	4

(a) Breakthrough percentage = amount on backtrap/amount on front trap x 100

poor analytical recovery from the corresponding front trap, or higher contamination on the back trap relative to the front trap, and it is likely that one of these conditions occurred for the compounds that had occasional high breakthrough values. Trichlorofluoromethane had breakthrough >10% for 4 of 14 samples, and dichloromethane had breakthrough >20% for 2 of 14 samples. However, dichloromethane had a high analytical blank value relative to the amount typically collected; therefore, the observed breakthrough may actually be related to variable blank contamination.

2.3.2.3 Sample Results

From July 1992 to July 1993, a total of 24 air samples (Table 2.4) were collected for volatile organic compounds at the 200-West Area, 300 Area, and Rattlesnake Springs locations on the Hanford Site (Figure 2.1). Two additional air samples were collected at the 200-East Area and the 100-N Area in July 1993 (Figure 2.1). The Rattlesnake Springs location is typically upwind of major Hanford Site facilities and is considered to be the background location for this study (Section 2.1.1.2; Figures 2.1 and 2.2). Average concentrations of volatile compounds for each sampling area are given in Table 2.8 and shown in Figure 2.5. A comparison of Hanford Site air concentrations of volatile organic compounds to concentrations at other locations is given in Table 2.6. Average DCFM concentrations were 2.4 ng/L, and this was the only compound with average concentrations above 1 ng/L. The concentration of DCFM should be taken as a lower limit because of substantial breakthrough during sampling. Each of the compounds was detected in at least 46% of the samples, with the exceptions of cis- and trans-1,3-dichloropropene, which were found in less than 30% of the samples. All detected volatile organic compound concentrations were orders of magnitude below the occupational threshold limit values given in Table 2.1. Comparisons of ambient air concentrations to occupational limits are given because of the absence of regulatory standards for volatile organic compounds in ambient air; therefore, caution should be

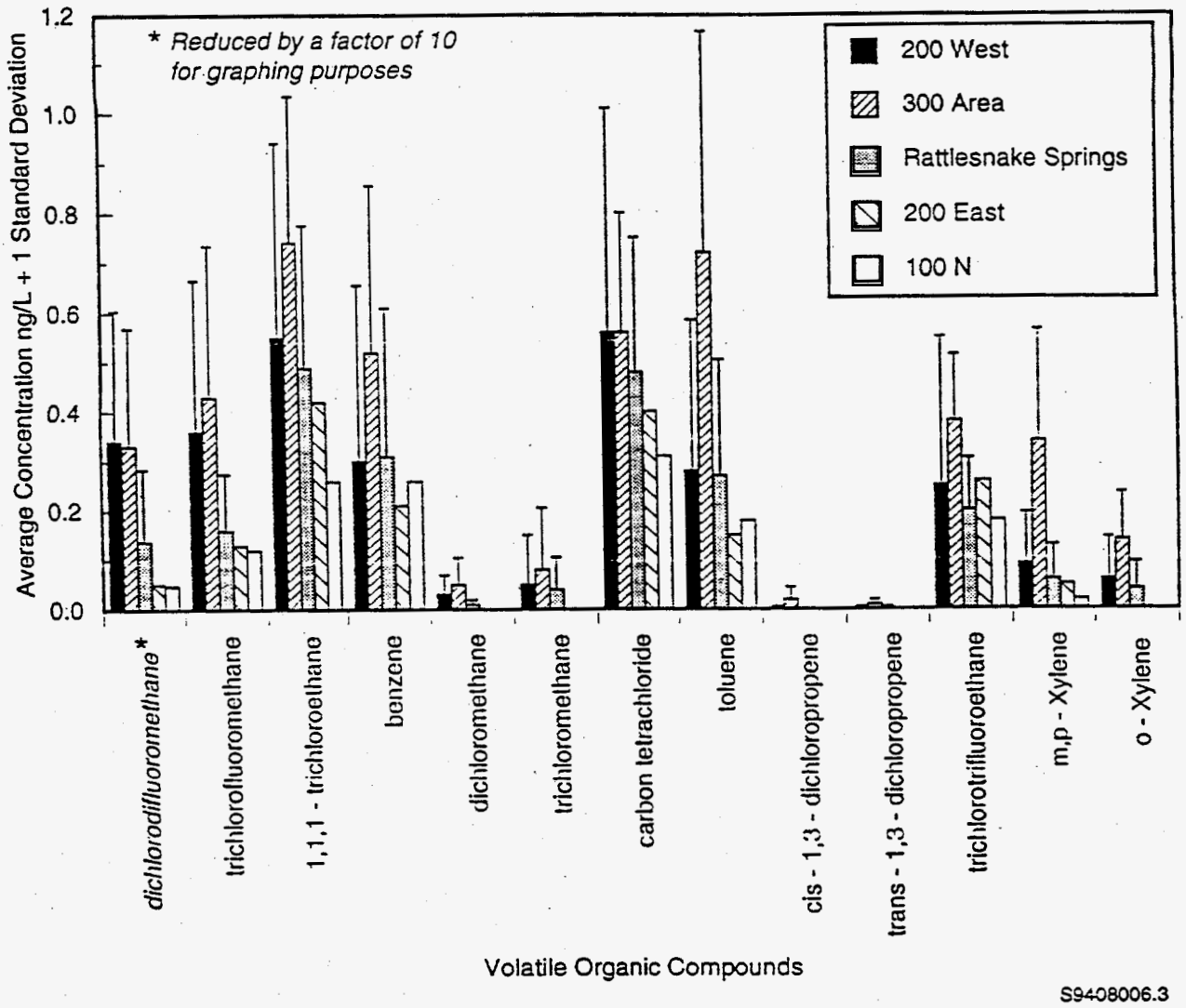

FIGURE 2.5. Average Volatile Organic Compound Concentrations in Air at the Hanford Site (Analysis by Air Toxics, Inc.)

used in interpreting this information for ambient air evaluations. A comparison of the measured ambient concentration to a risk-based criteria is presented in Section 4.0.

