POSTER SESSION ABSTRACTS

Use of Multi-Parameter Sensitivity Analysis to Determine Relative Importance of Processes Involved in Transport of Mining Contaminants

By Jungyill Choi, Judson W. Harvey, and Martha H. Conklin

ABSTRACT

Combining multi-parametric sensitivity analysis (MPSA) with stream transport modeling is proposed to determine the relative importance of physical and biogeochemical processes controlling transport of mining contaminants in natural stream systems. The MPSA is based on a large number of Monte-Carlo simulations to identify the sensitive parameters over a broad range of each parameter. This combined approach can provide an integrated view of transport processes of contaminants in natural stream system.

INTRODUCTION

The fate and transport of contaminants in streams and rivers are controlled by a variety of physical and biogeochemical processes. The physical processes play an important role in determining the fate of solutes in surface-water environments. These physical processes include advection, dispersion, hyporheic exchange, and ground-water interaction. In many situations, however, the transport of contaminants are also greatly affected by biogeochemical processes, such as sorption/desorption, oxidation/reduction, volatilization, hydrolysis, biodegradation, and other biochemical reactions. Therefore, transport of contaminants in natural streams and rivers is best described by considering all of the relevant physical and biogeochemical processes simultaneously (fig. 1).

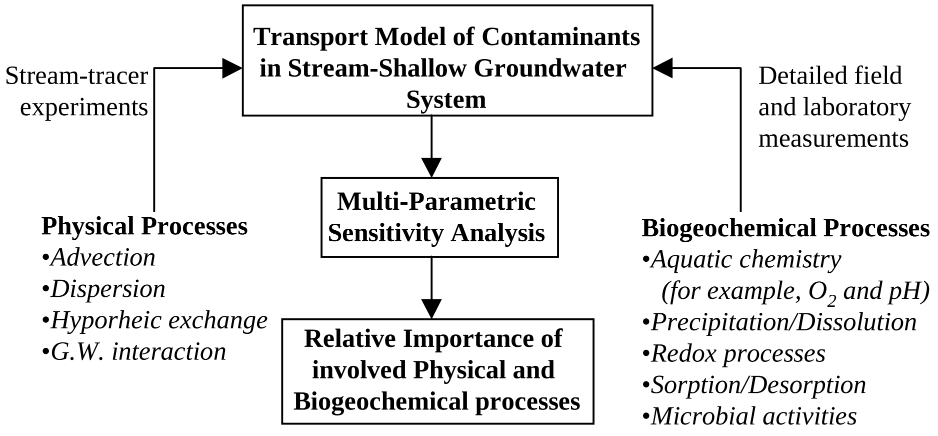

Figure 1. Coupling MPSA with transport model to identify the relative importance of physical and biogeochemical processes.

To answer the question about relative importance of factors, the sensitivity of a numerical transport model needs to be tested for the physical and biogeochemical parameters (processes) that are involved in the forward transport model. However, traditional parameter-sensitivity analysis pertains to a particular point (localized) in the parameter space, which is defined by all possible combinations of parameter values. Also, in the localized sensitivity analysis, the importance or sensitivity of a selected parameter can be affected greatly by the values of other parameters, because the significance of one selected process is usually dependent on other processes. Typically, the importance of biogeochemical processes are highly dependent on the physical processes, whereas the physical processes are not affected by the biogeochemical processes. For example, the biogeochemical reactions of solutes in the hyporheic sediments are enhanced by the prolonged retention time of solutes in these sediments. Therefore, to account for parameter interactions, the relative importance of the physical and biogeochemical processes of the transport model can be evaluated more accurately by a generalized (multi)-parameter sensitivity analysis, which encompasses the entire parameter space (fig. 1).

This paper presents the concepts and procedures of multi-parameter sensitivity analysis (MPSA) that is used to determine the relative importance of transport processes

METHODOLOGY

A numerical transport model may include detailed field measurements as well as ill-defined parameters that cannot be measured with a high degree of accuracy in the field or in the laboratory. These ill-defined parameters will severely limit the accuracy of any single simulation and increase the difficulty of assessing the relative importance. In an attempt to overcome this difficulty and to recognize the relative significance of parameters involved in the model, the sensitivities of simulations results to input parameters need to be evaluated by assigning either a range of variation or a degree of uncertainty to each parameter and implementing a generalized sensitivity analysis (Hornberger and Spear, 1980; Chang and Delleur, 1992; Choi, et al., 1998; Choi, 1998). This multi-parametric sensitivity analysis (MPSA) followed the procedure proposed by Chang and Delleur (1992) and Choi, et al. (1998). The procedure includes the following steps:

- Select the parameters to be tested.
- Set the range of each parameter to include the variations experienced in the field and laboratory measurement.
- For each selected parameter, generate a series of, for example, 500 independent random numbers with a uniform distribution within the design range.
- Run the model using selected 500 parameter sets and calculate the objective function values.
- Determine whether the 500 parameter sets are ‘acceptable’ or ‘unacceptable’ by comparing the objective function values to a given criterion (R).
- Statistically evaluate parametric sensitivity. For each parameter, compare the distributions of the parameter values associated with the acceptable and unacceptable results. If the two distributions are not statistically different, the parameter is classified as insensitive; otherwise, the parameter is classified as sensitive. Relative importance can be evaluated statistically if desired.

The objective function values of the sensitivity analysis usually are calculated from the sum of squared errors between observed and modeled values:

$$f = \sum_{i=1}^{n} [x_o(i) - x_c(i)]^2$$

where *f* is the objective function value and $x_C(I)$ and $x_0(I)$ are calculated and observed values, respectively. Observed values often are obtained from simulations that used the mid-points of the characteristic range for each parameters. The ranges for each parameter are determined from minimum to maximum values that are obtained from parameter estimations and field measurements through the study reaches. If the objective function value obtained from the simulation is less than a subjective criterion then the result is classified as acceptable, otherwise the result is classified as unacceptable. Three different objective function values often are tested for a subjective criterion. Those values typically define the 33, 50 and 66% divisions of 500 sorted objective functions.

The basic concept of MPSA is illustrated by using a hypothetical model with only two parameters (Figure 2). In addition, the modeling procedure of MPSA described above is summarized using a flowchart (Figure 3).

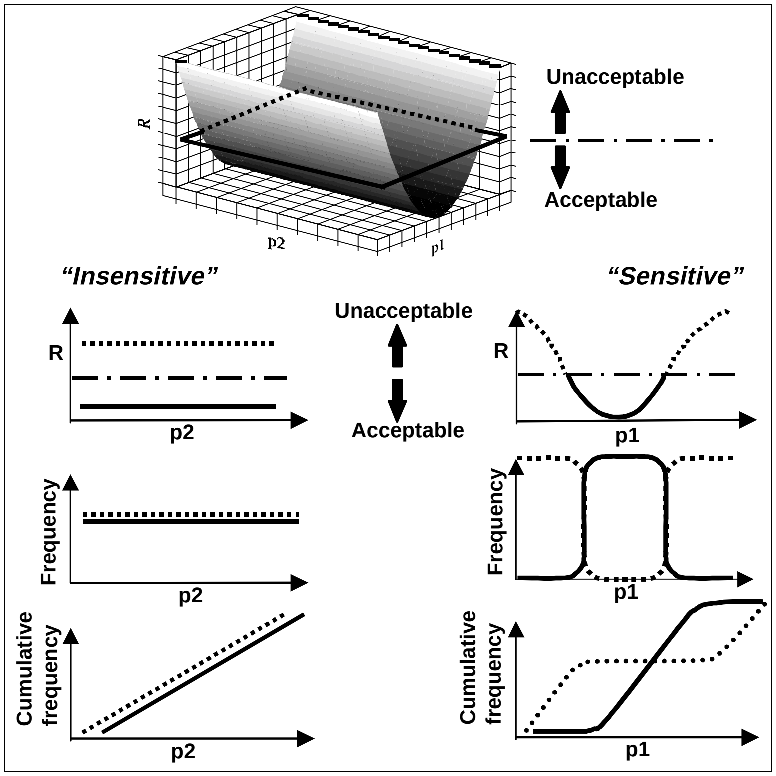

Figure 2. Basic concept of multi-parametric sensitivity analysis (MPSA) using a hypothetical model with only two parameters.

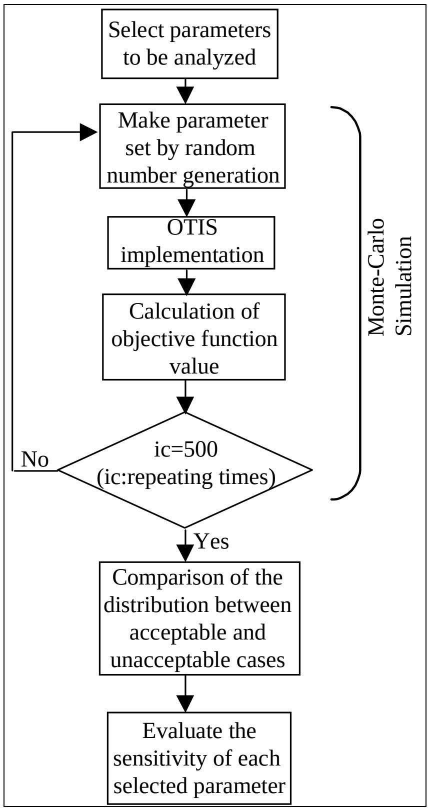

Figure 3. Flow chart illustrating the procedure of multiparametric sensitivity analysis (MPSA).

CONCLUSIONS

The combined efforts of forward modeling approach and generalized sensitivity analysis can provide an integrated view and better understanding of contaminant transport processes in natural stream systems. The multi- parametric sensitivity analysis especially helps identify the relative importance of physical and biogeochemical processes controlling the transport of contaminants. Furthermore, this methodology can provide a guide for future data-collection efforts and to order research priorities.

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Measurements of Plant and Algal Bioaccumulation of Metals in Pinal and Pinto Creeks, Arizona

By Justin C. Marble, Timothy L. Corley, and Martha H. Conklin

Dissolved Mn is an essential element for higher plant systems and is involved in photosynthesis (the Hill reaction) and activation of different enzyme systems (e.g., superoxide dismutase production) (Mukhopadhyay and Sharma, 1991). Critical deficiency levels of Mn(II) range between 0.01 to 0.02 microgram Mn per gram (mg Mn(II) g^{-1}) dry weight in dry mature leaves but vary tremendously between plants (Mukhopadhyay and Sharma, 1991). Vascular plants and algae also require certain amounts of other trace metals for normal plant growth (Zn, Ni, Cu, Fe, Co, Ca, and Mg).

Although Mn(II) supplements can increase growth yields of plants, large amounts of Mn(II) can interfere with the uptake of other trace metals (Mukhopadhyay and Sharma, 1991). In addition, excess concentrations of Zn, Ni, Cu, Fe, and Co can trigger an inherent defense mechanism that plants have developed that involves production of phytochelatins—polypeptides that bind metals (Ahner, et al., 1995). Phytochelatin production in response to high metal levels has been identified in land plants, vascular aquatic plants, fungi, and marine and freshwater algae. This mechanism results in an accumulation of the excess metals within the plants with the final metal concentration often being significantly higher than found in water supplied to the plants.

The work reported in this paper focuses on bioaccumulation of metals by aquatic plants, algae, and moss in Pinal Creek, an Arizona State Superfund site, near Globe, Arizona, that has been contaminated by acid-mining activities in the area. The primary purposes of this study were to determine the extent to which metals were taken up by the diverse plant community at Pinal Creek and to determine which plants were particularly effective at bioaccumulation of metals. To further aid in our assessment of the potential role of plants as a sink for metal contaminants in Pinal Creek (Figure 1), comparisons of metals uptake were made with other measurements reported for similar plants in Pinto Creek, also near Globe, Arizona. A comparison of typical surface water data for Pinal and Pinto Creeks is given in Table 1.

Plant grab samples were collected from several locations and rinsed with creek water to remove insects and loosely attached sediment material. At Pinal Creek, plant samples were collected from sites Z0, J^{2}-1, J^{2}-5, J^{2}-15, and Z11 (Figure 1). At Pinto Creek, grab samples were collected from two USGS stream gaging sites 09498501 (below Haunted Canyon near Miami, Arizona) and 09498502 (Pinto Creek near Miami, Arizona).

