

# Direct Measurement of Ground Water Contaminant Discharge to Surface Water

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## Biographical Sketches of Authors

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## Abstract

Defining zones of strongly discharging ground water is one way to characterize threats posed to surface water quality by contaminated ground water in both point source and non-point source settings. The three techniques most useful techniques for mapping areas of upward-discharging ground water and downward-discharging surface water are: temperature contrast, vertical gradient, and seepage flux. Pore water samples collected in zones of strong upward discharge show whether ground water contaminants affect surface water quality. Estimates of contaminant loading to surface water via the ground water pathway are made by combining pore water quality data with seepage flux rates.

At one site, the actual locations of contaminant discharge to surface water were not consistent with the conceptual model developed from up-gradient monitoring well data. Differences in streambed hydraulic conductivity are one factor in the departure. Hydrogeologic heterogeneity along or between flow paths, variations in recharge or natural attenuation capacity along flow paths, and other factors may play a role as well.

Although reductive dehalogenation of chlorinated ethenes does occur in the upgradient ground water, natural biodegradation processes do not appear to be enhanced in the hyporheic zone as ground water enters the surface water environment. This is consistent with the iron-reducing ground water geochemistry that predominates in the last 100 cm of ground water flow. Phospholipid and fatty acid analyses revealed variation in microbial community structure with depth, but this did not correlate to apparent attenuation of contaminants

## **Introduction**

Nationwide, 75% of RCRA and Superfund sites are located within one-half mile from surface water, and 50% of all Superfund sites have impacted surface water (Tomassoni, 2000). Yet ground water investigations rarely address the hyporheic zone, the hydraulically, chemically, and biologically complex zone comprising lakebed or streambed sediments. Conditions in the hyporheic zone do not necessarily resemble those in the greater part of the aquifer commonly examined by use of monitoring wells, and extrapolation of aquifer conditions to streambeds or lakebeds is often unjustified.

This paper discusses a simple two-step approach to defining ground water contaminant discharge to surface waters: 1) by defining zones of strong ground water discharge; and 2) by measuring the chemistry in those zones. A case study shows how a misleading portrayal of contaminant behavior can follow from sole reliance on a ground water conceptual model based on data collected from monitoring wells.

## **Site history**

A former dry cleaner supply company released approximately 450 kg of perchloroethene (PCE), contaminating a glacial outwash aquifer (Figure 1). The entire plume was defined during two phases of remedial investigation (Barr, 1992; Delta, 1989), consisting of 25 monitoring wells. PCE is the primary contaminant of concern, but trichloroethene (TCE), *cis*-1,2-dichloroethene (*cis*-DCE), *trans*-1,2-dichloroethene (*trans*-DCE), and vinyl chloride (VC) are also present in the dissolved chlorinated ethene plume more than 500 feet long and approximately 100 feet wide. The investigations supported conclusions that part of the plume discharged to Minnehaha Creek.

The initial remedial response in 1988 consisted of a single ground water extraction well, supplemented by a vacuum vaporizer well (Herrling et al., 1991; Lundy, 1995) which operated from 1994 until 1997. Other than extensive ground water sampling (Ferrety et al., 2001), no remedial efforts have been undertaken since 1997, but remaining concerns over possible ground water contaminants entering Minnehaha Creek prompted the current study.

## **Site geology, hydrogeology, and hydrogeochemistry**

The glacial outwash aquifer is continuous across the site and consists of poorly graded fine- to coarse-grained sands, fine gravels, and cobbles to a depth of 30 feet. The channel of Minnehaha Creek cuts the glacial outwash, and surface water flows at an elevation similar to that of the water table. Ground water flows to the east or southeast under a measured horizontal hydraulic gradient of 0.005 and an assumed effective porosity of 0.30. Aquifer pumping test data indicate a horizontal hydraulic conductivity ( $K_h$ ) of  $4.6 \times 10^{-2}$  cm/sec, yielding an expected average ground water velocity ( $v_x$ ) of 241 m/yr (790 ft/year). The water table is 3.0 to 3.7 m (10-12 ft) below grade. The aquifer is underlain by fine alluvium (sandy lean clay,  $K_h = 1.7 \times 10^{-4}$  cm/sec) and Paleozoic carbonate bedrock.

## **Methods**

Investigative methods used in this study were of three types: methods to map zones of strong ground water discharge; methods to obtain pore-water samples in zones of strong ground water discharge; and analysis of ground water geochemistry. The term "pore-water" refers to subsurface water, without designating its direction of flow. Pore-water moving upwards toward a discharge point to surface water is considered ground water.