3.0 ANALYSIS OF POLYCHLORINATED BIPHENYLS USING USEPA METHOD TO-4

3.1 INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of 209 organic chemicals composed of 1 to 10 chlorine atoms attached to biphenyl. They have tremendous commercial utility and were widely used as dielectric fluids for capacitors and coolants for transformers, with other uses as plasticizers, hydraulic and heat transfer fluids, inks, paints, and adhesives (Erickson 1992). Polychlorinated biphenyls were not produced as discrete compounds (referred to as congeners) but as technical mixtures of multiple PCB congeners in varying proportions. The production of PCBs in the U.S.A. from 1930 to 1974 is estimated at 590,000 metric tons, with most of the material marketed by Monsanto under the tradename Aroclor (National Research Council 1979). Production of PCBs in the U.S.A. peaked in 1970 (38,000 metric ton/yr), and production had essentially stopped by the late 1970s (Bidleman et al. 1990). World production of PCBs is estimated at 1,200,000 metric tons, with an estimated 65% still in use or in landfills, 4% degraded or incinerated, and 31% released and cycling in the global environment (Bidleman et al. 1990). Once released into the environment, PCBs are persistent, lipophilic, toxic at high doses, and possible human carcinogens. The environmental toxicology is complicated by the large number of congeners in the technical mixtures and the potential presence of other toxic compounds. In ambient air PCBs are distributed between the particle and vapor phases, whereas the volatile organic compounds exist primarily in the vapor phase. The saturation vapor pressure of PCBs range from 5.8 E-7 to 8.4 E-3 torr (7.7 E-5 to 1.1 Pa; Erickson 1992).

Ambient air samples for PCBs were taken at the Hanford Site using USEPA Sampling Method TO-4 (Winberry et al. 1988). USEPA Method TO-4 employs a high-volume air sampler equipped with a particle filter backed up by an adsorbent trap to collect the organic compounds. For this study only PCBs

were determined; however, Method TO-4 can be applied to other semivolatile organic compounds (e.g. pesticides, phthalates, polycyclic aromatic hydrocarbons, and chlorinated dibenzodioxins). Sample collection using Method TO-4 is a well documented and generally accepted technique. However, there are few commercial laboratories that have experience in preparing and analyzing these types of samples; therefore, careful evaluation of the laboratory's capabilities were required.

3.2 INITIAL TESTING (ANALYSIS BY U.S. TESTING, INC.)

3.2.1 General Procedure

General Metal Works PS-1 high-volume air samplers (Figure 3.1) equipped with dual (particle/vapor) sampling heads (Figure 3.2) were used to collect the samples. Air volumes of 361-1106 m^3 were pulled through 10.5-cm-diameter glass fiber filters (GFF) (Reeve Angle, Grade 934AH) and a 7.6-cm thick by 6.5-cm-diameter polyurethane foam plug (PUF) (polyether-type, density = 0.0225 g/cm^3) at flow rates of 0.206-0.288 m^3/min. Flow rates were determined by measuring the pressure drop behind the GFF/PUF traps with the Magnehelic gauge supplied with the PS-1 sampler. This pressure drop was related to volumetric flow by using the PS-1 calibration orifice.

Before sampling, the PUFs were cleaned by Soxhlet extraction by U.S Testing, Inc., Richland, Washington. The filters were wrapped in aluminum foil and baked overnight in a muffle furnace at 350° C. Clean PUFs were stored in glass jars with Teflon lids. The aluminum foil packets containing the GFF were stored in plastic bags. Sampling trains were loaded with GFF/PUF in the laboratory and transported to the field in plastic bags. Blank samples were carried to the field and stored with the actual samples. After sample collection the sampling trains were returned to the laboratory, and the GFF/PUF was removed and transported to the analytical laboratory. For the