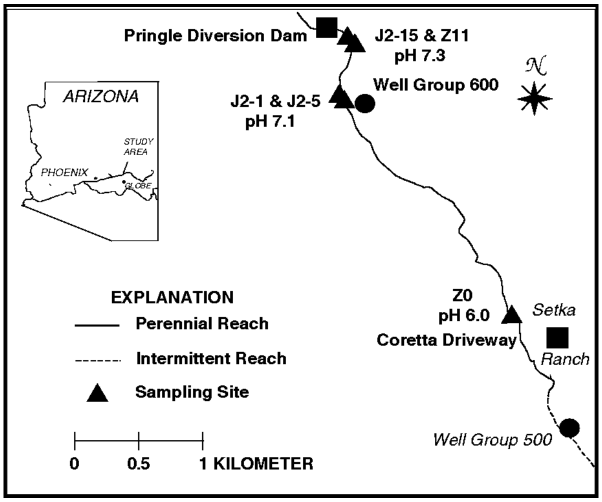

Figure 1. Study reach and sampling sites at Pinal Creek. Median pH values are shown for the study period.

	Pinal	**Pinto**
Parameter	Value	Value
pH	6.4	7.8
Oxygen	6.9	9.0
Alkalinity[1]	51	180
TDS	2,640	531
Co(II)	0.410	0.003
Cu(II)	0.050	0.010
Fe(II)	<0.130	0.0053
Mn(II)	72.0	0.0038
Ni(II)	0.790	0.010
Zn(II)	0.500	0.0060

[1] As $CaCO_3$.

Table 1. Physical and Chemical Values for Pinal Creek (Z0 on January 25, 1995) and Pinto Creek (near Miami, Arizona, on June 18, 1997, USGS). (mg L^{-1} except for pH which is in standard pH units).

After rinsing with creek water, the plant samples were placed in plastic bags and put into a cooler. Upon arrival at the laboratory, samples were dried at 60°C for 24 hours. Dried samples were ground and sieved, then digested with nitric acid. Digested plant samples were analyzed by flame or graphite atomic absorption spectroscopy for different metal concentrations. Results are reported as bioaccumulation, i.e., mg of metal per kg of dried plant material (mg kg^{-1}). The values reported represent the average of 2 subsamples with the maximum and minimum values measured being within ±2 percent of the average value.

The aquatic plant species found at Pinal Creek varied in type and density depending upon the time of year and the location. Before plant sampling started in 1996, water speedwell (*Veronica anagallis-aquatica*) and rabbitfoot grass (*Polypogon monspeliensis [L.] [Desf.]*) dominated the upstream portion of Pinal Creek (J^2-1) and algae (e.g., *Microcystis, Vaucheria*, and *Oocystis*) dominated in the downstream section (J^2-15). However, over the study period (November, 1996 through June, 1997), water speedwell, rabbitfoot grass, and algae were found along the entire study reach.

Water speedwell from Pinal Creek was collected from several field locations (Z0, J^2-1, and J^2-15) over a period of 8 months and analyzed for Mn(II). There was no obvious correlation between sampling date and bioaccumulation of Mn at J^2-1 and J^2-15 . A subset of the water speedwell samples from sites J^2-1 and J^2-15 were analyzed for other trace metals (Table 2). No trend with location was observed for concentrations of Fe, but Zn and Ni were higher at J^2-15 than at J^2-1 and Cu was higher at J^2-1 than at J^2-15. Bioaccumulation of Mn and Co exhibited consistently higher bioaccumulation at J^2-15 compared to J^2-1, about a factor of 2 difference.

Metal	Date	J2-1	J2-15
Mn	12/13/96	6450	18600
Mn	1/31/97	7990	16400
Fe	12/13/96	4400	1880
Fe	1/31/97	2520	2670
Ni	12/13/96	109	151
Ni	1/31/97	148	182
Cu	12/13/96	901	824
Cu	1/31/97	1750	1130
Co	12/13/96	80.5	158
Co	1/31/97	134	279
Zn	12/13/96	516	665
Zn	1/31/97	772	801

Table 2. Water speedwell bioaccumulation from Pinal Creek collected on December 1996 and January 1997 for Mn, Zn, Ni, Cu, Co, and Fe (units are mg kg-1).

Rabbitfoot grass samples from J^2-1 and J^2-15 were also analyzed for Mn, Zn, Ni, Co, and Fe (Table 3). Both upstream and downstream sampling sites had similar bioaccumulation values for Zn and Ni, but Mn, Cu, Co, and Fe values were larger at site J^2-1 than J^2-15. A factor of about 2 between values at J^2-1 and J^2-15was observed for Mn, Co, and Cu, and a factor of about 10 for Fe. Bioaccumulation of Mn at both sites was also greater than the other metals. Duckweed (*Lemna minor*) was less widely distributed than either water speedwell or rabbitfoot grass, and was typically only found in slow moving or stagnant water near the banks of the creek. However, a sample collected from J^2-5 on June 25, 1997 (pH 7.1, Mn(II) concentration 47.0 mg L^{-1}) had an Mn concentration of 10760 mg L^{-1}.

Metal	J^2-1	J^2-15
Mn	13600	5240
Fe	6890	691
Cu	1640	828
Ni	163	161
Co	237	130
Zn	581	534

Table 3. Rabbitfoot grass bioaccumulation in samples from Pinal Creek collected on January 31, 1997 (units are mg kg^{-1}).

Algae is prolific at both Pinal Creek and Pinto Creek and grab samples at both sites included the species *Microcystis*, *Vaucheria*, and *Oocystis*. Samples were collected from both creeks to compare bioaccumulation of Mn (Table 4). Although Pinal Creek samples had more bioaccumulation, the ratios of plant concentration to surface water concentration were greater in the Pinto Creek samples.

Site	Date	Mn
Pinal, Z11	7/17/96	49700
Pinal, Z11	11/15/96	90200
Pinal, J^2-15	12/12/96	5550
Pinal, J^2-15	1/31/97	79300
Pinto, Miami	6/18/97	240
Pinto, Miami	6/18/97	1460

Table 4. Algae samples from Pinal Creek and Pinto Creek: bioaccumulation of Mn (mg kg^{-1}).

Water speedwell collected from Pinto Creek had lower bioaccumulation of Mn than samples collected from Pinal Creek (Table 5). However, the ratios of Mn concentrations in water speedwell to the surface water concentrations were significantly higher in Pinto Creek than found for Pinal Creek. Similar differences were apparent from comparisons of the algae samples collected at Pinto and Pinal Creeks

Site	Date	Mn
Pinal, J^2-1	6/25/97	3870
Pinto, Haunted	6/18/97	505
Canyon	6/18/97	97
Pinto, Miami	6/18/97	47

Table 5. Water speedwell bioaccumulation (mg kg^{-1}) in Pinal and Pinto Creeks.

These studies indicate that water speedwell, rabbitfoot grass, and algae bioaccumulate Mn. Bioaccumulation of Zn, Ni, Co, Cu, and Fe was also observed in water speedwell and rabbitfoot grass. Comparisons between water speedwell and algae samples collected from Pinal Creek and Pinto Creek suggest that at Pinal Creek the plant capacity for metal uptake may have been reached and/or that metal toxicity effects must be considered. Water speedwell and other aquatic plants are prolific in Pinal Creek and could play a significant role in determining the fate of metal contaminants entering the stream. Additional data concerning the total biomass in the system, and the potential release of metals as plants die and decay, are required to assess the potential and actual contribution of plants to total metals removal in this system.

ACKNOWLEDGMENTS

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Tracing Groundwater Flow into Surface Waters by Application of Natural and Artificial Tracers

By D. Reide Corbett, William Burnett, Jeffrey Chanton, and Kevin Dillon

Submarine groundwater discharge (SGD) is an often overlooked yet possibly significant process in the geochemical and nutrient budgets of marine nearshore waters. According to Johannes (1980) “SGD should occur anywhere that an aquifer is hydraulically connected with the sea through permeable rocks or bottom sediments and where the head is above sea level.” Such conditions are met in most coastal areas. This process may be significant for transport of limiting nutrients in pristine coastal areas or, in the case of polluted aquifers, could be an important source of contamination to the marine environments. The problem is how to assess the extent of the groundwater flow and how to link environmental problems with specific sites of contamination. Due to the extreme temporal and spatial variability of many of these variables, the exact location of problematic discharges into coastal regions may be difficult to determine by monitoring standard water quality constituents (e.g., NO_X, turbidity). In this research, subsurface water movement was evaluated with natural and artificial tracers in the karst limestone of the Florida Keys (Figure 1).

In the Florida Keys, natural tracers (^{222}Rn and CH_4) were used to locate areas of increased groundwater/surface water interactions by reconnaissance surveys of the concentrations of radon and methane in the bay waters (Corbett, et al., 1999). These trace gases function as natural indicators of submarine groundwater discharge into standing bodies of water due to their significantly higher concentrations in groundwaters (Cable, et al., 1996a, b; Bugna, et al., 1996). General trends in surface water concentration were established by contouring data from each tracer survey with a kriging method by use of the software package Surfer® (Golden Software). Although kriging interpolates between data points, creating some artifacts, the general trends described are independent of the contouring

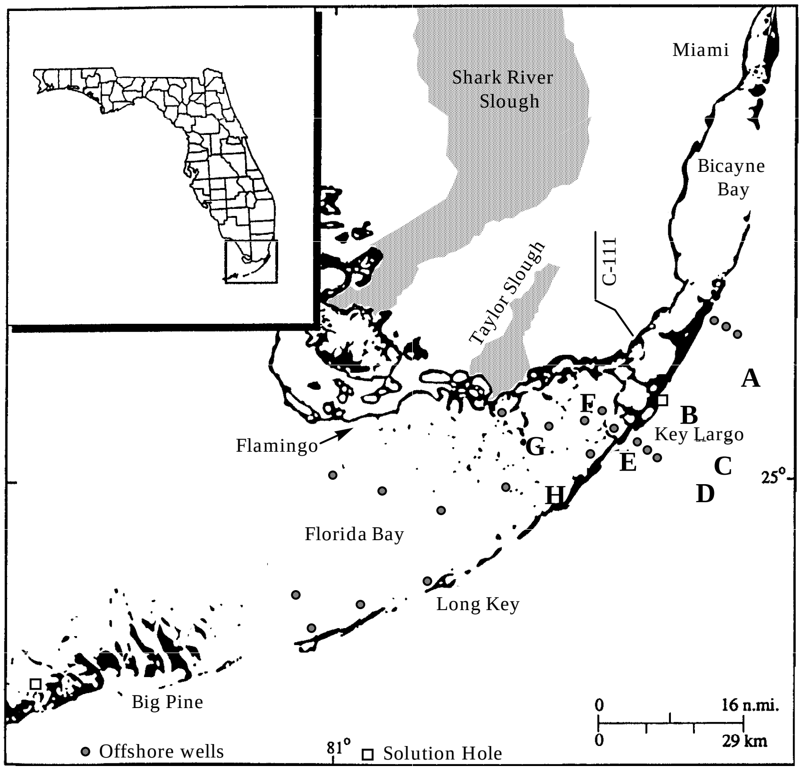

Figure 1. Florida Bay separates the Florida Keys, located off the southern tip of Florida, from the mainland. Water samples were collected primarily from north of Long Key and East of Flamingo. Groundwater samples from offshore wells were collected where indicated by the circles. Letters refer to locations mentioned in the text: A. Carysfort Reef; B. Algae Reef; C. French Reef; D. Molasses Reef; E. Rock Harbor; F. Porjoe Key; G. Black Betsy Keys; and H. Tavanier Basin. (Figure from Corbett et al., 1999)

method or a reasonable change in contouring concentration. Examination of these contour plots showed very little apparent seasonal variation throughout the study period. During each period we sampled, high concentrations of both tracers were observed near the Keys. Plots for ^{222}Rn and CH_4 in summer 1997 show the typical trends observed (Figure 2). Direct measurements of groundwater flux via seepage meters were also made in several different areas of Florida Bay. Radon and methane concentrations in water samples collected from wells, springs, canals, and Florida Bay showed a significant correlation, despite the fact that the two trace gases have independent source terms (Figure 3). Natural abundance of nitrogen isotopes measured on attached algae and seagrass also show greatest ^{15}N enrichment in areas near the keys. We observe a strong spatial gradient in ^{15}N of macrophytes (seagrasses and macroalgae) in Florida Bay, with relatively light (-1 to 4 ‰) macrophytes in western Florida Bay and relatively heavy (6 to 13 ‰) macrophytes in northeastern Florida Bay (Figure 4). This gradient is likely a function of two processes: (1) progressive denitrification of N brought into Florida Bay via tidal exchange with the Gulf of Mexico; and (2) entry of ^{15}N-enriched water from the subsurface adjacent to the Keys in northeastern Florida Bay. Collectively, these results indicate a greater flow of groundwater along the inside of the keys. Nutrient flux estimates, based on interstitial nutrient concentrations and groundwater flux measurements, suggest that groundwater in the eastern area of Florida Bay may provide as much nitrogen (110 ± 60 mmol N m^{-2} y^{-1}) and phosphate (0.21 ± 0.11 mmol PO_4^{3-} m^{-2} y^{-1}) as surface freshwater sources from the Everglades (i.e., Taylor Slough and C-111). However, the inputs are clearly not uniform and areas near solution holes/tidal springs may have a substantially greater nutrient flux into surface waters then these estimates (Corbett, et al., 1999).

