

# Distribution of Selected Volatile Organic Compounds Determined With Water-to-Vapor Diffusion Samplers at the Interface Between Ground Water and Surface Water, Centredale Manor Site, North Providence, Rhode Island, September 1999

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## Abstract

Volatile organic compounds are present in soils and ground water at the Centredale Manor Superfund Site in North Providence, Rhode Island. In September 1999, water-to-vapor diffusion samplers were placed in the bottom sediments of waterways adjacent to the site to identify possible contaminated ground-water discharge areas. The approximate 12-acre site is a narrow stretch of land between the eastern bank of the Woonasquatucket River, downstream from the U.S. Route 44 bridge and a former mill raceway. The samplers were placed along a 2,250-foot reach of the Woonasquatucket River, in the former mill raceway several hundred feet to the east and parallel to the river, and in a cross channel between the river and former mill raceway.

Volatile organic compounds were detected in 84 of the 104 water-to-vapor diffusion samplers retrieved. Trichloroethylene and tetrachloroethylene were the principal volatile organic compounds detected. The highest vapor concentrations measured for these two chemicals were from diffusion samplers located along an approximate 100-foot reach of the Woonasquatucket River about 500 feet downstream of the bridge; here trichloroethylene and tetrachloroethylene vapor concentrations ranged from about 2,000 to 180,000 and 1,600 to 1,400,000 parts per billion by volume, respectively. Upstream and downstream from this reach and along the former mill raceway,

trichloroethylene and tetrachloroethylene vapor concentrations from the diffusion samples were generally less than 100 parts per billion by volume. Along the lower reaches of the river and mill raceway, however, and in the cross channel, vapor concentrations of trichloroethylene exceeded 100 parts per billion by volume and tetrachloroethylene exceeded 1,000 parts per billion by volume in several diffusion samples. Although diffusion sample vapor concentrations are higher than water concentrations in surface waters and in ground water, and they should only be interpreted qualitatively as relative values, these values provide important information as to potential discharge areas of contaminants.

## INTRODUCTION

Polychlorinated biphenyls, dioxin, and volatile organic compounds (VOCs) have been detected in soils and VOCs have been detected in ground water at the Centredale Manor Superfund Site in North Providence, Rhode Island, the site of a former chemical company and a drum reclamation company (Anna Krasko, U.S. Environmental Protection Agency, written commun., 1999). In September 1999, the U.S. Geological Survey (USGS), in cooperation with the U.S. Environmental Protection Agency (USEPA), installed polyethylene-membrane water-to-vapor diffusion samplers (vapor diffusion samplers) at the interface between ground water and surface water at this site to identify possible discharge areas for contaminated ground water and for a preliminary evaluation of the distribution and concentrations of VOCs and contaminant pathways in

ground water. Vapor diffusion samplers were used because of their success as a reconnaissance tool in detecting and delineating VOC discharge locations at several New England sites during the last three years (Lyford and others, 1998; Lyford and others, 1999a; Lyford and others, 1999b; Mullaney and others, 1999; Savoie and others, 1999). Results from these studies have provided valuable insights on contaminant-transport pathways and interactions between ground water and surface water.

The Centredale Manor study area is an elongated stretch of land, about 12 acres in size, along the east bank of the Woonasquatucket River just downstream of the U.S. Route 44 bridge (pl. 1). A former mill raceway that is about 1,900-ft long and oriented nearly parallel to the river forms the approximate eastern boundary of the study area. For this portion of the overall Superfund Site investigations, the southern boundary of the site is 50 ft downstream of the confluence of the mill raceway and the Woonasquatucket River, about 2,250 ft downstream from the U.S. Route 44 bridge. A cross channel, about 175-ft long, connects the river to the mill raceway at about 600 ft upstream from this confluence. Vapor diffusion samplers were installed in bottom sediments of these waterways to measure vapor concentrations of VOCs.

The purpose of this report is to describe the use of vapor diffusion samplers for mapping VOC distribution at the Centredale Manor site and present the data collected. The USGS, with assistance from Anna Krasko, USEPA, constructed, installed, and retrieved the vapor diffusion samplers in September 1999. The vapor samples were analyzed on-site by Scott Clifford, USEPA.