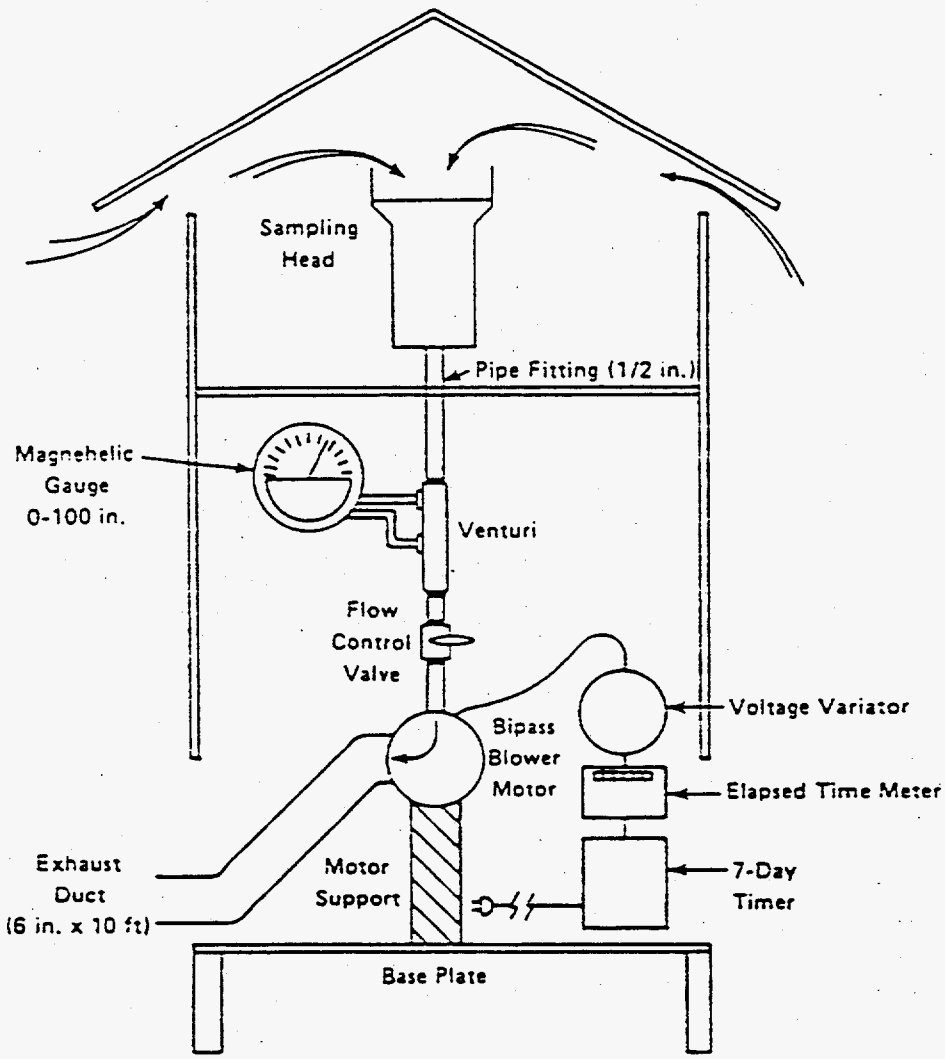

FIGURE 3.1. High-Volume Air Sampler for PCBs (TO-4) (from Winberry et al. 1988)

September 1990 samples, a second 7.6-cm PUF was added directly behind the primary PUF for two samples. This second PUF was used to monitor for breakthrough.

December 1989, April 1990, and May 1990 air samples were analyzed by U.S. Testing, Inc., Richland, Washington using USEPA SW-846 Method 8080 (USEPA 1986b). The samples were Soxhlet extracted and analyzed by gas chromatography

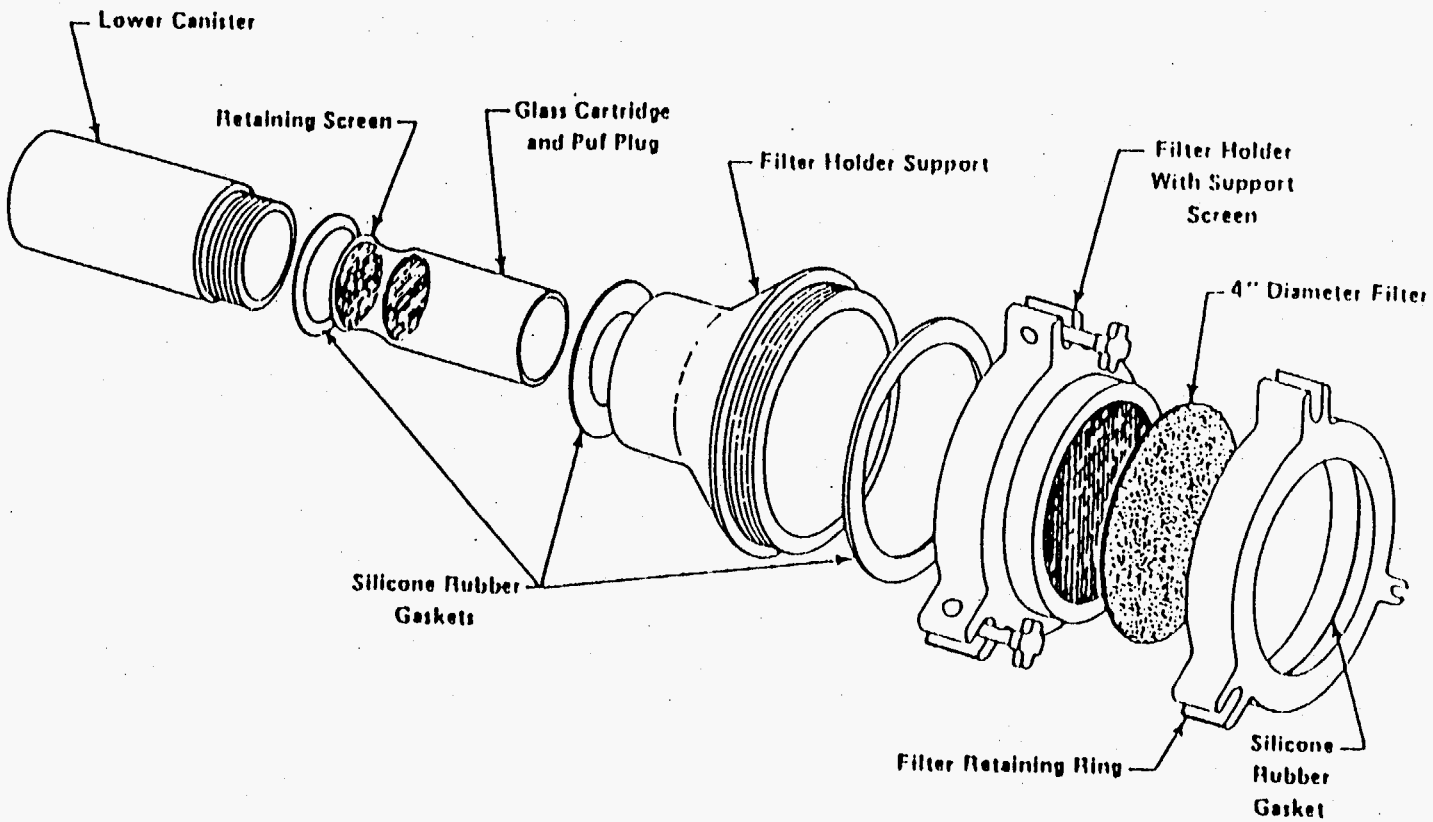

FIGURE 3.2. Exploded View of PCB Sampling Head (TO-4)

using electron capture detection. The surrogate standards dibutyl-chlorendate (DBC) and 2,4,5,6-tetrachloro-meta-xylene (TCMX) were added to the Soxhlet apparatus before sample extraction. Samples were analyzed for the following Aroclor (PCB) mixtures: 1242, 1248, 1254, and 1260. Aroclors 1016, 1221, and 1232 were also reported but are too volatile to be effectively retained by the GFF-PUF system and results should be considered qualitative data only. After the initial analysis, the December 1989 samples were cleaned by Florisil column chromatography, concentrated 10 fold below the original sample volume (to increase sensitivity), and reanalyzed.