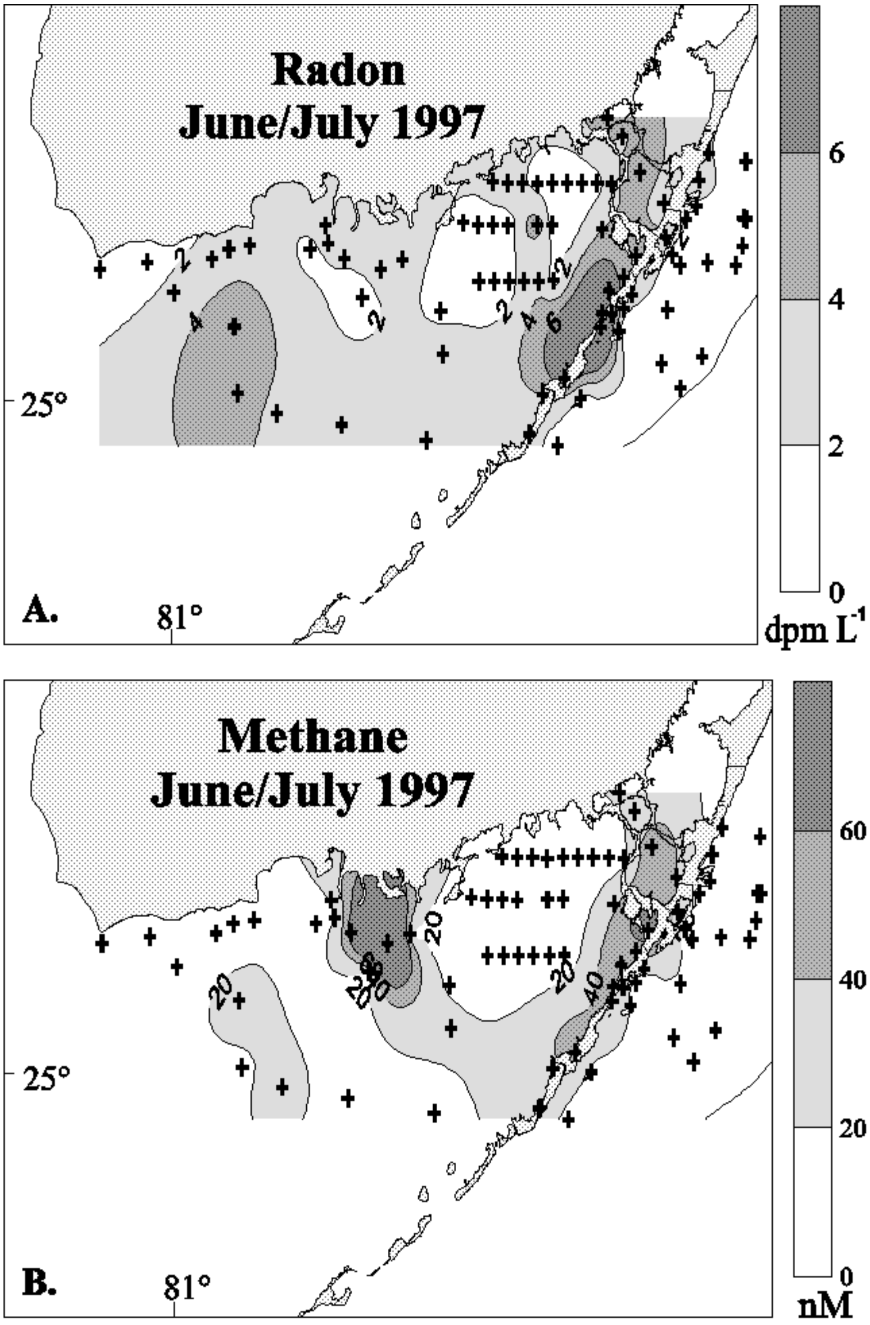

Figure 2. Contours of radon (A) in dpm L^{-1} and methane (B) in nM for samples collected in June/July 1997. Solid crosses indicate sampling locations. Note the darker contours, indicating higher concentrations of both parameters, near the upper Keys. (Figure from Corbett et al., 1999)

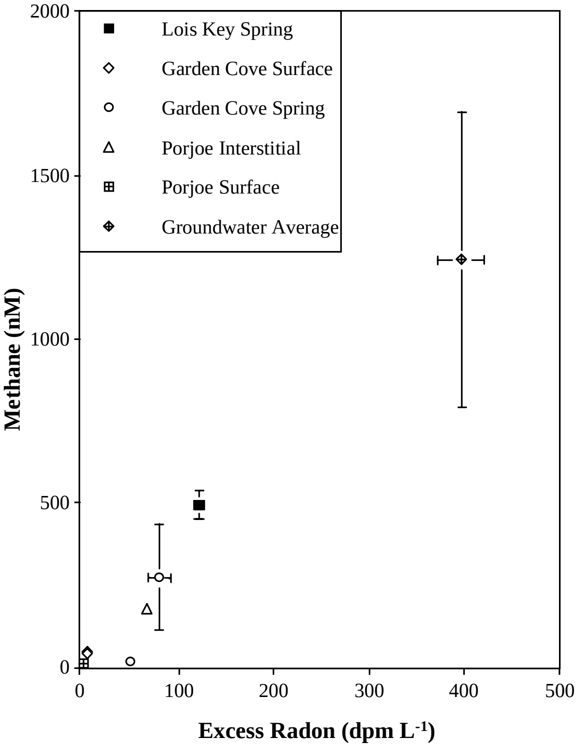

Figure 3. Radon and methane concentrations in waters sampled throughout the Keys. The groundwater tracer concentrations are based on the overall average of all samples collected. (Figure from Corbett et al., 1999).

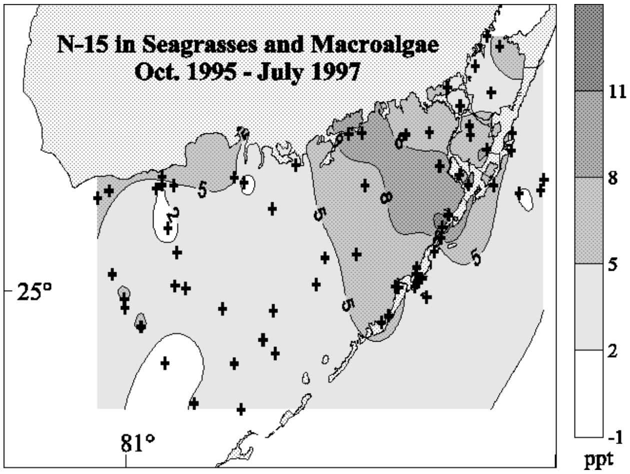

Figure 4. Contours of ^{15}N in macroalgae collected throughout the study period. Solid crosses indicate sampling locations. Note the darker contours, indicating higher enrichment, near the upper Keys. (Figure from Corbett et al., 1999).

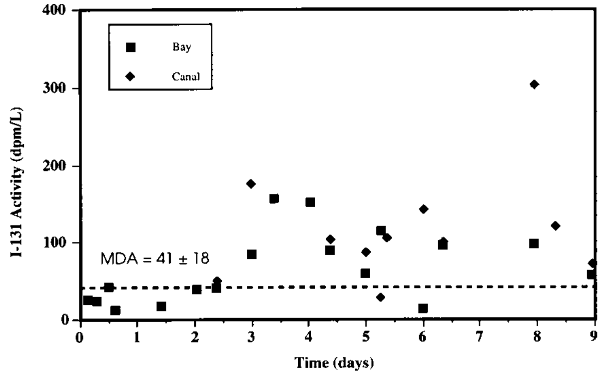

Figure 5. I-131 in surface waters sampled on both sides of Long Key, Florida Bay (closed square) and the Atlantic via a canal (closed diamonds). Radioactive iodine was added to a sewage injection well as a conservative tracer to track wastewater movement in the subsurface. Due to the rapid vertical and horizontal movement of wastewater in the subsurface, injected tracers appear in surface waters within 3 days after injection.

Artificial tracers (SF_6, ^{131}I, ^{32}P) were used to establish a direct link of contaminated groundwaters to surface waters. Tracers injected directly into sewage injection wells indicate rapid flow of groundwater beneath the keys. Experiments conducted on Long Key indicate two different types of transport: (1) rapid flow (0.20–2.20 m/hr), presumably through cracks and conduits present in the limestone; and (2) slow diffusive flow (<0.003-0.14 m/hr), associated with the limestone's primary porosity (Dillon, et al., 1999). Vertical flow of the wastewater effluent was comparable to horizontal flow due to the buoyancy of the relatively fresh wastewater compared to the surrounding saline groundwater. These experiments showed that solutes injected into the Key's subsurface have the potential to reach surface waters within a few days (Figure 5). Tracer experiments conducted using both a conservative tracer (SF_6, ^{131}I) and nutrients of interest (nitrogen and phosphorous) showed that both nitrate and phosphate have some non-conservative behavior. Either through microbial alteration or interaction with the limestone matrix, water from the wastewater injection appears to be polished as it flows through the subsurface.

In a review of the general subject of SGD, Johannes (1980) stated that "It is...clear that submarine groundwater discharge is widespread and, in some areas, of greater ecological significance than surface runoff." I agree with this appraisal and add that from my review of the available literature, I find that it has been largely the biological community which has recognized the potential importance of SGD. I maintain that the process of SGD may also be an important and overlooked part of the geochemical cycles of many elements. In the case of Florida Bay and the Florida Keys, SGD has been completely ignored in previous nutrient budgets in the area and has therefore not been considered as a potential threat of contaminants (e.g., sewage effluent) to the ecosystem. It is hoped that one of the main outcomes of this research will be the development of an approach which integrates geochemical and hydrogeological techniques for assessing directions and rates of subsurface flow and, specifically, how to quantify the flow into surface waters.

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Considerations for Calculating the Mass Loading of Metal Contaminants to a Marine Embayment: ASARCO Superfund Site, Tacoma, WA

By Gayle Garman and ASARCO Sediments/Groundwater Task Force

INTRODUCTION

The Asarco Superfund Site is located along the southern shore of Commencement Bay, an industrialized marine embayment in southeastern Puget Sound, approximately 30 miles south of Seattle, WA. The first industries on the site were sawmills that deposited woodwaste along the shoreline. A lead smelter that began operations in 1890, was purchased by Asarco in 1905 to process copper ore from other locations. By-products of copper smelting were further refined to produce additional products, including arsenic, sulfuric acid, liquid sulfur dioxide, and slag. Smelter operations ended in 1985 (Hydrometrics, 1996).

Arsenic, cadmium, copper, lead, zinc, and other trace elements were released into soil, air, and surface water as a result of the smelting and refining operations. There are six upland source areas where the highest measured concentrations of contaminants in soils are found: The Stack Hill area, Cooling Pond area, Arsenic Kitchen area, Copper Refinery area, the Fine Ore Bins building, and the Southeast Plant/DMA area where sulfuric acid spills were frequent. Metals from soil releases and from slag have migrated to groundwater at the Site (Hydrometrics, 1996).