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## **USE OF VAPOR DIFFUSION SAMPLERS FOR MONITORING OF VOLATILE ORGANIC COMPOUNDS**

Polyethylene-membrane vapor diffusion samplers were constructed in accordance with methods described by Vroblesky and others (1996). A sampler consists of a 40-milliliter, uncapped glass bottle secured inside two polyethylene bags with cable ties. Duplicate samples for quality control were constructed by placing two polyethylene-wrapped glass bottles in the outer bag. The sampler is attached to a survey flag for marking and retrieval. Samplers were placed manually 6 to 10 in. deep in channel sediments, with the bottle opening facing downward, after a shovel blade was used to part the sediments to the depth of insertion.

The organic vapors from VOCs in water or saturated sediments diffuse into the bottle through the two layers of polyethylene. The time required for vapor in the air-filled bottle to equilibrate with VOC concentrations in the saturated sediment has been shown to be 24 hours or less in a controlled laboratory setting (Vroblesky and others, 1996). Additional time is considered necessary after placement of the samplers in a field setting to allow concentrations of VOCs in ground water to re-equilibrate due to the disturbance of channel bed sediment when installing the sampler; a period of two weeks is recommended (Don Vroblesky, oral commun., 1997). Once the sampler has been retrieved, the outer bag is removed to shed attached sediment, and a cap is immediately screwed onto the bottle over the inner bag.

Vapor diffusion samplers were installed at 115 sites at Centredale Manor on September 8 and 9, 1999 (pl. 1). Samplers were placed in the bed sediment of the Woonasquatucket River, the former mill raceway, and the cross channel that connects the river and mill raceway at 114 of these sites. A sampler was placed in water in the cross channel at one additional site. Duplicate samplers were installed at 11 of these 115 sites. Samplers were identified in numerical order as installed. Distance between sampling sites was 50 ft, except in reaches of the river and cross channel where the USEPA had indicated possible discharge of contaminants; sampler interval placement in these locations was 25 ft or less.

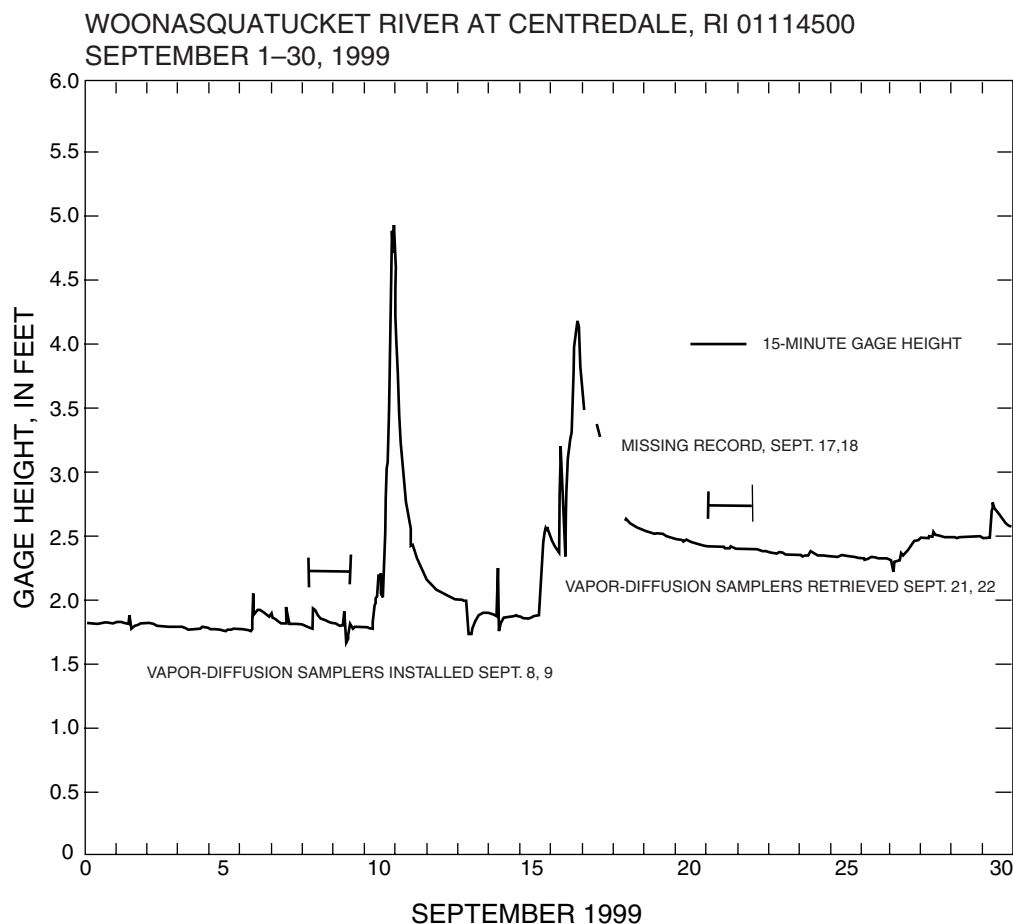
Sixty-two samplers (samplers VS-001 to VS-062) were installed in the coarse-grained, gravelly bottom sediments near the east bank along a 2,250-ft