3.2.2 Results and Discussion

A total of six air samples were taken at the 200-West Area and the 300 Area on the Hanford Site (Figure 2.1) between December 1989 and May 1990. Results were received for only four of the samples and are given in Table 3.1. The overall analytical service contract with U.S. Testing, Inc., was

TABLE 3.1. Concentrations (ng/m^3) of PCBs at the Hanford Site (Analysis by U.S. Testing, Inc.)

	December 1989				December 1989 Retest[a]				May 1990				Blanks[b]		
	200-West Area		300 Area		200-West Area		300 Area		200-West Area		300 Area		µg	PUF	
PCB Mix	GFF	PUF	GFF	PUF	GFF	PUF	GFF	PUF	GFF	PUF	GFF	PUF	GFF	#1	#2
1016[c]	<3	<3	<3	<3	<3	<0.3	<0.3	<0.3	<13	<13	<1.3	<1.3	<1	<1	<0.1
1221[c]	<6	<6	<6	<3	<6	<6	<0.6	<0.6	<25	<25	<2.7	<1.3	<2	<2	<0.2
1232[c]	<3	<3	<3	<3	<3	<0.3	<0.3	<0.3	<1.3	<1.3	<1.3	<1.3	<1	<1	<0.1
1242	<3	<3	<3	<3	<3	<0.3	<0.3	<0.3	<1.3	<1.3	<1.3	<1.3	<1	<1	<0.1
1248	<3	<3	<3	<3	<3	<0.3	<0.3	<0.3	<1.3	<1.3	<1.3	<1.3	<1	<1	<0.1
1254	<3	<3	<3	<3	<3	<0.3	<0.3	<0.3	<1.3	<1.3	<1.3	<1.3	<1	<1	<0.1
1260	<3	<3	<3	<3	<3	<0.3	<0.3	<0.3	<1.3	<1.3	<1.3	<1.3	<1	<1	<0.1

(a) Retested samples were cleaned with Florisil columns and concentrated 10 fold below the original samples (to increase sensitivity).
(b) GFF, n = 2. PUF #1, n = 2. PUF #2, n = 1, retested samples.
(c) Because the Aroclor mixture was not effectively retained by the PUF-GFF system, this is a qualitative value only.

terminated by Pacific Northwest Laboratory in June 1990 and the analysis of the samples in progress was not completed (Woodruff et al. 1991). Percent recoveries for the surrogate standards were 89% ± 23% for DCB (n = 16) and 109% ± 50% for TCMX (n = 15); one result was eliminated by use of a Q-test (Skoog and West 1980). No PCBs were detected on either the GFF or PUF for any of the ambient samples or blanks, including the December 1989 samples that were given a more sensitive retest. Total concentration for each Aroclor mixture (sum of GFF + PUF) was <6 ng/m^3 for December 1989, <3.3 ng/m^3 for December 1989 retested samples, and <2.6 ng/m^3 for May 1990 samples. The Hanford air concentrations for PCBs are compared to literature values in Table 3.2. Air surveillance using similar systems, sample volumes, and analytical laboratory during a remedial investigation of the 1100-EM-1 Site at Hanford also reported nondetectable amounts of PCBs (Glantz and Laws 1990).

TABLE 3.2. Comparison of the Range of Concentrations of PCBs in Hanford Air to Other Locations

	ng/m^3					
Hanford[a] Site	PCB Landfill[b] Uncontrolled	PCB Landfill[b] Controlled	Indiana[c] Urban	Midwest[d] Urban	Remote[d] & Rural	Arctic[e] Canada
<0.6 - <6[f]	80 - 193,000	<20	0.3 - 4	7	0.5 - 2	0.02 - 0.1
<0.2 - 4[g]						

(a) Individual Aroclors 1242, 1248, 1254, and 1260 (Tables 3.1 and 3.5).
(b) Sum of 1242 + 1260 (Lewis et al. 1985).
(c) Sum of individual congeners (Hermanson and Hites 1989).
(d) Review of literature, quantitation methods not given (Murphy et al. 1985).
(e) Sum of individual congeners (Patton et al. 1991).
(f) Table 3.1 (analysis by U.S. Testing, Inc.).
(g) Table 3.5 (analysis by General Physics Environmental Services, Inc.).

The occupational exposure limit for PCBs is 1000 ng/m^3 (DHHS 1985). Ambient air concentrations at Hanford were less than 6 ng/m^3 for each Aroclor, which are more than 160 times below the TLV. A human risk assessment for the Hanford Site PCB air concentrations is given in Section 4.0.

3.3 ENVIRONMENTAL SURVEILLANCE FOR PCB (ANALYSIS BY GENERAL PHYSICS ENVIRONMENTAL SERVICES, INC.)

3.3.1 General Procedure

Air samples for PCB analysis were collected at the Hanford Site from April 1992 to December 1993 (Table 3.3) using the same method and materials as described in Section 3.2.1 (USEPA Method TO-4). Samples were analyzed by General Physics Environmental Services, Inc., Gaithersburg, Maryland, using USEPA SW-846 Method 8080 (USEPA 1986b). Before sample collection the PUFs were cleaned by General Physics Environmental Services, Inc., and stored in precleaned glass jars with Teflon lids (PUFs were not wrapped in aluminum foil as in Section 3.2.1). Samples were temporarily stored in a refrigerator before shipment on dry ice to the analytical laboratory. Samples were analyzed for the following Aroclor mixtures: 1242, 1248, 1254, and 1260. Aroclor 1016, 1221, and 1232 were also reported but are too volatile to be effectively retained by the PUF adsorbent, and results should be considered qualitative data only. For some samples the GFF and front PUF were combined for a single analysis to improve the overall analytical detection limit and reduce cost (Table 3.3).