Many of the smelter buildings and structures are on slag fill. In addition, Asarco extended the existing shoreline by pouring molten slag into Commencement Bay. The upland area consists of both gradual and steep slopes extending down to the slag filled shoreline, where slag bluffs extend as much as 30 ft above the natural sandy substrate. These slag bluffs are very porous, and are subject to twice daily tides that fluctuate up to 12 ft. vertical (Cross-Section D-D’).

The adjacent 23-acre Breakwater Peninsula is composed of massive and granulated slag that were placed into Commencement Bay between 1917 and 1970. An estimated 15 million tons of slag exist at the smelter property and slag peninsula (Hydrometrics, 1996).

SEDIMENTS/GROUNDWATER EVALUATION

Sediments as far as 1,000 ft from shore exhibit toxicity in bioassays, and are being evaluated for remedial action. The preferred alternative is to place a clean sand cap over the contaminated sediment to prohibit slag contact with marine organisms (Parametrix 1996). Reviewers of the proposed remedial action asked whether metal contaminants in site groundwater would recontaminate the clean cap. The Asarco Sediments Groundwater Task Force (ASGTF) was organized to evaluate this question.

Upland geological cross-sections were extended to the shoreline based on boring logs for nearshore monitoring wells and offshore cores. These cross-sections indicated that the slag formation did not discharge through sediment to the Bay, but rather, discharged directly to the Bay surface water. In order to assess the influence of the tides on the hydrologic parameters of the site, 15 slag wells were monitored over four complete tidal cycles in January 1998 and a multi-well pump-test was conducted at new slag well MW-206. This new data was combined with slug-test data from the upland Remedial Investigation. The distribution of hydraulic conductivities suggested the slag was characterized by four corridors, indicated as A, B, C and D on the Figures. Later, corridor A was subdivided into corridors A1 and A2 (Figure 1). Discharge rates were calculated for the slag aquifer and the underlying marine sand aquifer in each corridor by using site data and Darcy's law (ASGTF Group 1, 1998):

$$Q = Kibw$$

Where:

Q = groundwater discharge rate (ft3/day)
K = hydraulic conductivity (ft/day)
i = hydraulic gradient (ft/ft)
b = aquifer thickness at the shoreline (ft)
w = width of groundwater flow path (ft)

APPROACH TO CONTAMINANT FLUX ESTIMATION

The ASGTF recognized that Darcy's law "provides an estimate of the net groundwater flow discharging from the site to Commencement Bay." This net groundwater flow originates as recharge in upgradient water-bearing zones, as infiltration of surface water run-on, and as precipitation onto the slag. While the twice daily tides, with ranges to 12 vertical feet, are known to cause recurrent inflow and outflow of seawater in nearshore areas of both the slag and marine sand aquifers, it is assumed that the net tidal flow is zero (ASGTF, Group 1 Memo).

The mass flux of a contaminant is calculated by multiplying the groundwater discharge rate by the contaminant concentration. However, when (fresh) groundwater mixes with seawater, there are changes in geochemistry that alter the solubility, and consequently the mobility, of the metal contaminants of concern at this site.

Arsenic (As) is the primary contaminant of concern in upland areas of the site. Dissolved arsenic concentrations to 30 mg/ℓ have been measured in groundwater near the Fine Ore Bins. The chronic marine AWQC (Ambient Water Quality Criterion) for arsenic is 0.036 mg/ℓ.

DATA AND FIGURES [1]

Data are collected at site monitoring wells each Spring and Fall. The ASGTF used data from March 1994 through September 1998, thus, the Figures show the mean of ten measurements for each parameter. The Figures are taken directly from the ASGTF Group 4 Technical Memorandum, (December 1998) and consequently, are not numbered sequentially in this presentation. The contaminant isopleths were drawn by hand.

ARSENIC ATTENUATION

Figure 10 shows the intrusion of seawater (chloride) for hundreds of feet into the slag formation along the shoreline. Chloride in upland groundwater is negligible. The landward intrusion of seawater into the slag is least in corridor D and greatest in corridor A1. The chloride concentrations in both deep and shallow wells on the breakwater peninsula approximate the chloride concentrations in Commencement Bay surface water.

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[1] Editor's note: Figures follow the text. Figures are not consecutively numbered.

Figure 2 shows that the arsenic concentration is an order of magnitude greater in the deeper breakwater wells (B) than in the shallow breakwater wells (A). The breakwater peninsula is composed entirely of smelter slag. The ASGTF concluded that the lower oxygen exchange capacity for water deep within the breakwater peninsula, and the associated lowered redox condition, increase the solubility of slag arsenic.

Figure 11 shows that dissolved oxygen, in general, diminishes in proportion to distance from the shoreline and more rapidly in the less permeable corridors, e.g., Corridor D. However, it is difficult to get accurate field measurements of dissolved oxygen, so the distribution of manganese, which rapidly precipitates in the presence of dissolved oxygen, also was evaluated.

Figure 6 shows the distribution of dissolved manganese which corroborates the mechanism of arsenic precipitation, described below. Manganese concentrations decline by an order of magnitude as site groundwater approaches the shoreline and mixes with oxygen-rich seawater that has intruded into shoreline slag.

In upland areas of the site (not the slag peninsula, which is entirely slag), the greatest groundwater flow occurs in the slag formation, which is above the natural geologic formations. The slag, in turn, is topped by a thin layer of filled soil. Upland groundwater has low oxygen content relative to seawater, so the geochemistry of the upland groundwater is reducing in comparison to the water of Commencement Bay. At the shoreline, the tides of Commencement Bay enter the porous seaward face of the slag formation, forcing seawater into the slag. Thus, as the upland reduced groundwater migrates toward the shoreline, it gains oxygen by mixing with tidal seawater within the slag. The solubility of the arsenic then decreases, and most of the dissolved arsenic is precipitated as secondary minerals in the slag and does not discharge to Commencement Bay. The presence of secondary arsenic minerals has been confirmed by a mineralogic study of material recovered when MW-206 was installed (US EPA, 1998). Thus, the changing redox condition of the groundwater explains the attenuation of the primary contaminant of concern, arsenic. However, understanding the mechanism that controls arsenic solubility does not answer the question of how to calculate the mass flux of arsenic to the Bay (ASTGF 1998, Group 4).

RELEASE OF COPPER

Figure 3 shows an area in Corridor D where the average dissolved copper concentration in groundwater is greater than in any other nearshore area. Unlike arsenic, copper is generally more soluble when there is more dissolved oxygen. However, the shallow (A) wells on the Breakwater Peninsula, where oxygen is available from seawater and atmospheric exchange, do not have copper concentrations as great as the wells in Corridor D. The ASGTF concluded there must be another geochemical parameter causing copper to dissolve from slag in corridor D (ASGTF 1998, Group 4).

Figure 14 shows that acidity may be controlling copper concentrations in Corridor D. Acidity is measured in logarithmic pH units. The pH of Commencement Bay water is about 8.0. Wells in the southeast plant/DMA area have average pH values less than 6.0, indicating acid concentrations two orders of magnitude greater than Commencement Bay. The southeast plant/DMA area is the location of previous liquid sulfur dioxide and sulfuric acid manufacture. Materials remaining at this location apparently continue to acidify the groundwater, releasing copper from the slag matrix. Even the intrusion of seawater does not overcome this effect, as the Corridor D well nearest the shoreline has an average dissolved copper concentration of 3.6 mg/ℓ, more than an order of magnitude greater than any other shoreline well. By comparison, the copper acute marine AWQC is 0.0029 mg/ℓ (a chronic copper marine AWQC has not been adopted).

Figure 13 shows the distribution of dissolved iron in shoreline wells, which helps corroborate the mechanism of copper solubility. Like copper, iron is more soluble in a low pH (acid) environment (e.g., landfill leachate). Higher concentrations of iron are found in the Southeast Plant/DMA source area where pH was low and copper was high. Thus, both copper and iron exhibit increased solubility here because of the lower pH (higher acidity). However, unlike copper, the average dissolved iron concentrations are quite similar in all the wells closest to the shoreline (ASGTF 1998, Group 4). This suggests that when the dissolved copper and iron in acidified groundwater in corridor D encounter intruding seawater within the shoreline slag, that the reaction of iron with the oxygen and alkalinity of the seawater forming an iron precipitate is more rapid than the similar reaction of copper.

CONCLUSIONS

The wells closest to the shoreline have mean dissolved copper concentrations at least three orders of magnitude greater than the marine acute/chronic AWQC of 0.0029 mg/ℓ. The greatest volume of groundwater discharges through the fractured slag into the marine water column rather than through contaminated subtidal sediment. Thus, the groundwater process that is having the greatest effect on marine biota is probably copper discharge to water, not arsenic discharge to sediment.

Mass loading of contaminants in general is a simple calculation that multiplies the average contaminant concentration by the corresponding average water (volume) discharge rate. This calculation is valid as long as the contaminant concentration is the concentration in the volume of water that is discharged. The calculation of contaminant mass loading rates to Commencement Bay is complicated by the geochemical changes that occur in the shoreline slag as the fresh groundwater mixes with marine surface water, altering the solubility of the metal contaminants; and by the difficulty in determining the corresponding volume (discharge rate) of water, which is influenced at the shoreline by the twice daily tidal flux. Wells nearest the shoreline, where contaminant concentrations are most representative of discharges to the Bay, are affected by the influx and efflux of tidal water, i.e., the volume of discharging water characterized by the contaminant concentration measured in the shoreline wells, is likely greater than the *net* groundwater flux from the site.

The ASGTF has not yet found a satisfactory method for resolving this problem.

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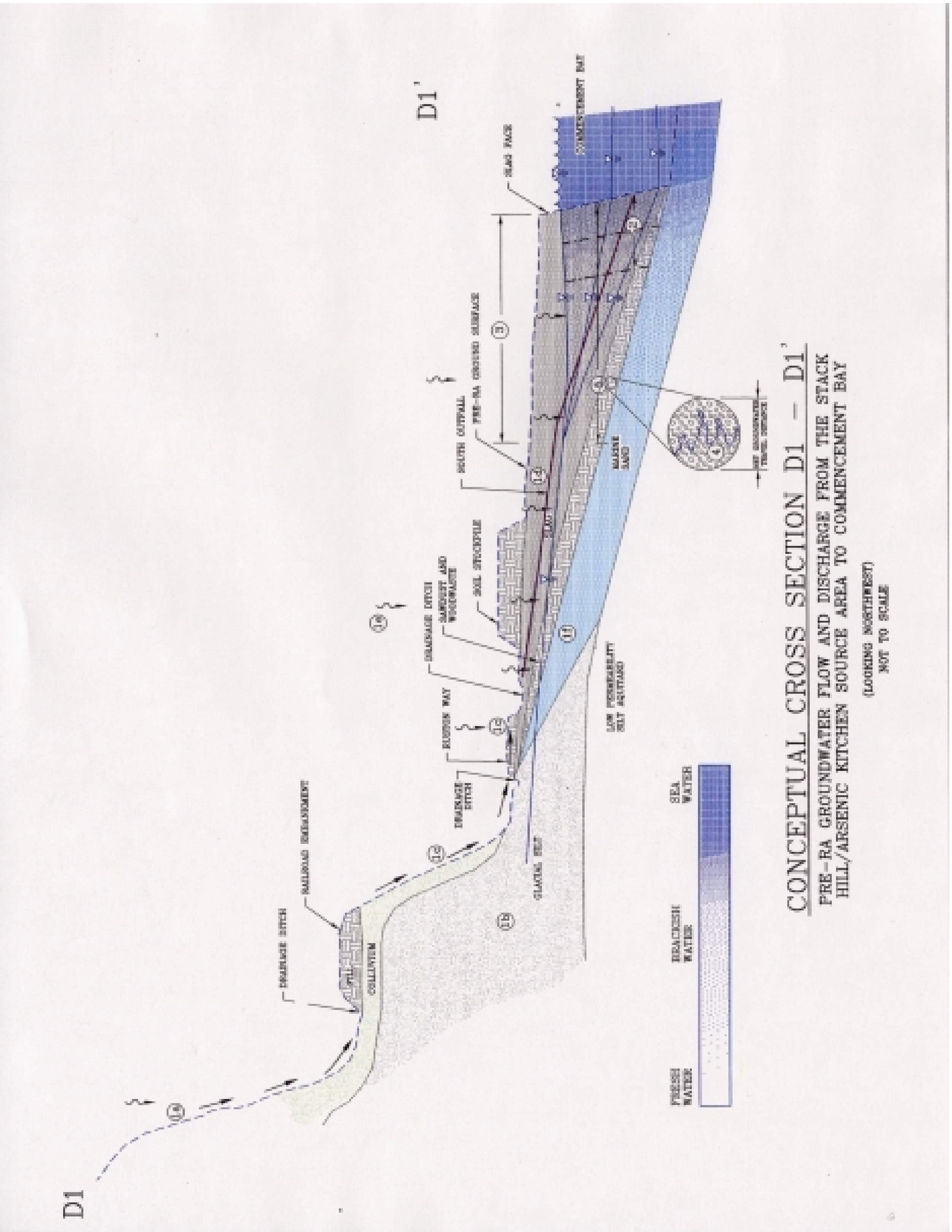