Seepage between ground water and surface water is affected by geologic heterogeneity, and is rarely uniform (Winter, 2000). Contaminants commonly move to surface water by pathways of most rapid ground water flow. Finding zones of rapid ground water discharge to surface water using thermal mapping, gradient mapping, and seepage, can therefore guide sampling location selection.

*Thermal mapping.* A six-foot long steel probe with a retractable 10-cm long screen and drive point was hand-driven, and the screen was exposed to the sediment. Common summer surface water temperatures in Minnesota are 20-25 degrees C. Typical ground water temperatures are 10-12 degrees C. Pore-water temperatures close to

ambient surface water temperatures suggest downward surface water leakage. Pore-water temperatures close to ambient ground water temperatures suggest upward discharging ground water. Pore-water temperatures between the surface water and ground water temperatures suggest a mixture, or rapidly changing conditions.

*Vertical gradient measurement.* A device with a probe similar to the temperature probe was used to measure relative head difference between the underlying pore water and the surface water. Separate tubing and screen assemblies allow surface and pore-water to be pumped simultaneously allowing a measurement of relative head difference. Vertical gradient was computed by dividing the head difference by the depth of the exposed screen beneath the sediment-surface water interface.

*Seepage measurements.* Water flux between pore- and surface water was measured using a device similar to Lee (1977). The cut-off top of a plastic 30-gallon drum was first pushed gently into the sediment, allowing no residual air inside. A 7-L collection bag with a known water volume was connected to the seepage drum for a specified period of time, then removed. The volume change divided by the time of collection equals the seepage rate over the area covered by the drum.

*Pore-water sample collection.* Based on the above measurements, we selected eight stations to install simple multi-level samplers (MLS). The MLS were constructed of 3/8-inch ID/1/4-inch OD polyethylene tubing. Holes were drilled into the bottom end of each sampler, and scrim was cable-tied to exclude sediment for a screened interval of 5 cm. Each MLS consisted of four samplers installed to depths of 25 cm, 50 cm, 75 cm, and 100 cm. Additional samples were collected in selected locations using Henry PushPoint samplers (<http://www-personal.engin.umich.edu/~markhen/index.htm>). We used dedicated plastic syringes to draw ground water samples.

*Analytes.* A modified EPA Method 624 was used to quantify chlorinated ethenes. Field measurements of dissolved oxygen, nitrate, iron (II), manganese (II), and sulfide were accomplished with field test kits (Hach Co., Loveland, CO).

Ground water samples collected from 25, 50, 75, and 100 cm depths at station 219 were analyzed for phospholipid fatty acids (PLFA; Microbial Insights, Inc., Rockford, TN). Lipids were extracted from the 1-L aqueous samples with a chloroform-methanol solution. The PLFA were fractionated on a silicic acid column, followed by esterification of the polar-lipid fractions. The PLFA were quantified through GC/MS analysis, and the microbial community structure was determined at different depths based on the PLFA patterns present in the ground water samples.

## **Results**

The area investigated (Figure 1) included the area of expected plume discharge on the northern bank of the creek. Twenty-two stations approximately 7.5 m (25 ft) apart were numbered consecutively beginning with station 201 on the western end of the area investigated.

*Temperature.* Forty-five temperature measurements were made at 34 locations along the northern stream bank, with additional measurements (at some stations) in the middle of the stream channel. Measurement depths ranged from 15-95 cm, and most depths were in the range of 15-65 cm. All pore water temperatures were in the range of 16.7-26.0 degrees C, colder than the creek temperature (26.5 degrees C).

*Vertical gradient.* We measured 30 vertical gradients at 24 locations along the northern stream bank, with additional measurements (at some stations) in the middle of the stream channel. Measurement depths ranged from 15-105 cm, and most depths were 15-45 cm. Vertical gradients were 0.004 to 0.01 in the upward direction, and -0.001 to -0.2 in the downward direction.

*Seepage.* Seepage was measured 18 times at four locations (Table 1), along the northern stream bank. Seepage measurement attempts in other locations were frustrated by bed materials and shallow water. Measured seepage rates ranged from less than 1 cm/day to 52 cm/day.