reach of the Woonasquatucket River downstream from the U.S. Route 44 bridge (pl. 1). Forty-three samplers were installed in the former mill raceway. Twenty-four of these samplers (samplers VS-092 to VS-115) were installed in the predominately fine-grained, organic-rich sediments in the upper (northern) part of raceway, which is about 1,050 ft long. Below this point to its confluence with the Woonasquatucket River, a distance of about 850 ft, the mill raceway is more characteristic of coarse-grained bed sediments. Nineteen samplers (samplers VS-063 to VS-077 and VS-088 to VS-091) were installed along this lower section of the mill raceway, two of which were installed short distances up small tributary channels (samplers VS-071 and VS-091). Nine samplers (samplers VS-078 to VS-086) were installed in the fine-to-coarse-grained organic-rich bottom sediments of the 175-ft cross channel. Sampler VS-087 was placed in water in the cross channel next to sampler VS-079 to compare the VOC vapor concentration measured in the water with concentrations measured in the sediment below. Every

tenth sampler installed contained an additional bottle for a duplicate sample, which resulted in six duplicate samples in the river, four in the mill raceway, and one in the cross channel.

During installation of the vapor diffusion samplers, distances between samplers were determined by using a cloth measuring tape. Locations of samplers were then determined with a global positioning system (GPS) during retrieval of the samplers. GPS location data were checked by comparing the data with measured distances between samplers and known locations, such as marked stakes and proximity to buildings and parking lots.

Vapor diffusion samplers were retrieved on September 21 and 22, 1999. Sixty of the sixty-two samplers installed in the Woonasquatucket River were retrieved despite two near-flood flows in the two weeks after they were installed (fig. 1), which is most likely when the two samplers were lost. Eight of the nineteen samplers installed in the lower section of the mill raceway were not found. It is suspected that these



**Figure 1.** Gage height of Woonasquatucket River, U.S. Route 44 bridge, North Providence, Rhode Island, during September 1999.

samplers were either washed away or buried in recently re-worked bed sediments which was a result of the high flows. One additional sampler was found hanging in grasses several feet above the water level, but, due to its exposure to air, any VOC vapor contained would have already diffused out of the sampler. All of the samplers installed in the upper section of the mill raceway and in the cross channel were retrieved. Three of the 11 samplers lost included duplicate samplers, bringing the total number of samplers lost to fourteen. Approximate locations of the samplers that were lost are shown in plate 1.

Vapor samples were analyzed on site for VOCs in accordance with the USEPA Region I standard air screening method, Ambient Air Grab Sample Analysis for Volatile Organic Compounds (U.S. Environmental Protection Agency, 1998). A gas chromatograph equipped with a 4-ft by 1/8-in. SE-30 column and photoionization detector, a gas chromatograph equipped with a 30-m by 0.53-mm DBPS-624 column photoionization, and electron capture detectors were used. Samples were analyzed within eight hours of sample collection. Target compounds for analysis were benzene, chlorobenzene, ethylbenzene, tetrachloroethylene (PCE), 1,1,1-trichloroethane (111 TCA), trichloroethylene (TCE), toluene, meta/para-xylene, and ortho-xylene. The minimum reporting limits for these target compounds in this study, which are based on the analytical methods used, are shown in table 1.

**Table 1.** Minimum reporting limits for target volatile organic compounds at Centredale Manor, North Providence, Rhode Island, September 1999

Compound	Minimum reporting limit (parts per billion by volume)
Benzene	6
Chlorobenzene	40
Ethylbenzene	40
Tetrachloroethylene (PCE)	10
Toluene	30
1,1,1-Trichloroethane (111 TCA)	8
Trichloroethylene (TCE)	6
meta/para-xylene	40
ortho-xylene	60

The concentrations of VOCs in air-filled sample bottles are vapor concentrations and are reported in units of parts per billion by volume (ppb v). Under equilibrium conditions, vapor concentrations can be several times the concentrations in water, which are reported in units of micrograms per liter ( $\mu\text{g/L}$ ). For example, according to Henry's Law, the concentration of TCE and PCE in air in ppb v can be 20 times or more than the concentration in water in  $\mu\text{g/L}$ , depending largely on the temperature of the fluid (Rathbun, 1998). Other factors that affect the concentration of VOCs in air relative to concentrations in water are molecular weight of a particular compound, pressure, and the presence of multiple compounds. Although these vapor concentrations may be much higher than actual concentrations in the surface waters and in ground water, and should only be interpreted qualitatively as relative values, they provide important information about potential discharge areas of contaminants.