Conceptual Cross-Section D1 – D1'

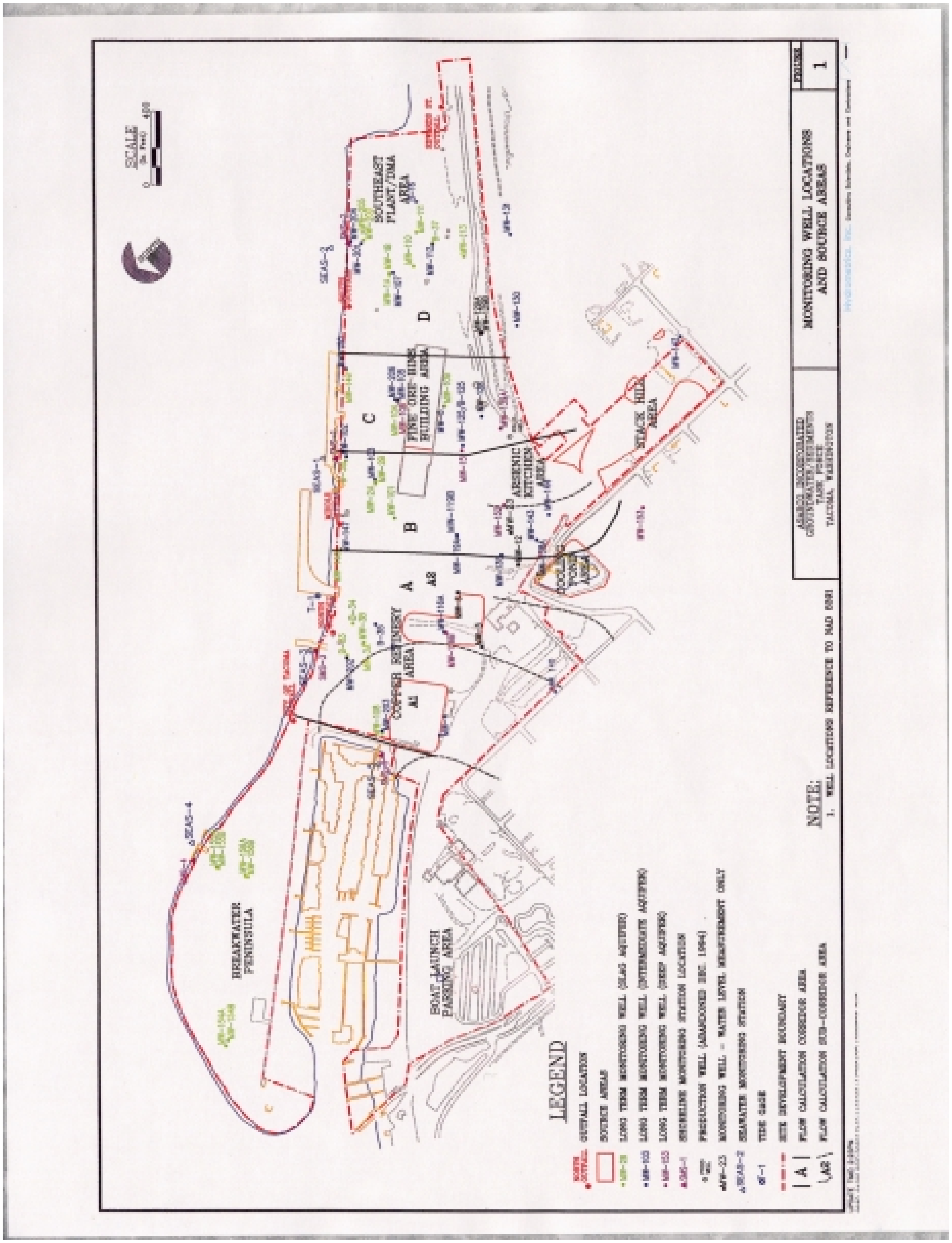
LEGEND
OUTFALL LOCATION
SOURCE AREAS
LONG TERM MONITORING WELL (SLAG AQUIFER)
LONG TERM MONITORING WELL (INTERMEDIATE AQUIFER)
LONG TERM MONITORING WELL (DEEP AQUIFER)
SHORELINE MONITORING STATION LOCATION
PRODUCTION WELL (ABANDONED DEC. 1994)
MONITORING WELL - WATER LEVEL MEASUREMENT ONLY
SEAWATER MONITORING STATION
TIDE GAGE
SITE DEVELOPMENT BOUNDARY
FLOW CALCULATION CORRIDOR AREA
FLOW CALCULATION SUB-CORRIDOR AREA
BREAKWATER PENINSULA
BOAT LAUNCH PARKING AREA
COPPER REFINERY AREA
FINE ORE BIN BUILDING AREA
ARSENIC KITCHEN AREA
STACK HILL AREA
SOUTHEAST PLANT/DMA AREA
A
B
C
D
SCALE (in feet)
0
400
NOTE:
1. WELL LOCATIONS REFERENCE TO NAD 83/91
ASARCO INCORPORATED
TACOMA, WASHINGTON
MONITORING WELL LOCATIONS AND SOURCE AREAS
FIGURE
1

Figure 1

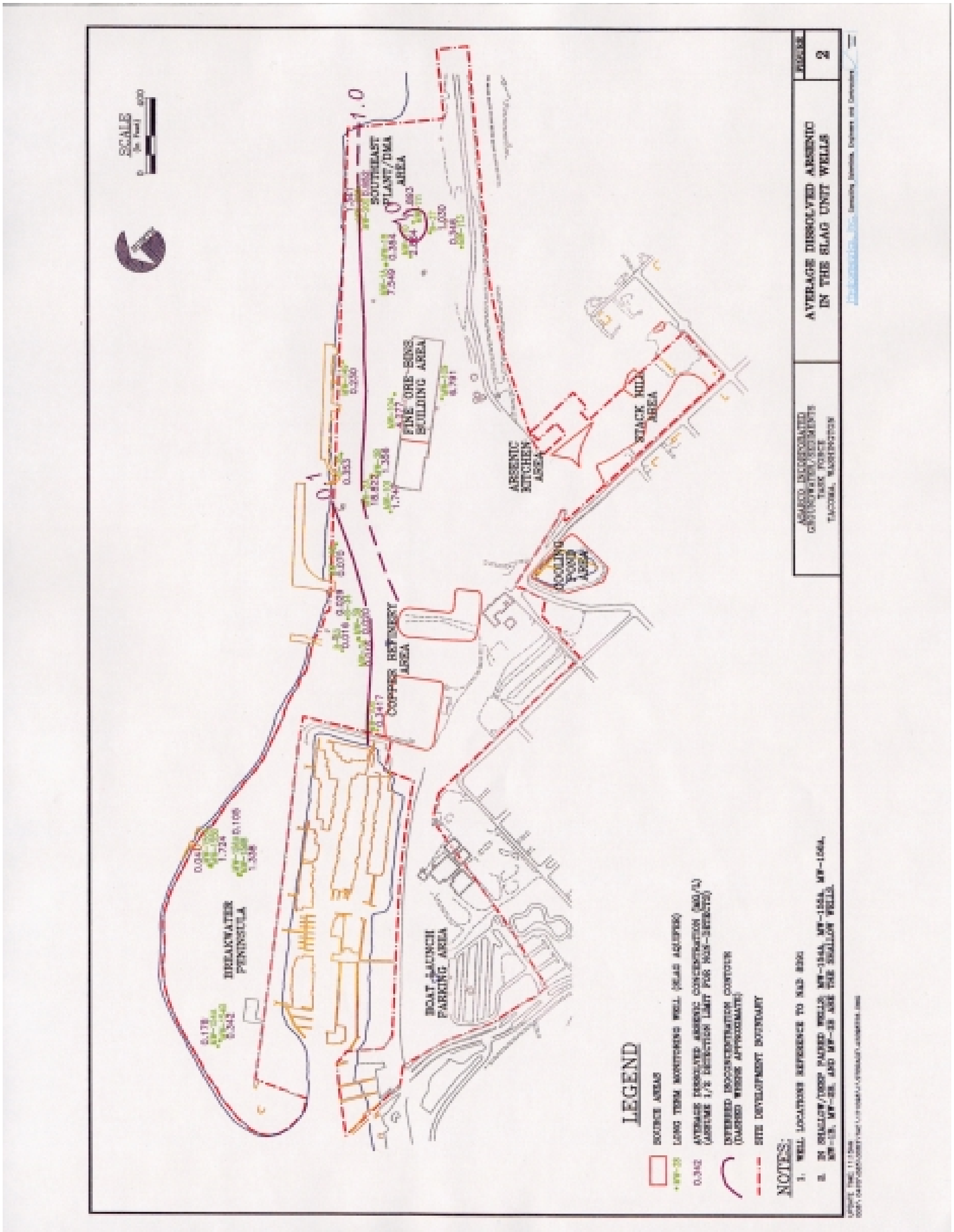
SCALE
(in Feet)
BREAKWATER PENINSULA
BOAT LAUNCH PARKING AREA
COPPER REFINERY AREA
FINE ORE BINS BUILDING AREA
ARSENIC KITCHEN AREA
STACK HILL AREA
COOLING POND AREA
SOUTHEAST PLANT/DMA AREA
LEGEND
NOTES:
AVERAGE DISSOLVED ARSENIC IN THE SLAG UNIT WELLS
FIGURE
2

Figure 2


AVERAGE DISSOLVED COPPER IN THE SLAG UNIT WELLS
FIGURE
3
SCALE
LEGEND
NOTES:
BREAKWATER PENINSULA
BOAT LAUNCH PARKING AREA
COPPER REFINERY AREA
FINE ORE BINS BUILDING AREA
SOUTHEAST PLANT/DMA AREA
ARSENIC KITCHEN AREA
STACK HILL AREA
COOLING POND AREA

Figure 3


SCALE
BREAKWATER PENINSULA
BOAT LAUNCH PARKING AREA
COPPER REFINERY AREA
FINE ORE BINS BUILDING AREA
SOUTHEAST PLANT/DMA AREA
ARSENIC KITCHEN AREA
STACK HILL AREA
COOLING POND AREA
1.0
LEGEND
SOURCE AREAS
NOTES:
ASARCO INCORPORATED
TACOMA, WASHINGTON
AVERAGE DISSOLVED MANGANESE IN THE SLAG UNIT WELLS
FIGURE
6