*Redox.* Figure 2 illustrates  $[\text{Fe}^{+2}]$ ,  $[\text{Mn}^{+2}]$ , and  $[\text{SO}_4^{-2}]$  in ground water 25 cm below the creek bed. Sulfate concentrations ranged from 20 to 35 mg/L; sulfide was not detected at any location.  $[\text{Fe}^{+2}]$  and  $[\text{Mn}^{+2}]$  varied widely by location. Reduced iron was not detected in any of the ground water samples collected from the 25 cm depth at locations 213, 218 or 219, while reduced manganese was detected and increased in concentration to over 5 mg/L at location 219. Dissolved oxygen was present only at location 218 at 4 mg/L.

*Chlorinated ethenes.* The highest chlorinated ethene concentrations were at locations 213 and 219, and somewhat lower concentrations at location 202 (Table 2). While total chlorinated ethene concentrations varied greatly depending on location, there was little vertical variation over the 100 cm interval at any particular location (data not shown). The highest chlorinated ethene concentrations were present where reduced iron concentrations were low.

*Phospholipids.* Microbial biomass was determined by the total PLFA mass at location 219. Biomass decreased as a function of sediment depth (Table 3). Although PLFA analysis indicated that eukaryotic organisms were present at every depth, the bulk of the biomass was bacterial. Phospholipids unique to metal-reducing bacteria increased four-fold from the surface water sample to the ground water sample collected at a depth of 100 cm. The proportion of phospholipid unique to the sulfate-reducing *Desulfotobacter* sp. increased by an order of magnitude over the same interval.

## **Discussion**

Temperature measurement is rapid and easy, and is a good indicator of stations that warrant more detailed study. Where upward vertical gradients were measured, the range of pore-water departures from stream temperature was 2.1-9.8 degrees C (19 measurements). The average pore-water temperature difference from stream temperature in zones of measured upward vertical gradient was 4.4 degrees C. At each location where a downward vertical gradient was measured, the pore-water departure from stream temperature was low, ranging from 0.0-4.7 degrees C, averaging 1.6 degrees C (8 measurements). These findings suggest that pore-water temperature is a good indicator of the direction (and perhaps also the strength) of the vertical hydraulic gradient. Temperature departures greater than about 4 degrees C suggest upward ground water discharge.

Repetition of seepage measurements assured good precision (Table 1). Low seepage rates measured at stations 215A and 216 coincided with field observations of probable low-permeability materials (clay), not observed at other locations. Using seepage measurements at stations 218 and 219 to characterize the entire zone of plume discharge to the creek yielded a ground water discharge rate of approximately 7,490 L/day. Computing Darcy flux by use of bulk aquifer parameters yields a ground water discharge rate along the same stream reach of approximately 9,200 L/day.

Contaminant mass flux to the stream for each station is the product of the water flux and contaminant concentration (Table 2). For this analysis, each measurement station represents an area of the stream halfway to the next measurement station. Water flux is computed as the product of the measured seepage rate and area the measurement represents. These calculations indicate that approximately 271 g of chlorinated ethene mass discharged to the creek in 2002.

A typical conceptual model developed from ground water monitoring data predicts a smooth increase in contaminant concentrations along a transverse plume cross-section from plume flank to plume axis, and a smooth decrease in contaminant concentrations from plume axis to the opposite plume flank. Assuming a bulk hydraulic conductivity for the entire aquifer, the conceptual model predicts a similar distribution of contaminant mass flux to the creek. Table 2 and Figure 3 indicate that this pattern of contaminant discharge is not the case. Instead, contaminant discharge is focused at station 213 (177 mg/day), 218A (114 mg/day), and 219 (112 mg/day).

Negligible or zero contaminant flux is present at several stations (214-218) located on the plume axis where maximum concentrations and contaminant flux are predicted by the conceptual plume model. Data collected in the ground water discharge zone appear to challenge the conceptual plume model in two fundamental ways: 1) contaminants are absent where expected; and 2) contaminants are present where unexpected.

Since multiple source areas have been ruled out, the effect may be partly accounted for by variable streambed vertical hydraulic conductivities or uneven infiltration (due to pavement). However, these factors cannot completely explain significant contaminant flux (66 mg/day) at station 202, approximately 200 feet upstream of the zone of expected plume discharge. With only one source area, the occurrence of contamination at station 202, far outside of the expected zone, likely arises due to preferred pathways of contaminant movement within the aquifer. Such zones are often unanticipated in glacial outwash sediments, but they may in fact be common (e.g., Freeze and Cherry, pp.147-148). Investigating exact preferred flow paths by conventional means would be cost-prohibitive, but their discharge points can be conveniently mapped.