Field spikes were prepared by pipetting 2 mL of an acetone solution of several Aroclor standards (Ultra Scientific, North Kingstown, Rhode Island) onto precleaned PUFs (from General Physics Environmental Services, Inc.). The spiked plugs were handled, shipped to the laboratory, and processed in the same manner as actual samples.

TABLE 3.3. PCB Sample Collection Dates and Sample Types (Analysis by General Physics Environmental Services, Inc.)

	Location						
Date	200-West Area	300 Area	Rattlesnake Springs	Blank	Blank	Spike	Detection Limit (ng/sample)
04/24/92	GFF[a],F[b],B[c]	GFF,F,B	GFF,F,B	GFF,F,B	x[d]	x	100
06/11/92	GFF,F,B	GFF,F,B	GFF,F,B	GFF,F,B	x	x	100
07/02/92	GFF,F	GFF,F,B	GFF,F,B	GFF,F	F	6*F	100
08/07/92	GFF,F,B	GFF,F,B	GFF,F,B	GFF,F,B	x	x	100
09/04/92	GFF,F,B	GFF,F,B	GFF,F,B	GFF,F,B	x	x	100
10/01/92	C[e]	C,B	C,B	C,B	x	x	100
10/28/92	C	C,B	C	C,B	x	4*F	100
02/08/93	GFF,F,B	GFF,F,B	GFF,F,B	GFF,F,B	x	x	33.5
04/02/93	C,B	C,B	C,B	C,B	x	x	100
05/03/93	x	C,B	C,B	C,B	x	x	50
06/07/93	C,B	C,B	C,B	C,B	x	x	50
09/10/93	C,B	C,B	C,B	C,B	x	x	50
12/17/93	C,B	C,B	C,B	C,B	x	x	50

(a) GFF = glass fiber filter.
(b) F = front polyurethane foam plug (PUF).
(c) B = back PUF.
(d) x = no sample.
(e) C = GFF + F combined for analysis.

3.3.2 Results and Discussion

Analytical recoveries for the spiked PUFs are given in Table 3.4. In all cases the laboratory correctly identified the spiked Aroclor (i.e., no false positive or false negative results). Two sets of spiked plugs were sent to the laboratory. The first set (test 1) had low recoveries (25% to 37%) for Aroclor mixtures spiked at 10 times the detection limit and extremely high recoveries (600%) for Aroclors spiked at twice the detection limit. Because of the poor and variable recoveries, a second set of spiked plugs was submitted. The second set (test 2) consisted of Aroclor 1254 spiked at 10 times the detection limit and showed reasonable recoveries of 67% to 72%.

TABLE 3.4. Analytical Recoveries of PCBs from Spiked PUFs (Analysis by General Physics Environmental Services, Inc.).

	Aroclor	Spiked (μg)	Recovered (μg)	Detection Limit (μg)	Percent
Test 1	1242	0.2	1.2	0.1	600
		0.2	1.2	0.1	600
		0.2	1.2	0.1	600
		1.0	0.25	0.1	25
		1.0	0.29	0.1	29
		1.0	0.30	0.1	30
	1254	0.2	1.2	0.1	620
		0.2	1.3	0.1	635
		0.2	1.2	0.1	620
		1.0	0.3	0.1	34
		1.0	0.3	0.1	33
		1.0	0.4	0.1	37
Test 2	1254	1.0	0.67	0.1	67
		1.0	0.69	0.1	69
		1.0	0.72	0.1	72
		1.0	0.72	0.1	72

A total of 38 ambient air samples from the Hanford Site were analyzed by General Physics Environmental Services, Inc., with the results given in Table 3.5. Results for 10 samples were above the detection limit for Aroclor 1254, with results ranging from 0.25 to 3.9 ng/m^3. All other results for the Aroclor mixtures were below a general detection limit of $\leq$100 ng/sample component for each PCB mixture. Air volumes for samples with nondetectable results ranged from 580 to 1500 m^3, which yields air concentrations below 0.2 ng/m^3 for each Aroclor mixture. The sampling method used (USEPA Method TO-4) specifies a general detection limit of 1 ng/m^3; therefore, the results below the detection limit exceeded the required sensitivity.

The PCB concentrations measured in Hanford Site air were well below the National Institute of Occupational Safety and Health (DHHS 1985) occupational air limits of 1000 ng/m^3 (10-h time-weighted average). No regulatory limits for PCBs in ambient air have been established. A human risk assessment for the Hanford Site PCB air concentrations is discussed in Section 4.0. A comparison of the Hanford Site air concentrations to other locations is given in Table 3.2. The Hanford Site air concentrations (or detection limits) for PCBs are similar to those in remote or rural locations.