Figure 6

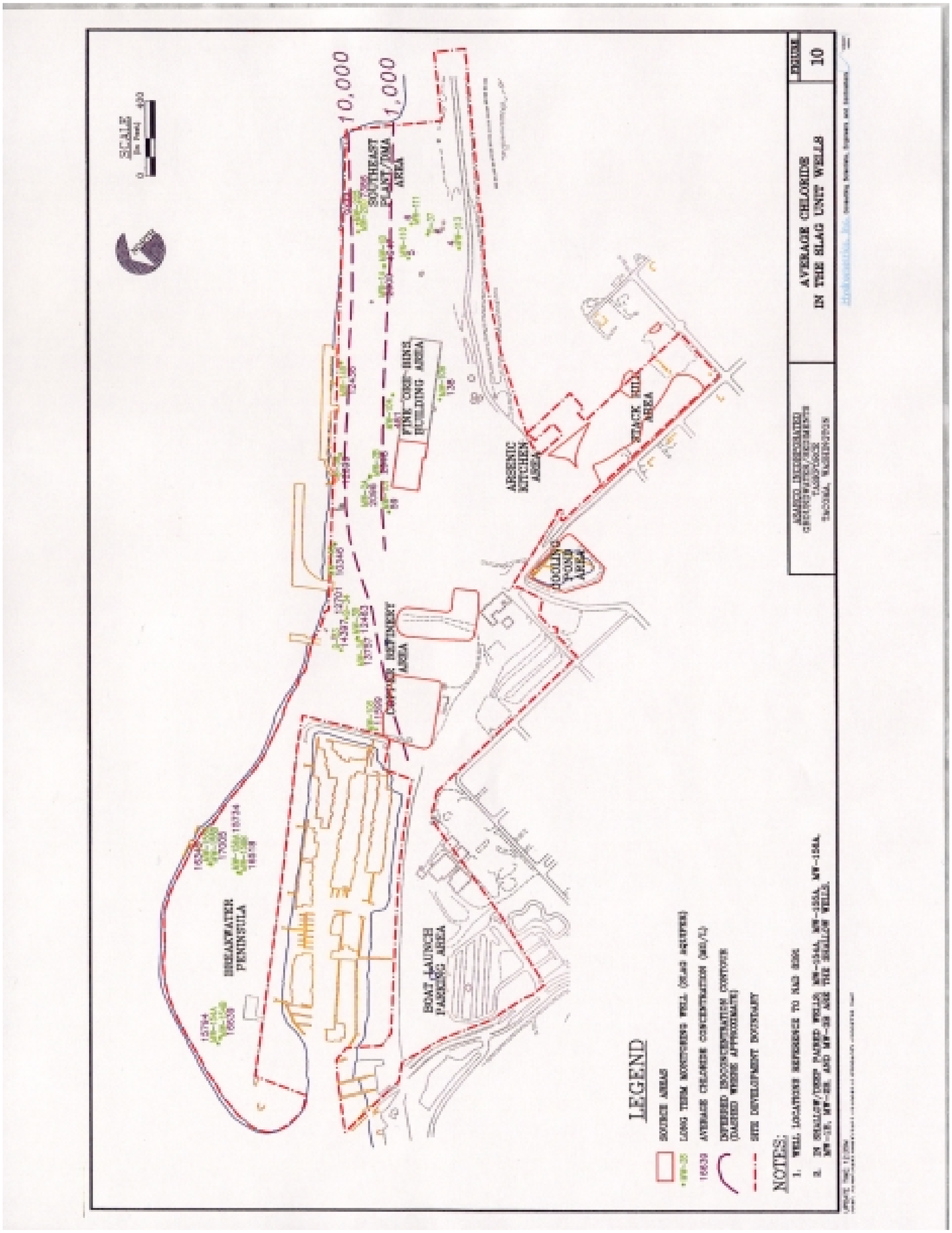
SCALE
10,000
1,000
SOUTHEAST PLANT/DMA AREA
FINE "ORE" BINS BUILDING AREA
ARSENIC KITCHEN AREA
STACK HILL AREA
COOLING POND AREA
COPPER REFINERY AREA
BREAKWATER PENINSULA
BOAT LAUNCH PARKING AREA
LEGEND
SOURCE AREAS
LONG TERM MONITORING WELL (SLAG AQUIFER)
AVERAGE CHLORIDE CONCENTRATION (mg/L)
INFERRED ISOCONCENTRATION CONTOUR (DASHED WHERE APPROXIMATE)
SITE DEVELOPMENT BOUNDARY
NOTES:
AVERAGE CHLORIDE IN THE SLAG UNIT WELLS
TACOMA, WASHINGTON
FIGURE
10

Figure 10

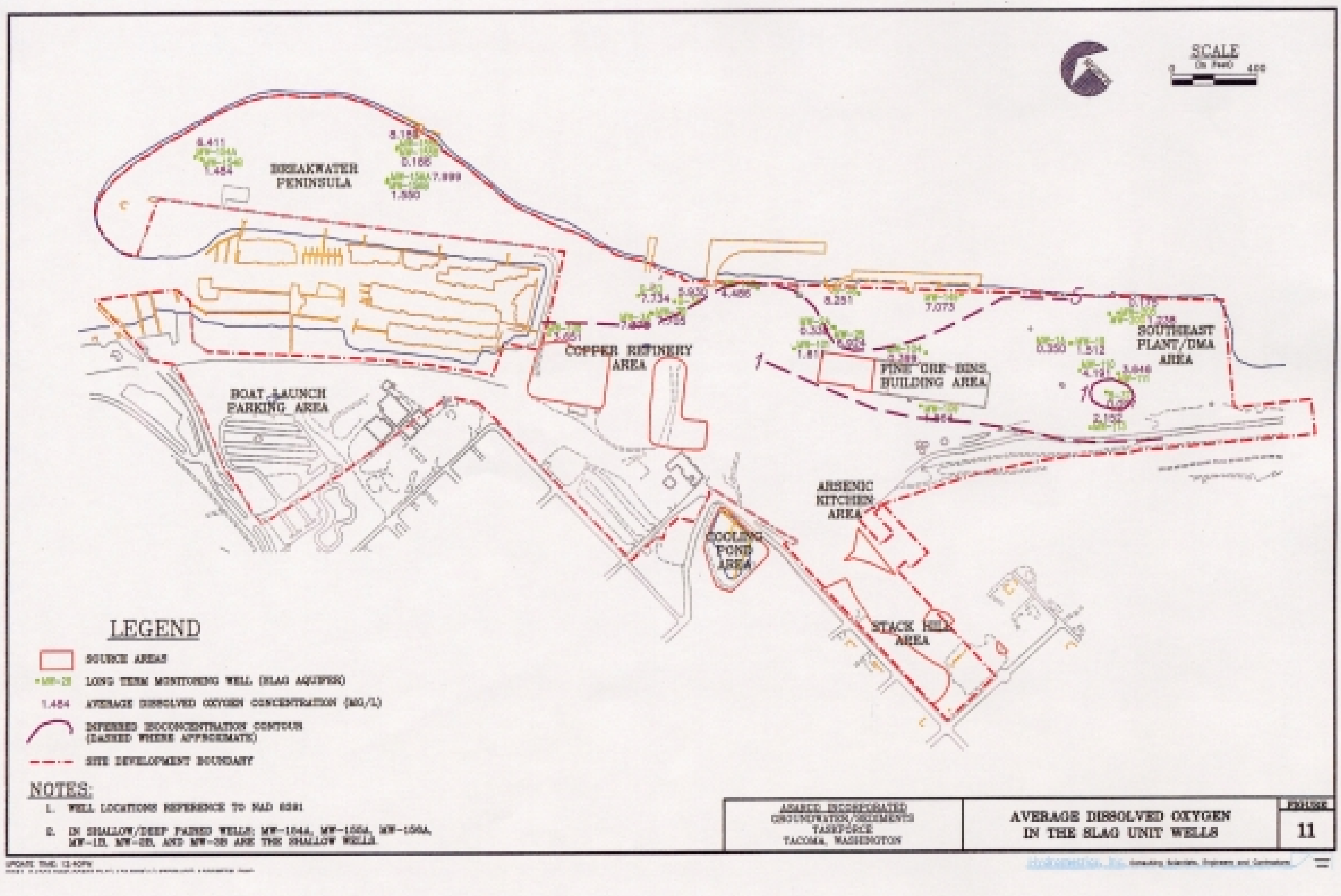
SCALE
(In Feet)
0
400
BREAKWATER PENINSULA
8.411
1.454
0.188
7.899
1.550
COPPER REFINERY AREA
7.734
5.930
4.488
8.251
7.075
FINE ORE BINS BUILDING AREA
SOUTHEAST PLANT/DMA AREA
BOAT LAUNCH PARKING AREA
ARSENIC KITCHEN AREA
COOLING POND AREA
STACK HILL AREA
LEGEND
SOURCE AREAS
MW-28 LONG TERM MONITORING WELL (SLAG AQUIFER)
1.454 AVERAGE DISSOLVED OXYGEN CONCENTRATION (MG/L)
INFERRED ISOCONCENTRATION CONTOUR (DASHED WHERE APPROXIMATE)
SITE DEVELOPMENT BOUNDARY
NOTES:
1. WELL LOCATIONS REFERENCE TO NAD 83/91
2. IN SHALLOW/DEEP PAIRED WELLS: MW-104A, MW-105A, MW-106A, MW-1D, MW-2B, AND MW-3B ARE THE SHALLOW WELLS.
ASARCO INCORPORATED
GROUNDWATER/SEDIMENTS TASKFORCE
TACOMA, WASHINGTON
AVERAGE DISSOLVED OXYGEN IN THE SLAG UNIT WELLS
FIGURE
11
Hydrometrics, Inc. Consulting Scientists, Engineers and Contractors

Figure 11


LEGEND
SOURCE AREAS
LONG TERM MONITORING WELL (SLAG AQUIFER)
AVERAGE DISSOLVED IRON CONCENTRATION (MG/L)
SITE DEVELOPMENT BOUNDARY
NOTES:
1. WELL LOCATIONS REFERENCE TO NAD 83
SCALE
BREAKWATER PENINSULA
BOAT LAUNCH PARKING AREA
COPPER REFINERY AREA
FINE ORE BINS BUILDING AREA
SOUTHEAST PLANT/DMA AREA
ARSENIC KITCHEN AREA
STACK HILL AREA
COOLING POND AREA
1.0
10
ASARCO INCORPORATED
TACOMA, WASHINGTON
AVERAGE DISSOLVED IRON IN THE SLAG UNIT WELLS
FIGURE
13

Figure 13


SCALE
(In Feet)
0
400
SOUTHEAST PLANT/IMA AREA
FINE ORE BINS BUILDING AREA
COPPER REFINERY AREA
ARSENIC KITCHEN AREA
STACK HILL AREA
COOLING POND AREA
BREAKWATER PENINSULA
BOAT LAUNCH PARKING AREA
7.417
7.594
7.887
7.713
7.974
8.738
8.863
8.714
LEGEND
SOURCE AREAS
LONG TERM MONITORING WELL (SLAG AQUIFER)
AVERAGE FIELD pH (STANDARD UNITS)
INFERRED DECONCENTRATION CONTOUR (DASHED WHERE APPROXIMATE)
SITE DEVELOPMENT BOUNDARY
NOTES:
ASARCO INCORPORATED
TACOMA, WASHINGTON
AVERAGE pH (FIELD) IN THE SLAG UNIT WELLS
FIGURE
14

Figure 14

The Interaction of Ground Water and Surface Water within Fall Chinook Salmon Spawning Areas in the Hanford Reach of the Columbia River

By David R. Geist

INTRODUCTION

The Hanford Reach is the last unimpounded section of the mainstem Columbia River in the United States and supports a large run of fall chinook salmon (*Oncorhynchus tshawytscha*) that returns there annually to spawn (Dauble and Watson 1997). Previous studies have shown that adult salmon repeatedly spawn in definite locations within the Reach (Geist 1999; Geist and Dauble 1998; Dauble and Watson 1997), but the physical characteristics associated with these areas are variable and poorly understood. More information on the spawning habitat characteristics of fall chinook salmon that utilize large rivers is needed to recover stocks listed on the Endangered Species Act.

The association between fall chinook salmon spawning and physical habitat characteristics was previously examined in the Hanford Reach at Locke Island and Wooded Island (Geist 1999). Although the physical habitat characteristics, e.g., depth, substrate, and water velocity, at the two sites were similar, only the Locke Island site had extensive salmon spawning. Additional measurements were taken to determine if the interaction of ground water and surface water within the hyporheic zone could explain this discrepancy in habitat use between the two sites. Hyporheic discharge was assumed to affect spawning site selection by providing cues (chemical, temperature, and physical) for pre-spawning adults to locate spawning reaches (usually 2 to 5 km in length). Once these reaches were “discovered,” hyporheic discharge was assumed to correlate with the distribution of redd clusters (500 to 800 m in length, 120 m in width; Geist 1999) within these river reaches

METHODS

During the fall chinook salmon spawning seasons (October and November; Dauble and Watson 1997) from 1995 to 1997, mini-piezometers (Lee and Cherry 1979) and internal-drive-rod piezometers (Geist, et al. 1998) were installed within the two sites. Piezometers were installed within the river channel in groups of three or four, and hyporheic water within the piezometers was sampled 2 to 7 times each year for specific conductance (µS/cm at 25°C), water temperature (T, °C), dissolved oxygen (DO, mg/ℓ), and hydraulic head (h, cm). These same parameters were also measured on a contiguous river sample.