The results of this study indicate that generalized conceptual plume models should be viewed skeptically. These plume models suggest a smooth spread of ground water contaminant discharge to surface water, but at this site ground water contaminant discharge to surface water was erratic. Moreover, a generalized plume model did not predict the discharge of contaminants well upstream of the ground water “plume” inferred from monitoring well data.

*Contaminant fate.* The pathway for biological reductive dehalogenation of chlorinated ethenes occurs under redox conditions governed by sulfidogenic or methanogenic processes (Vogel and McCarty, 1985). PCE degrades at a significant rate (-2.43/yr) in the aquifer upgradient of the creek through reductive dehalogenation (Ferrey et al, 2001). However, contaminant fate in the last meter of flow path into surface water was not clear. Under the organic carbon-rich conditions found in the surface water sediment, we anticipated that reductive dehalogenation processes might be enhanced along the last meter of ground water flow, thereby reducing the contaminant loading to the overlying surface water.

We found no evidence of strongly reducing conditions in the sediments at any depth below the creek bed. Sulfide was not present, and the absence of reduced iron at several locations indicated that redox conditions were unfavorable to the reductive dehalogenation of chlorinated ethenes, particularly at location 218 where oxygen was detected at 4 mg/L. Under these conditions, appreciable degradation of PCE or other chlorinated ethenes is not expected.

The highest contaminant concentrations and flux to the surface water coincided with very low reduced iron concentrations in the ground water. At stations 213 and 219, where the flux of total chlorinated ethenes to surface water was 177 and 112 mg/day, respectively, reduced iron was absent from ground water at each of the four depths sampled to 100 cm. High reduced manganese concentrations at station 219 indicate an elevated oxidation-reduction ground water condition in this area. These conditions are consistent with relatively high concentrations of chlorinated ethenes at these locations, as these compounds tend to be recalcitrant under redox conditions dominated by iron-, manganese-, or nitrate-reducing processes (Bouwer, 1994).

Microbial PLFA analysis showed that microbial biomass decreased significantly over the 1 meter depth of sediment, which we anticipated due to the decrease in organic carbon provided by the surface water ecosystem. However, PLFA analysis demonstrated that the population of sulfate reducing *Sulfotobacter* sp. increased significantly in the deepest ground water sampled at 100 cm below the creek bed. *Sulfotobacteria* and other sulfur reducing bacteria are able to effectively dehalogenate chlorinated ethenes (Wiedemeier et al, 1999). However, we found no evidence that reductive dehalogenation was enhanced along the last vertical meter of ground water flow in the sediment. The absence of sulfide from the ground water samples at this location suggested that sulfur-reducing bacteria were not metabolically predominant. The presence of *cis*-DCE and VC in aquifer water upgradient of the creek indicates that reductive dehalogenation is occurring. However, PCE, TCE,

*cis*-DCE, and VC concentrations were remarkably consistent in the ground water samples collected from depths ranging from 100 cm to 25 cm below the creek bed.

The results of this study are consistent with other studies showing that ground water flux to surface water is rarely uniform (e.g., Rosenberry et al., 2000; Winter, 2000). In addition, there are considerable variations in the redox environment and the corresponding microbial consortia in the hyporheic zone. While we did not detect accelerated breakdown of the chlorinated contaminants in the stream sediments at this site, it is clear that detailed investigation of ground water flux to surface water can yield valuable information upon which to focus remediation decisions and risk assessments.

### **Acknowledgement**

The authors thank Dr. Frank Chapelle, USGS, for assistance and advice with the microbial PLFA analysis.

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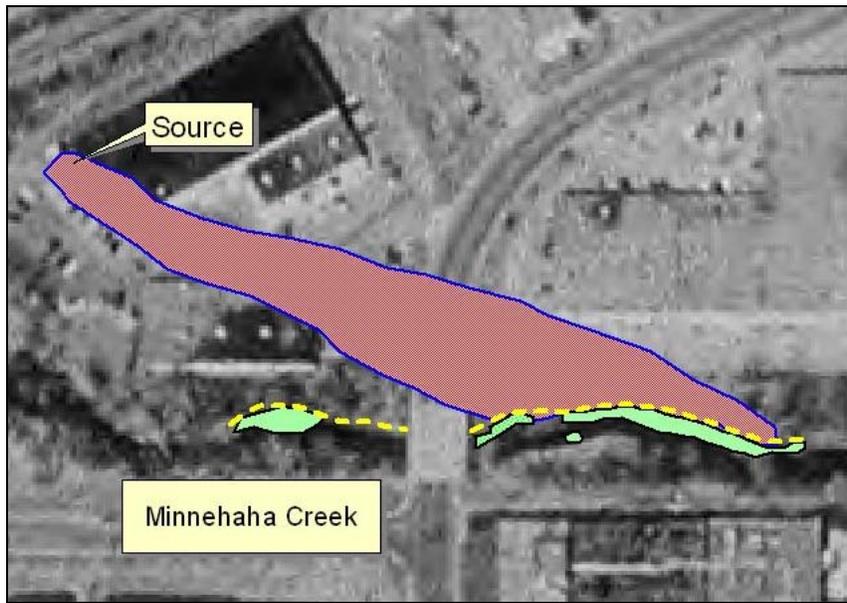