## VOLATILE ORGANIC COMPOUNDS DETECTED IN VAPOR DIFFUSION SAMPLES

VOCs were detected above their respective reporting limits in vapor diffusion samples at 84 of the 104 sites at Centredale Manor where samplers were retrieved. Among the 60 samples retrieved from the eastern edge of the Woonasquatucket River, VOCs were detected in 58 samples (pl. 1, table 2). TCE and PCE were the principal VOCs detected of the nine target compounds (table 1). The highest TCE and PCE vapor concentrations of 182,000 and 1,390,000 ppb v, respectively, were measured in sample VS-013 (table 2). This sample was located about 525 ft downstream of the U.S. Route 44 bridge (pl. 1). Within the first 475-ft reach downstream from the bridge, which includes samples VS-001 to VS-011, the highest vapor concentrations of TCE and PCE were 19 and 156 ppb v, respectively. In the next 50-ft reach, vapor concentrations increased sharply to the values reported above for sample VS-013. Vapor concentrations of TCE and PCE in the next 125 feet, which includes samples VS-014 to VS-018, decreased to 11 and 147 ppb v in sample at the end of this reach.

**Table 2.** Concentrations of volatile organic compounds in vapor diffusion samplers at Centredale Manor Site, North Providence, Rhode Island, September 1999

[Concentrations in parts per billion by volume. Numbers in parentheses indicate reporting limit in parts per billion by volume. Target compounds Ethylbenzene and 1,1,1-Trichloroethane not detected above reporting limits in any of the diffusion samples. **PCE and TCE:** trace, compound identified on chromatograph but at concentration below reporting limit; PCE, Tetrachloroethylene; TCE, Trichloroethylene. D, duplicate; No., number; ns, no sample; --, not detected above reporting limit]

Sample No.	Benzene (6)	Chlorobenzene (40)	PCE (10)	TCE (6)	Toluene (30)	meta/para-xylene (40)	ortho-xylene (60)
<b>Woonasquatucket River (downstream direction; north to south)</b>							
VS-001	--	--	--	trace	--	--	--
VS-002	--	--	--	--	--	--	--
VS-003	--	--	--	trace	--	--	--
VS-004	--	--	--	25	--	--	--
VS-005	--	--	132	10	--	--	--
VS-006	--	--	--	--	--	--	--
VS-007	--	--	90	14	--	--	--
VS-008	--	--	--	11	--	--	--
VS-009	--	--	40	--	--	--	--
VS-010	--	--	43	14	--	--	--
VS-010D	--	--	40	11	--	--	--
VS-011	--	--	156	19	--	--	--
VS-012	--	--	4,270	2,720	--	--	--
VS-013	--	--	1,390,000	182,000	--	--	--
VS-014	--	--	219,000	51,000	--	--	--
VS-015	--	--	1,610	2,330	--	--	--
VS-016	--	--	15,000	3,830	--	--	--
VS-017	--	--	322	85	--	--	--
VS-018	--	--	147	11	--	--	--
VS-019 <sup>1</sup>	--	--	100	33	64	240	430
VS-020	--	--	67	49	--	--	--
VS-020D	--	--	56	44	--	--	--
VS-021	--	--	66	23	--	--	--
VS-022	--	--	25	25	--	--	--
VS-023	--	--	22	61	--	--	--
VS-024	--	--	45	22	--	--	--
VS-025	--	--	91	10	--	--	--
VS-026	--	--	45	29	--	--	--
VS-027	--	--	71	8	--	--	--
VS-028	--	--	19	42	--	--	--
VS-029	--	--	136	18	--	--	--
VS-030	--	--	16	--	--	--	--
VS-030D	--	--	16	--	--	--	--
VS-031	--	--	117	11	--	--	--
VS-032	--	--	10	--	--	--	--
VS-033	--	--	42	11	--	--	--
VS-034	--	--	104	17	--	--	--
VS-035	--	--	35	9	--	--	--
VS-036	--	--	21	16	--	--	--
VS-037	--	--	--	7	--	--	--