It was assumed that water discharging from the hyporheic zone into the river was a combination of ground water and surface water. Specific conductance was the primary measure used to differentiate undiluted ground water from surface water; specific conductance of undiluted ground water adjacent to the Hanford Reach averages 300-400 µS/cm while the river water averages ~150 µS/cm. The differences in temperature (T) and hydraulic head (h) were based on the piezometer reading (hyporheic water) minus the reading from its paired river sample. Differences in hydraulic head between the river and hyporheic waters were used to calculate a vertical hydraulic gradient (VHG) between the two

(VHG = h/depth of piezometer). Slug tests were used to estimate the volume of hyporheic discharge from the sediments into the river channel.

RESULTS AND DISCUSSION

The results showed that fall chinook salmon spawning locations were highly correlated with hyporheic discharge that was composed of mostly river water and not undiluted ground water. Hyporheic water that discharged into fall chinook salmon spawning locations was consistently greater in magnitude, and had higher dissolved oxygen and lower specific conductance than discharge into non-spawning locations. However, there was no significant difference in temperature between hyporheic and river water. These results were true when comparisons were performed between Locke Island (spawning site) and Wooded Island (non-spawning site) (Figure 1), and also true when spawning and non-spawning clusters within the Locke Island site were evaluated (Figure 2).

Slug tests showed that substrate permeability decreased with increasing distance below the river bed at Wooded Island but did not change over the depths monitored at Locke Island (Figure 3). This suggested the mixing zone where river water penetrated into the river bed was greater within the spawning site than within the non-spawning site. Specific discharge calculations gave an average flux out of the sediments on the order of 9.0 x 10^{-4} cm/s at Locke Island and 3.0 x 10^{-4} cm/s at Wooded Island. Thus, specific discharge of hyporheic waters was approximately 3 times larger at Locke Island than Wooded Island.

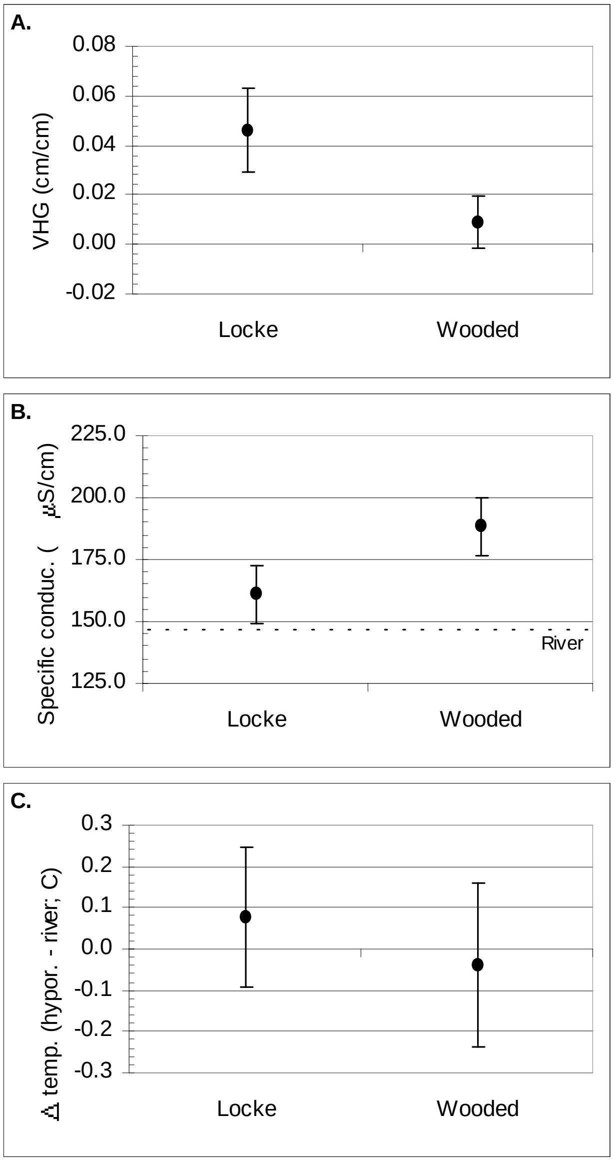

Figure 1. Physiochemical data collected from piezometers installed and monitored at the Locke Island and Wooded Island study sites during October and November, 1995. Bars above and below the points represent the 95% confidence interval of the mean. (A) Vertical hydraulic gradient (VHG) between hyporheic and surface waters where positive values indicated potential upwelling and negative values downwelling, (B) specific conductance of hyporheic and surface waters, and (C) differences in water temperatures of hyporheic and surface waters.

River water was presumed to have entered highly permeable riverbed substrate at locations upstream of spawning areas. Geomorphic bed features (i.e., islands, gravel bars, riffles) of alluvial rivers are able to create hydraulic gradients sufficient to direct surface water into the bed (Stanford, et al. 1996; Brunke and Gonser 1997). River water is able to penetrate deeper into hyporheic habitats if the riverbed is composed of alluvium that is highly permeable (Vaux 1962, 1968; White 1993). The more permeable the alluvium, the more that the physiochemical characteristics of the hyporheic waters will resemble surface water rather than ground water. In contrast, the relative proportion of phreatic ground water in hyporheic waters will be greater if the riverbed sediments are of low hydraulic permeability because

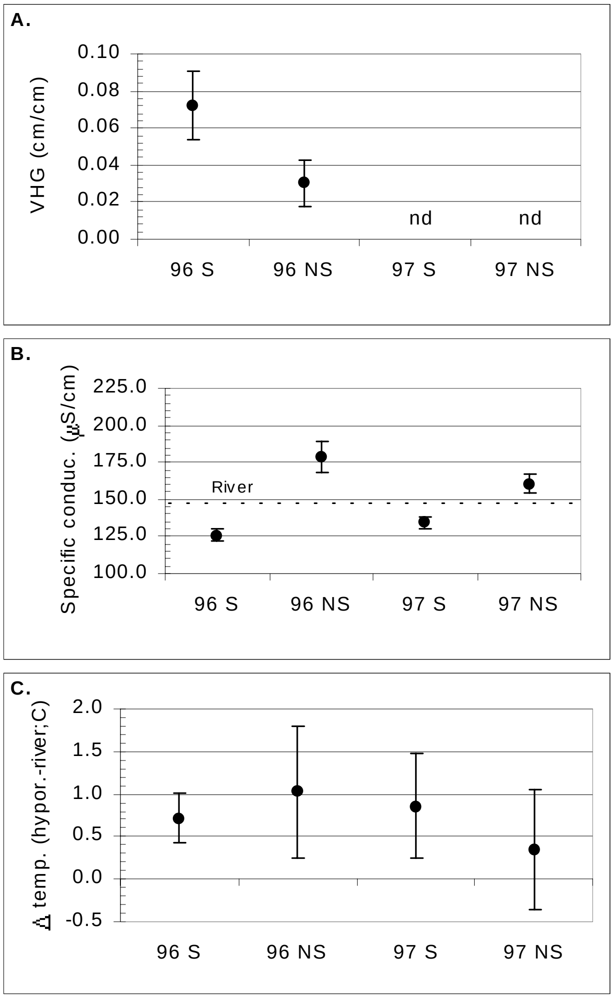

Figure 2. Physiochemical data collected from piezometers installed and monitored within the Locke Island site at spawning (S) and non-spawning (NS) sites during October and November, 1996 and 1997. Bars above and below the points represent the 95% confidence interval of the mean. ND = no data.

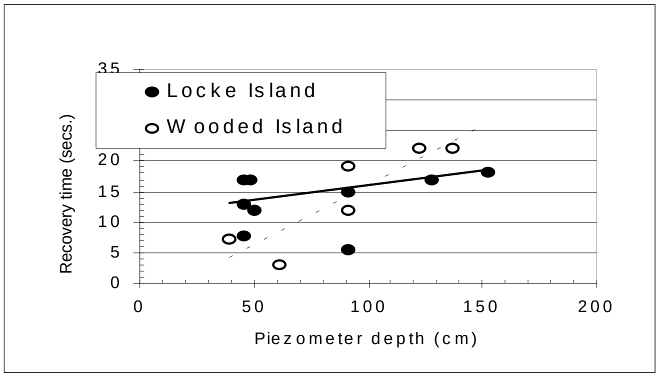

Figure 3. Recovery time to 37% of the initial hydraulic head following a slug-test within piezometers installed at Locke Island and Wooded Island. The trend line at the Wooded Island site (dashed line) was significant (P = 0.02, r^2=0.78) but not significant at Locke Island (P = 0.42, r^2= 0.08).

river water will not be able to readily enter the substrate and dilute the ground water (White 1993; Brunke and Gonser 1997). I concluded river water that became entrained into the "hyporheic corridor" had a strong influence on vertical hydraulic gradients and influenced the use of salmon spawning habitat. Knowledge of the three-dimensional connectivity between rivers and ground water within the hyporheic zone can be used to improve the definition of fall chinook salmon spawning habitat.

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Integrated Acoustic Mapping of Surface Waters: Implications for Ground-Water/Surface-Water Linkages

By Chad P. Gubala, Ullrich Krull, Joseph M. Eilers, Mike Montoya, and Jeff Condiotty

The study of aquatic systems has historically been approached in a traditional scientific manner. "Representative" sections or components of lakes and rivers have been examined intensively through a combination of laborious sampling methods. Broader assessments of specific aquatic ecosystems have then been statistically constructed through the assembly of discrete study elements. Changes in aquatic ecosystems have then been documented by repeating a similar regimen of sampling at varying time intervals. Aquatic ecosystem analyses and risk-based management plans have been developed on the basis of discreet and/or empirical numeric models of aquatic ecosystems, deriving from the original field investigations.

The efficacy of aquatic assessments and/or risk-based management plans depends upon the completeness and accuracy of the original data collection and analysis scheme. In order to assemble an accurate model of an entire aquatic ecosystem, data must be collected in a manner that minimizes the major components of uncertainty: measurement, spatial and temporal. Most researchers have been able to adequately minimize measurement error throughout intensive, small-scale research studies or monitoring exercises. However, precise and accurate measurements distributed over a small section of a large domain frequently lead to inaccurate conclusions. This phenomenon derives from the uncertainty of interpolating the conditions of an unknown domain, such as a river reach or lake region, through interpolation or extrapolation from a limited data-base.

A need exists to develop better monitoring techniques for the dynamic management of aquatic ecosystems. Combinations of current and emerging technologies, drawn from a variety of application areas may provide for faster, more cost-effective means of acquiring aquatic systems data and information. Linking mobile sensors such as hydroacoustic arrays with Global Positioning System (GPS) navigation have already yielded effective methods for rapidly delineating the bathymetric, morphometric and hydrologic features of lakes and rivers. Expansion of the role of acoustics has also permitted the spatial analysis of aquatic biological communities within complex spatial domains. The coupling of standard aquatic sensor arrays, such as temperature, conductivity or velocity probes, with GPS will provide multiple parameters for a system in a cost-effective manner. Integration of advanced sensor probes, such as real-time DNA detectors for identification of aquatic microorganisms will also greatly enhance the ability to detect and manage change in aquatic ecosystems.

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Mike Montoya, Ute Tribal Nation, Jeff Condiotty, Simrad, Inc.

Delineation of VOC-Contaminated Groundwater Discharge Zone, St. Joseph River, Elkhart, Indiana

By John H. Guswa, Jonathan R. Bridge, and Michael J. Jordan

A hydrogeologic study was conducted to locate and delineate the portion of the St. Joseph river within which VOC contaminated groundwater observed in monitoring wells in the study area was discharging. The principal groundwater contaminants are trichloroethene (TCE) and carbon tetrachloride (CCl_4). Water samples were collected at a depth of approximately two to five feet below the river bed using a GeoProbe® from a pontoon boat. The samples were analyzed for the purpose of delineating VOC concentrations in groundwater directly beneath the river bed. The results of this hydrogeologic study were used to select sampling locations for a benthic macroinvertebrate investigation to determine if there were any ecological effects resulting from the discharge of VOC-contaminated groundwater to the river.