TABLE 3.5. PCB Concentrations[a] for Air Samples Collected on the Hanford Site in 1992 and 1993 (Analysis by General Physics Environmental Services, Inc.; ng/m^3)

	200-West Area				300 Area				Rattlesnake Springs			
Date	C[b]	GFF[c]	F[d]	B[e]	C	GFF	F	B	C	GFF	F	B
04/24/94	-[f]	<0.17[g]	<0.17	<0.17	-	<0.18	<0.18	<0.18	-	<0.16	<0.16	<0.16
06/11/92	-	<0.17	<0.17	<0.17	-	<0.16	<0.16	<0.16	-	<0.16	<0.16	<0.16
07/02/92	-	<0.17	<0.17	-	-	<0.17	<0.17	<0.17	-	<0.17	<0.17	<0.17
08/07/92	-	<0.18	<0.18	<0.18	-	<0.18	<0.18	<0.18	-	<0.17	<0.17	<0.17
09/04/92	-	<0.17	<0.17	<0.17	-	<0.18	<0.18	<0.18	-	<0.16	<0.16	<0.16
10/01/92	<0.11	-	-	-	<0.11	-	-	<0.11	<0.11	-	-	<0.11
10/28/92	<0.18	-	-	-	<0.18	-	-	<0.18	<0.17	-	-	-
02/08/93	-	<0.07	<0.07	<0.07	-	<0.07	<0.07	<0.07	-	<0.06	<0.06	<0.06
04/02/93	<0.11	-	-	<0.11	<0.12	-	-	<0.12	<0.11	-	-	<0.11
05/03/93	-	-	-	-	0.25[h]	-	-	<0.04	<0.04	-	-	<0.04
06/07/93	0.44[h]	-	-	<0.04	0.34[h]	-	-	<0.03	<0.03	-	-	<0.03
09/10/93	2.8[h]	-	-	<0.08	3.5[h]	-	-	<0.09	3.9[h]	-	-	<0.08
12/17/93	0.86[h]	-	-	<0.04	1.2[h]	-	-	<0.04	0.75[h]	-	-	<0.04

(a) Polychlorinated biphenyl (PCB) concentrations reported from the analysis of the following Aroclors: 1016, 1221, 1232, 1242, 1248, 1254, and 1260 using USEPA Methods TO-4 and SW-8080. Samples of PCBs were collected by pulling air through a glass fiber filter (GFF) to collect particle-associated PCBs, and then through front and back PUFs to collect vapor-phase PCBs. The back PUF was used to monitor for breakthrough. Samples were analyzed for either individual components (filters and PUF separate) or with the GFF and front PUF combined to increase analytical sensitivity.
(b) Data in column C are the combined extract from GFF and front PUF for analysis.
(c) GFF (glass fiber filter).
(d) F = Front Polyurethane Foam Plug (PUF).
(e) B = Back Polyurethane Foam Plug.
(f) - = not applicable.
(g) < indicates value for each Aroclor was below the given detection limit.
(h) Only Aroclor 1254 was detected.

4.0 ESTIMATE OF CARCINOGENIC AND NONCARCINOGENIC HUMAN HEALTH RISKS POSED BY MONITORED VOLATILE ORGANIC COMPOUND AND PCB AMBIENT AIR LEVELS

An evaluation of potential human health risks resulting from exposure to volatile organic compounds and PCBs at the maximum ambient air level concentrations measured on the Hanford Site during the environmental surveillance portion of this study (Sections 2.3 and 3.3) was performed using a USEPA risk assessment method (USEPA 1989) and the Hanford Site Baseline Risk Assessment Methodology (HSBRAM) (DOE 1992).

Because similar air concentrations were measured on the Hanford Site and at the Rattlesnake Springs background location, these risk estimates are indicative of the regional air concentrations and do not imply a Hanford source for the measured pollutants. A more realistic estimate of the Hanford Site's contribution of pollutants to the regional air concentrations could be generated by subtracting the background concentrations from the Hanford Site values; however, this was not attempted because of the limited number of samples. Another method to estimate the Hanford Site's contribution to pollutant concentrations would be to use source-term data (stack releases) and atmospheric dispersion models to estimate the air concentrations; however, this type of study is beyond the scope of this paper.

Risks from both carcinogenic and noncarcinogenic health effects were calculated based on a "residential exposure" scenario that is described in detail in HSBRAM (DOE 1992) and Risk Assessment Guidance for Superfund (USEPA 1989). The residential exposure scenario estimates the risks for a hypothetical individual residing on the Hanford Site for 30 years and continually exposed to the maximum measured concentration of the air pollutants. Only exposure variables for the air pathway were examined in this risk assessment with no other media pathways (e.g., soil, groundwater, biota)

TABLE 4.1. Maximum Hanford Site Air Concentrations, Occupational Limit Values, Ambient Air Level Goals, Cancer Slope Factors, and Reference Doses for Risk Assessment.

Compound	Maximum Concentration Detected, Table 2.8 (ng/L)	TLV Occupational Limit (ng/L)	Ambient Air Level Goals (ng/L)	Cancer Slope Factor (mg/kg-d)		Reference Dose (mg/kg-d)	
				Ingestion	Inhalation	Ingestion	Inhalation
dichlorodifluoromethane	7.00	4,950,000	NA[a]	NA	na	0.2[b]	0.05[c]
trichlorofluoromethane	0.83	5,620,000	NA	NA	na	0.3[b]	0.2[c]
1,1,1-trichloroethane	1.17	1,910,000	36400	NA	na	0.3[d]	NA
benzene	0.99	32,000	0.096	0.029[b]	0.029[b]	NA	NA
dichloromethane	0.11	174,000	0.1	0.0075[b]	0.0016[b]	0.06[b]	0.9[c]
trichloromethane	0.27	49,000	0.022	0.0061[b]	0.081[b]	0.01[b]	0.01[e]
carbon tetrachloride	1.27	31,000	0.053	0.13[b]	0.053[b]	0.0007[b]	NA
toluene	0.92	377,000	1400	NA	na	0.2[b]	0.1[b]
cis-1,3-dichloropropene	0.01	4,500	NA	0.18[c]	0.13[c]	0.0003[b]	0.006[b]
trans-1,3-dichloropropene	0.01	4,500	NA	0.18[c]	0.13[c]	0.0003[b]	0.006[b]
trichlorotrifluoroethane	0.87	NA	NA	NA	NA	NA	NA
m,p-xylene	0.26	434,000	57	NA	NA	2[b]	0.086[c]
o-xylene	0.19	434,000	290	NA	NA	2[b]	0.086[c]
				Cancer Slope Factor (mg/kg/d)		Reference Dose (mg/kg/d)	
Chemical	Maximum Concentration Detected, Table 3.5 (ng/m^3)	TLV Occupational Limit (ng/m^3)	Ambient Air Level goals (ng/m^3)	Ingestion	Inhalation	Ingestion	Inhalation
Aroclor-1254	3.9	1,000	NA	7.7[b][e]	7.7[b][e]	NA	NA