Figure 1. Study site showing conceptual ground water contaminant plume. Minnehaha Creek flows eastward. The area of expected plume discharge is where the conceptual plume intersects the northern stream bank. Investigation area indicated by dotted line. Areas of upward discharging ground water indicated by light pattern in stream (see text).

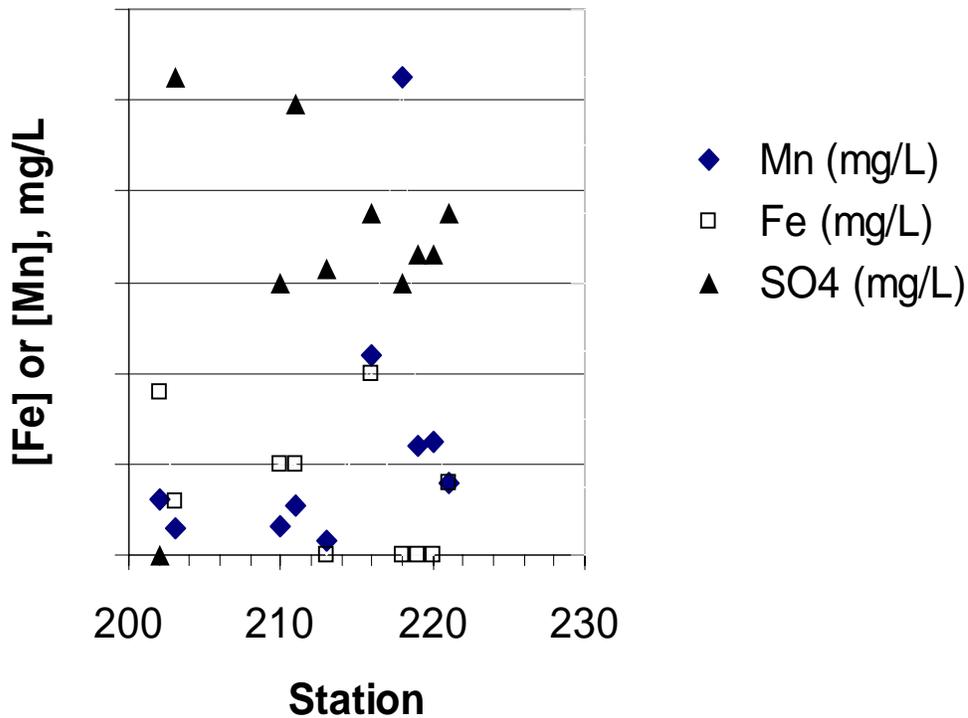


Figure 2. Plot of Mn, Fe, and SO<sub>4</sub> vs. station, at a depth of 25 cm beneath stream bed.