**Table 2.** Concentrations of volatile organic compounds in vapor diffusion samplers at Centredale Manor Site, North Providence, Rhode Island, September 1999—*Continued*

Sample No.	Benzene (6)	Chlorobenzene (40)	PCE (10)	TCE (6)	Toluene (30)	meta/para-xylene (40)	ortho-xylene (60)
<b>Woonasquatucket River (downstream direction; north to south)—<i>Continued</i></b>							
VS-038	--	--	10	--	--	--	--
VS-039	--	--	17	19	--	--	--
VS-040	--	--	22	19	--	--	--
VS-040D	--	--	22	19	--	--	--
VS-041	--	--	36	16	--	--	--
VS-042	--	--	62	9	--	--	--
VS-043	--	--	29	12	--	--	--
VS-044	--	--	39	22	--	--	--
VS-045	--	--	--	15	--	--	--
VS-046	--	--	93	11	--	--	--
VS-047	--	--	93	11	--	--	--
VS-048	--	--	86	11	--	--	--
VS-049	--	--	86	8	--	--	--
VS-050	ns	ns	ns	ns	ns	ns	ns
VS-050D	ns	ns	ns	ns	ns	ns	ns
VS-051	--	--	65	8	--	--	--
VS-052	--	--	72	8	--	--	--
VS-053	--	--	65	10	--	--	--
VS-054	--	--	273	14	--	--	--
VS-055	--	--	302	11	--	--	--
VS-056	--	--	trace	30	--	--	--
VS-057	--	--	50	34	--	--	--
VS-058	--	--	718	42	--	--	--
VS-059	--	--	1,470	17	--	--	--
VS-060	--	--	71	10	--	--	--
VS-060D	--	--	89	19	--	--	--
VS-061	--	--	248	8	--	--	--
VS-062	ns	ns	ns	ns	ns	ns	ns
<b>Former Mill Raceway, upper section (north to south)</b>							
VS-115	--	--	--	--	--	--	--
VS-114	--	--	--	--	--	--	--
VS-113	--	--	--	--	--	--	--
VS-112	--	--	--	--	--	--	--
VS-111	--	--	--	--	--	--	--
VS-110	--	--	--	--	--	--	--
VS-110D	--	--	--	--	--	--	--
VS-109	--	--	--	--	--	--	--
VS-108	--	--	--	6	--	--	--
VS-107	9	--	--	--	--	--	--
VS-106	--	--	--	--	--	--	--
VS-105 <sup>1</sup>	--	59	--	6	--	--	--
VS-104 <sup>1</sup>	--	248	--	12	--	--	--
VS-103 <sup>1</sup>	--	260	--	--	--	--	--
VS-102	--	--	--	--	--	--	--

**Table 2.** Concentrations of volatile organic compounds in vapor diffusion samplers at Centredale Manor Site, North Providence, Rhode Island, September 1999—*Continued*

Sample No.	Benzene (6)	Chlorobenzene (40)	PCE (10)	TCE (6)	Toluene (30)	meta/para-xylene (40)	ortho-xylene (60)
<b>Former Mill Raceway, upper section (north to south)—<i>Continued</i></b>							
VS-101	--	--	--	10	--	--	--
VS-100	--	--	--	--	--	--	--
VS-100D	--	--	--	--	--	--	--
VS-099	--	--	--	--	--	--	--
VS-098	--	--	--	--	--	--	--
VS-097	--	--	24	--	--	--	--
VS-096	--	--	--	--	--	--	--
VS-095	--	--	--	--	--	--	--
VS-094	--	--	456	266	--	--	--
VS-093	--	--	54	225	--	--	--
VS-092	--	--	54	178	--	--	--
<b>Former Mill Raceway, lower section (north to south)</b>							
VS-091	ns	ns	ns	ns	ns	ns	ns
VS-090	ns	ns	ns	ns	ns	ns	ns
VS-090D	ns	ns	ns	ns	ns	ns	ns
VS-089	ns	ns	ns	ns	ns	ns	ns
VS-088	ns	ns	ns	ns	ns	ns	ns
VS-077	ns	ns	ns	ns	ns	ns	ns
VS-076	--	--	13	11	--	--	--
VS-075	--	--	170	333	--	--	--
VS-074	--	--	21	17	--	--	--
VS-073	--	43	45	35	--	--	--
VS-072	--	--	57	6	--	--	--
VS-071	--	--	32	74	--	--	--
VS-070	ns	ns	ns	ns	ns	ns	ns
VS-070D	ns	ns	ns	ns	ns	ns	ns
VS-069	--	--	67	309	--	--	--
VS-068	--	--	1,410	46	--	--	--
VS-067	--	--	12	85	--	--	--
VS-066	--	--	--	--	--	--	--
VS-065	ns	ns	ns	ns	ns	ns	ns
VS-064	ns	ns	ns	ns	ns	ns	ns
VS-063	ns	ns	ns	ns	ns	ns	ns
<b>Cross Channel (west to east)</b>							
VS-086	--	--	80	12	--	--	--
VS-085	--	--	99	20	--	--	--
VS-084	--	--	--	--	--	--	--
VS-083	--	--	--	6	--	--	--
VS-082	--	--	--	34	--	--	--
VS-081	--	--	1,310	140	--	--	--
VS-080	--	--	1,200	331	--	--	--
VS-080D	--	--	1,230	331	--	--	--
VS-079	--	--	37	273	--	--	--
VS-087	--	--	52	59	--	--	--
VS-078	--	--	1,740	87	--	--	--