(a) NA = not applicable.
(b) Source-Information Risk Information System (IRIS, USEPA 1993).
(c) Source-Health Effects Assessment Summary Tables (HEAST, USEPA 1992).
(d) Source-Superfund Technical Support Center.
(e) No slope factor available for Aroclor-1254, thus, the Aroclor-1260 injection slope factor was used.

included. The residential scenario was used because it provided a conservative estimate of the potential risk to the nonresident public exposed to the ambient air levels detected in this study.

A summary of the assumptions and example calculation used in determining contaminant uptake through the air exposure pathway using the USEPA/HSBRAM residential exposure scenario is presented below.

Residential Exposure

Inhalation of Airborne (Vapor Phase) Chemicals

$$\text{Intake (mg/kg-day)} = \frac{CA * IR * ET * EF * ED}{BW * AT}$$

Where:

- CA = Contaminant concentration in air (ng/m^3)
- IR = Inhalation rate (0.83 m^3/h)
- ET = Exposure time (24 h/day)
- EF = Exposure frequency (365 day/yr)
- ED = Exposure duration (30 yr)
- BW = Body weight (70 kg)
- AT = Averaging time [period over which the exposure is averaged (25,550 day)]

Exposure Information

Daily Intake Rate	20 m^3
Frequency	365 day/yr
Duration	30 yr
Body Weight	70 kg (adult)
Intake Factor	Air inhalation 1.3 E-1, Dust inhalation 6.1 E-9
Breathing Rate	20 m^3/day (adult)
Air Quality Standard	50 $\mu g/m^3$

The incremental cancer risk is the probability of an individual developing cancer over a lifetime from exposure to a potential chemical

carcinogen. Incremental cancer risk (ICR) was calculated by multiplying the estimated daily intake from the above residential exposure scenario by the chemical's reported slope factor.

$$\text{Cancer Risk} = \text{Intake} * \text{Slope Factor}$$

The USEPA typically considers a cancer risk value of 1 E-6 or greater to be an action level. Table 4.1 provides the maximum Hanford Site air concentrations, cancer slope factor, and reference dose values used in the risk assessment. It is important to note that the public is continually exposed to trace levels of the organic compounds detected in this study, with indoor air providing the major health risk compared to outdoor air (Wallace 1986; Travis and Hester 1990). For example, the estimated lifetime cancer risk from background exposure for benzene, carbon tetrachloride, chloroform (trichloromethane), and PCBs are all above the 1 E-4 risk level (Travis and Hester 1990).

The cancer risk estimates for maximum air concentrations of organics measured on the Hanford Site are given in Table 4.2. The maximum measured air concentration for all of the following chemicals exceeded the typical USEPA cancer risk level of 1 E-6: benzene, trichloromethane, carbon tetrachloride, and Aroclor 1254. Benzene had the highest cancer risk with an estimated value of 3.5 E-5 for the maximum measured concentration. Trichloromethane (chloroform) was the only other organic compound with a cancer risk estimate above 1 E-5 for the maximum air concentrations. The total estimated cancer risk from the maximum concentrations of volatile organic compounds and PCBs measured in Hanford Site air is 7.4 E-5, with benzene and chloroform representing 80% of the potential cancer risk. This total estimated cancer risk was generated by summing the cancer risks for individual compounds and does not take into account any potential synergistic effects between pollutants. Air inhalation was the major exposure pathway for both the volatile organic compounds and the semivolatile PCBs. Risks from exposure by dust inhalation (calculated by HSBRAM) were orders of magnitude lower than for air inhalation (Table 4.2).

TABLE 4.2. Estimated Cancer Risk and Hazard Quotient Values for the Maximum Measured Concentrations of Volatile Organic Compounds and PCBs in Hanford Site Air.

Compound[a]	Cancer Risk		Hazard Quotient	
	Dust Inhalation	Air Inhalation	Dust Inhalation	Air Inhalation
dichlorodifluoromethane	NA[b]	NA	4.4E-09	8.8E-02
trichlorofluoromethane	NA	NA	1.3E-10	2.6E-03
benzene	1.8E-12	3.5E-05	NA	NA
dichloromethane	1.1E-14	2.2E-07	3.8E-11	7.6E-04
trichloromethane	1.3E-12	2.7E-05	8.40E-09	1.70E-01
carbon tetrachloride	4.1E-13	8.2E-06	NA	NA
toluene	NA	NA	2.9E-10	5.8E-03
cis-1,3-dichloropropene	8.0E-15	1.6E-07	5.2E-11	1.0E-03
trans-1,3-dichloropropene	8.0E-15	1.6E-07	5.2E-11	1.0E-03
total xylene[c]	NA	NA	9.4E-11	1.9E-03
Aroclor-1254[d]	1.8E-13	3.7E-6	NA	NA
Sum =	3.7E-12	7.4E-05	1.3E-08	2.7E-01
Total Cancer Risk = 7.4E-05			Hazard Index = 2.7E-01	

(a) No toxicity data were available for trichlorotrifluoroethane or 1,1,1-trichloroethane.
(b) NA = not applicable.
(c) Maximum value obtained for m,p,o-xylene was used in the risk calculation; toxicity information is for "total Xylene".
(d) Because no reference information was available for Aroclor 1254, Aroclor 1260 data were substituted.