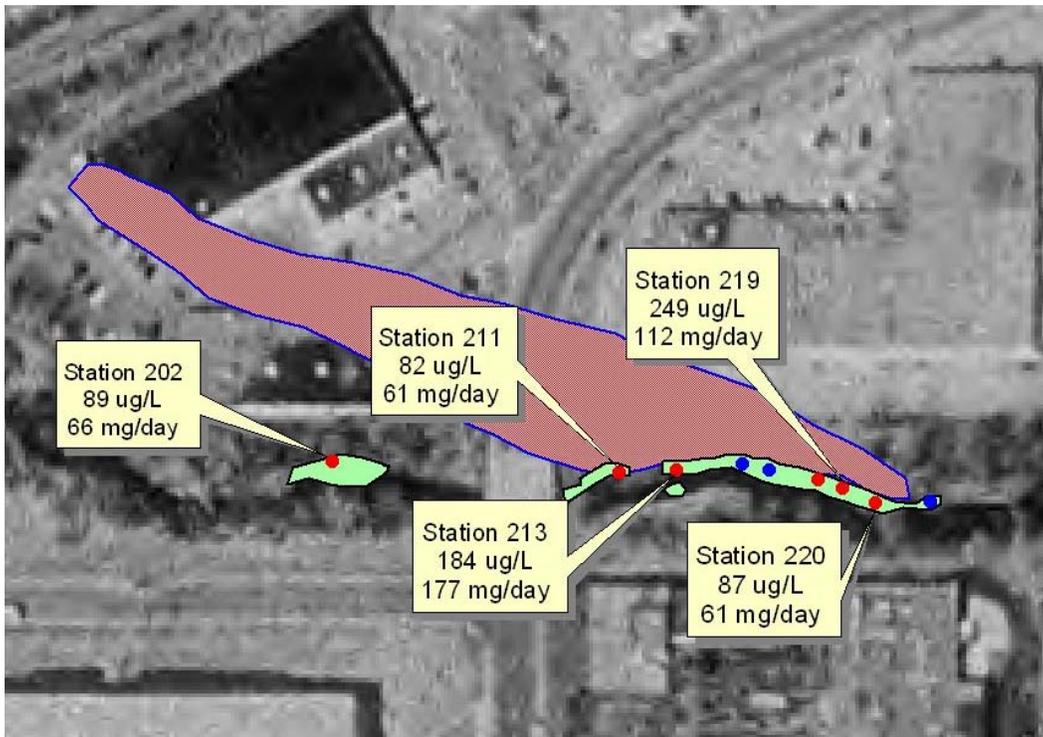


Figure 3. Station numbers, total chlorinated ethene concentrations, and contaminant mass flux in discharging ground water. Blue dots denote contaminants not present.

<b>Station</b>	<b>Trial</b>	<b>Seepage (cm/day)</b>	<b>Kv (cm/sec)</b>
215a	1	5	1.62E-02
	2	2	7.48E-03
	3	3	9.15E-03
	4	3	1.08E-02
	5	2	6.00E-03
	<b>Average</b>	<b>3</b>	<b>9.36E-03</b>
216	1	1	2.92E-04
	2	1	3.80E-04
	3	0.3	1.31E-04
	4	0.5	2.19E-04
	5	1	2.77E-04
	<b>Average</b>	<b>0.8</b>	<b>2.50E-04</b>
218	1	47	3.27E-02
	2	46	3.20E-02
	3	52	3.59E-02
	<b>Average</b>	<b>48</b>	<b>3.35E-02</b>
219	1	24	4.80E-02
	2	27	5.23E-02
	3	24	4.70E-02
	4	26	5.20E-02
	5	24	4.75E-02
	<b>Average</b>	<b>25</b>	<b>4.93E-02</b>

Table 1. Seepage and calculated streambed vertical hydraulic conductivity.

Station*	Chlorinated ethenes (ug/L)	Seepage (cm/day)	Area (cm <sup>2</sup> )	Water flux (L/day)	Contaminant mass flux (mg/day)
201		37	25000	925	0
202	89	37	20000	740	66
202A	26	37	18000	666	17
203	4	37	20000	740	3
203A	2	37	13000	481	1
209A	11	37	13000	481	5
210	37	37	21000	777	29
211	82	37	20000	740	61
213	184	37	26000	962	177
214		37	20000	740	0
215		<b>3</b>	30000	90	0
216		<b>1</b>	36000	36	0
217		37	34000	1258	0
218		<b>48</b>	16000	768	0
218A	132	48	18000	864	114
219	249	<b>25</b>	18000	450	112
219A	204	25	19000	475	97
220	87	25	28000	700	61
221		37	11000	407	0
			<b>Total</b>	12300	L/day
				743	mg/day
				0.743	g/day
				271	g/year

Table 2. Estimated contaminant mass flux to the stream. Blank cells indicate contaminants not detected. Shading denotes area of expected plume discharge based on conceptual plume model. Bold italicized numbers denote measured seepage (others estimated).

	Cell equiv. (cells/mL)	Bacteria biomass	Eukaryote biomass
Surface water	$7.0 \times 10^5$	20	15
25 cm	$4.0 \times 10^5$	17	3
50 cm	$2.6 \times 10^5$	9	4
75 cm	$1.0 \times 10^5$	9	2
100 cm	$9.9 \times 10^4$	4	1

Table 3. Results of PLFA analysis at location 219. Biomass values are in picomoles PLFA mL<sup>-1</sup> sample.