<sup>1</sup> Sample contained unidentified peaks.

Vapor concentrations of TCE from this point to the outlet of the mill raceway (about 1,550 ft; samples VS-019 to VS-049 and VS-051 to VS-061) were detected in 39 of the 42 samples, with the highest concentration of 61 ppb v in sample VS-023. Vapor concentrations of PCE along this same reach were detected in 40 samples with the highest concentration of 1,470 ppb by volume about 100 ft upstream of the mill raceway outlet (sample VS-059). Other VOCs along the Woonasquatucket River were detected only in sample VS-019: toluene, meta/para-xylene, and ortho-xylene at vapor concentrations of 64, 240, and 430 ppb v, respectively. The target compounds ethylbenzene and 1,1,1-trichloroethane were not detected in any of the diffusion samples in the river, nor were they detected in any samples from the mill raceway and the cross channel.

VOCs were detected in 10 of the 24 samples retrieved along the approximate 1,050-ft upper section of the mill raceway (samples VS-092 to VS-115) (pl. 1, table 2). In the upper 925 ft of this section (samples VS-095 to VS-115), the highest vapor concentration of TCE was 12 ppb v (sample VS-104) and of PCE was 24 ppb v (sample VS-097). In the lower 125 ft of this section (VS-092 to VS-094), vapor concentrations of TCE ranged from 178 to 266 ppb v and PCE ranged from 54 to 456 ppb v. Other VOCs detected were benzene (vapor concentration of 9 ppb v in sample VS-107) and chlorobenzene (vapor concentrations of 260, 248, and 59 ppb v in samples VS-103, VS-104, and VS-105).

VOCs were detected in 9 of the 10 samplers retrieved from the lower part of the mill raceway (samples VS-066 to VS-069 and VS-071 to VS-076) (pl. 1, table 2). As in the samples from the river, TCE and PCE were the principal VOCs detected. TCE vapor concentrations ranged from 6 to 333 ppb v and PCE vapor concentrations ranged from 12 to 1,410 ppb v. The only other target VOC detected was chlorobenzene (vapor concentration of 43 ppb v from sample VS-073).

In the cross channel (samples VS-078 to VS-086), TCE and PCE were the only VOCs detected (pl. 1, table 2). TCE was detected in 8 of the 9 samples from the sediment and vapor concentrations ranged from 6 to 331 ppb v. PCE was detected in 6 of these 9 samples and vapor concentrations ranged from 37 to 1,740 ppb v. Sampler VS-087 was secured in water next to sampler VS-079. TCE and PCE vapor concentrations in the water were 59 and 52 ppb v,

respectively, compared to TCE and PCE vapor concentrations in sediment of 273 and 37 ppb v, respectively.

The effects, if any, of the high flows that occurred between installation and retrieval of the diffusion samplers (fig. 1) on the VOC vapor concentrations in the bottom sediment of the Woonasquatucket River, the former mill raceway, and the cross channel are not known. These high flows can alter the direction and magnitude of exchange of surface water and ground water at the stream channel bed and banks from the exchange that may occur during lower flows. This in turn may affect the VOCs discharged into the waterways and the vapor concentrations of VOCs in the diffusion samplers. The effects of this alternating exchange of water on vapor diffusion samples concentrations, however, have not been determined at this site.

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