An independent evaluation of the estimated health effects calculated above (USEPA/HSBRAM method) can be made by comparing the results to ambient air level goals (AALGs) developed by Calabrese and Kenyon (1991). The AALGs are nonregulatory, nonbinding limits that were developed for use as health-based guidelines for risk assessments and are somewhat analogous to the USEPA's maximum contaminant level goals for water. The AALG values are used

as a comparative tool in this report because no regulatory standards have been developed for these compounds in ambient air. Table 4.1 gives the maximum detected air concentrations of organics at the Hanford Site and the corresponding AALG values. Maximum air concentrations approached or exceeded the AALG values for benzene, dichloromethane (methylene chloride), trichloromethane (chloroform), and carbon tetrachloride. Ambient air level goals have not been developed for all of the compounds detected in Hanford Site air; however, for the available values there was reasonable agreement between the estimated health risk for both the AALG approach and the USEPA/HSBRAM approach.

The potential for noncarcinogenic effects is evaluated by comparing an exposure level to a laboratory-derived chemical reference dose. The hazard quotient is defined as the exposure level (intake) divided by the reference dose (effect level).

Hazard Quotient = Intake / Reference Dose
Hazard Index = Sum of All Individual Hazard Quotients

A hazard quotient or hazard index value of 1.0 or greater indicates that there may be concern for noncancer health effects. The hazard quotients for the maximum concentration of organics measured on the Hanford Site are given in Table 4.1. None of the chemicals evaluated had a hazard quotient value that would indicate a noncarcinogenic health problem. The sum of the hazard quotients for all measured compounds provided a hazard index value that was below 0.3, with chloroform composing 63% of the total.

5.0 CONCLUSIONS

5.1 VOLATILE ORGANIC COMPOUNDS

Two USEPA sampling methods for volatile organic compounds in ambient air were evaluated for use by the Hanford Site Surface Environmental Surveillance Project. In addition, preliminary environmental monitoring samples were collected. The low-volume sampling methods evaluated were USEPA Method TO-2, which uses carbon-based adsorbent traps for sample collection, and USEPA Method TO-14, which uses stainless steel Summa canisters for sample collection. The sampling methods were evaluated for their collection efficiency, analytical recoveries, background contamination, detection limits, and practicality. Both sampling methods were found to be appropriate for Hanford Site ambient air monitoring.

Following the method evaluation, a series of environmental samples were collected for 14 volatile organic compounds using Sampling Method TO-2. Compounds selected for monitoring included chlorofluorocarbons, benzene, dichloromethane, trichloromethane, carbon tetrachloride, and toluene. Average concentrations for 13 of these volatile organic compounds were below 1 ng/L. Dichlorodifluoromethane (DCFM) concentrations averaged 2.4 ng/L; however, the DCFM value should be taken as a lower limit because of breakthrough of this compound past the adsorbent traps (see Section 2.3.2.2).

5.2 POLYCHLORINATED BIPHENYLS (PCBs)

Air samples for PCB analysis were collected using USEPA Sampling Method TO-4, which uses a high-volume air sampler equipped with both a particle filter and polyurethane foam plug (PUF) adsorbent trap. During the study, samples were submitted to two independent laboratories for PCB analysis as Aroclor mixtures. Air sample results were below detection limits

(<0.2-<6 ng/m^3) for all Aroclor mixtures, except for Aroclor 1254, which was detected in 10 of 42 samples (results from both labs), with detected concentrations ranging from 0.25 to 3.9 ng/m^3.

5.3 ESTIMATED HUMAN HEALTH RISK (VOLATILE ORGANIC COMPOUNDS AND PCBs)

All measured ambient air concentrations were orders of magnitude below occupational threshold limit values; however, occupational air standards are not directly applicable to ambient air. Thus, a conservative risk-based human health evaluation was conducted for the ambient air concentrations measured at the Hanford Site. Because of the limited number of samples, it was not possible to determine the specific Hanford Site contribution to the measured air concentrations. It should be noted that the public is constantly exposed to trace levels of the organic compounds measured in this study with exposure to indoor air providing the major health risk compared to outdoor air (Wallace 1986). The lifetime cancer risk from background exposure for benzene, carbon tetrachloride, chloroform, and PCBs are all above the 1 E-4 risk level (Travis and Hester 1990).

Compounds whose maximum measured air concentrations on the Hanford Site exceeded the cancer risk level of 1 E-6 were benzene, trichloromethane (chloroform), tetrachloromethane (carbon tetrachloride), and Aroclor 1254 (a PCB mixture). Benzene had the highest cancer risk with an estimated value of 3.5 E-5 for the maximum concentration measured. Trichloromethane was the only other organic compound with a cancer risk above 1 E-5. The total estimated cancer risk for the maximum concentrations of volatile organic compounds and PCBs was 7.4 E-5 (sum of individual risks), with benzene and trichloromethane representing 80% of the potential risk. An independent evaluation of the estimated human health risk was made by comparison to the non-regulatory ambient air level goals developed by Calabrese and Kenyon (1991). Maximum air concentrations exceeded the AALG values (comparable to the 1 E-6 risk level)

for benzene, trichloromethane, tetrachloromethane, and dichloromethane (methylene chloride); an AALG value was not found for Aroclor 1254.

The potential for non-cancer effects from exposure to the maximum air concentrations measured on the Hanford Site were also evaluated using a hazard quotient and hazard index (sum of hazard quotients) approach. A hazard quotient or hazard index value above 1.0 indicates that there may be a potential health concern. Trichloromethane had the highest hazard index with a value of 0.17 for air inhalation. None of the compounds evaluated had a hazard quotient that would indicate a noncarcinogenic health problem, and the hazard index for all compounds was below 0.3.

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