Groundwater and surface water samples were initially collected from selected wells and sampling stations on the river and analyzed for the inorganic analytes listed in Table 1. The purpose of this sampling was to identify whether there were inorganic analytes that could be used as “tracers” to ensure that the samples collected from beneath the river bed were groundwater samples and not induced river water. The concentrations of none of the inorganic analytes proved to be consistently different between the surface water samples and the groundwater samples. Therefore this group of inorganic analytes could not be used as “tracers.” Other field measured parameters, in particular pH, temperature and specific conductance were more useful in this regard, and were used for that purpose. The pH of the river water was approximately one pH unit higher than the groundwater. The river water temperature was approximately 8°C higher than the groundwater temperature and the specific conductance of the groundwater was generally higher than the river water.

Table 1. Results of preliminary inorganic analyses, in mg/ℓ.

Sampling Location	CATIONS				ANIONS		
	calcium	magnesium	sodium	potassium	bicarbonate	carbonate	sulfate
Groundwater							
MW-7S	94.3	25.6	7.7	ND*	280	ND	28.7
MW-7D	89.9	24.3	31.7	ND	230	ND	41.2
MW-8S	76.8	18.6	22.2	ND	230	ND	20.3
MW-8D	81.0	19.9	31.4	ND	230	ND	26.3
MW-9	75.9	19.5	ND	ND	210	ND	10.9
MW-10S	82.8	20.1	14.5	ND	230	ND	28.6
Surface Water							
SW-01	83.0	23.4	15.8	ND	180	ND	2.7
SW-02	81.1	22.8	13.7	ND	220	ND	43.5
SW-03	66.5	22.7	21.1	ND	210	ND	27.0

*ND= Not Detected

Groundwater samples were collected from beneath the river bed at 73 locations located along 19 transects. The initial sampling locations were based on evaluation of water quality data from upgradient monitoring wells and evaluation of groundwater flow direction. Subsequent transect and sampling locations were selected by reviewing daily analytical results received from an on-site field laboratory. The water samples were collected by driving a GeoProbe®, from a pontoon boat, approximately two to five feet below the bed of the river. The one foot long GeoProbe® screen was then exposed, and water was pumped to the surface using a peristaltic pump. The GeoProbe® was fitted with a thermocouple to permit in-situ measurement of groundwater temperature. A schematic of the GeoProbe® sampling device is shown on Figure 1. At some locations the GeoProbe® screen became clogged with fine sediment from the river bed. When this happened the screen was flushed with deionized water to clear the screen. The sampling then proceeded using a low-flow sampling protocol.

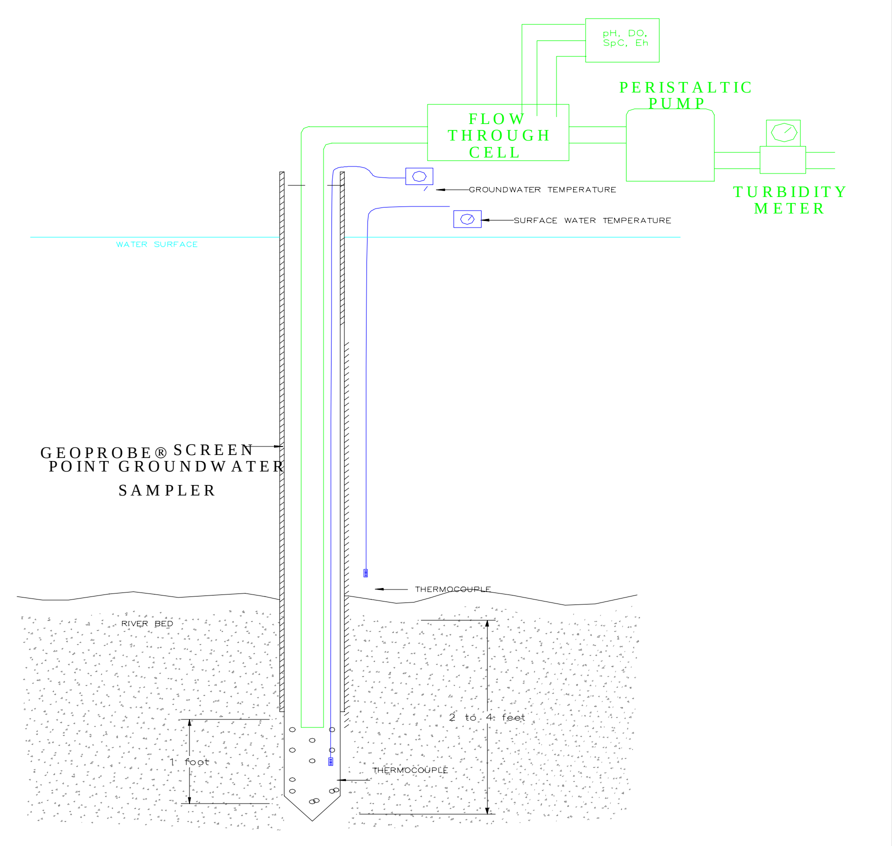

Figure 1. Schematic of sub-riverbed sampling equipment

During pumping, the water quality parameters pH, Eh, specific conductance, dissolved oxygen, temperature, and turbidity were measured in the field. The pH, Eh, specific conductance dissolved oxygen and temperature were measured utilizing a flow through cell with a YSI model 6820 multi parameters instrument. Turbidity was measured using an HF model DRT-15CE turbidity meter. A surface water sample at each sampling location was also analyzed for the field water quality parameters. The sampling point was purged until the field water quality parameters stabilized. After the field parameters stabilized the surface water results and the stabilized results from the sampling point were compared to be certain that groundwater, and not surface water, was being sampled. The field analyses indicated that pH, temperature and specific conductance were good indicator parameters for this comparison. The collected sub-river bed samples were then analyzed for the nine VOCs listed in Table 2. VOC analyses were performed in the field laboratory using a modification of EPA Method SW-846 8021.

Table 2. VOC Analytes

Trichloroethene
Carbon Tetrachloride
1,1,1-Trichloroethane
Chloroform
Vinyl Chloride
Tetrachloroethene
1,1-Dichloroethene
Chloromethane
1,2-Dichloroethene

The results of the sampling and analyses indicated that TCE contaminated groundwater is discharging into the river along a 5'500 foot length of the river. The maximum TCE concentration detected was 1'600 micrograms per liter (µg/ℓ). Groundwater containing CCL_4 is discharging to the river along a 2'500 foot length of the river, and the CCl_4 discharge zone is contained within the TCE discharge zone. The maximum CCL_4 concentration was 940 µg/ℓ. The sampling locations, and the TCE and CCl_4 distribution in the sub-riverbed groundwater, are shown on Figure 2. Based on the results of this investigation, sampling locations for a benthic macroinvertebrate investigation were selected.

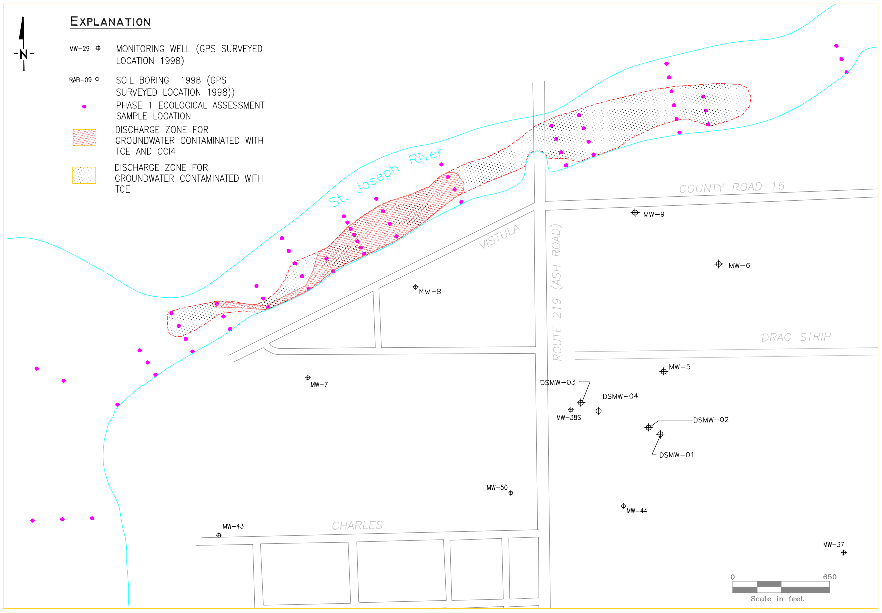

Figure 2. Sampling grid and contaminant discharge area

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Measuring Enhanced Removal of Dissolved Contaminants in Hyporheic Zones and Characterizing Causes and Consequences for Water Quality

By Judson W. Harvey, Christopher C. Fuller, and Martha H. Conklin

ABSTRACT

Characterizing both the causes and consequences of enhanced oxidation of dissolved manganese (Mn) in the hyporheic zone at Pinal Creek basin, AZ required measurements with spatial resolution varying across five orders of magnitude. Our measurements ranged in scale from that of the fundamental interactions between surface and ground water (centimeters) to the scale of the perennial stream that receives ground-water discharge from the entire drainage basin (kilometers). Because of the lower uncertainty of the stream-tracer approach for estimating the average reaction rate, that method provided the most reliable basin-scale simulation of the effects of enhanced Mn-removal in hyporheic zones. The stream-tracer characterization alone, however, could not determine that the removal of manganese was pH-dependent, or even that the reaction occurred in hyporheic zones (as opposed to slow-moving zones in surface water). Laboratory and *in situ* measurements within hyporheic zones provided the crucial evidence to support interpretations about the causal processes.

INTRODUCTION

Hydrologic exchange of streamwater and ground water back and forth across channel beds of rivers and streams enhances chemical transformations in shallow groundwater beneath the streambed (hyporheic zone). The hyporheic zone is defined hydrologically by flow paths that route streamwater temporarily through the subsurface and chemically by subsurface water that can be shown to receive greater than 10% of its water from the surface (Triska and others, 1993). Steep chemical gradients in dissolved oxygen, dissolved organic carbon, and pH in hyporheic zones enhance biogeochemically mediated transformations of solutes, such as nitrification and denitrification (Grimm and Fisher, 1984; Triska and others, 1993), oxidation of metals (Benner and others, 1995), and biodegradation of volatile organic compounds (Heekyung and others, 1995). Hyporheic flow paths are typically small in their spatial dimensions, but if chemical reaction rates are fast enough, and if enough exchange occurs between flowing water and sediment, then the effects can accumulate downstream and affect water quality (Harvey and Fuller, 1998).

This short paper considers three types of measurements at different spatial scales of resolution. The three measurement types are: (1) laboratory-batch experiments that quantify solute-sediment interactions at the millimeter-scale, i.e. the scale of individual sediment grains, (2) *in situ* measurements in hyporheic flow paths at the scale of centimeters beneath the streambed, and (3) stream-tracer experiments that quantify removal rates at the scale of experimental subreaches in the perennial stream (approximately 500 meters) or at the scale of the perennial stream that receives ground-water discharge from the entire drainage basin (3 kilometers).

A number of physical and chemical measurements of the hyporheic zone have been made as part of our investigations, including the hyporheic-zone depth, hydrologic residence time in the hyporheic zone, net removal-rate constant for dissolved manganese (Mn), and percent removal of Mn in hyporheic flow paths. Previously, we found good agreement across scales of measurement based on a relatively limited data set (Harvey and Fuller, 1998). In this paper, we update with new data the means and standard deviations for manganese removal-rate constants and compare them among the three measurement types. Field methods, analyses, and modeling calculations for reach-scale and in-situ measurements are presented in Harvey and Fuller (1998), Fuller and Harvey (1999), and Duff, et al., (1998). Laboratory methods and analyses are given by Marble and others (1999) and Harvey and Fuller (1998).

COMPARISON OF REMOVAL-RATE CONSTANTS ACROSS SCALES

In situ rate constants (cm-scale) in the hyporheic zone were determined at a total of eleven sites in 1994, 1995, and 1997. Rate constants were determined for sub-reaches of the perennial stream (500-m scale) by averaging results from stream-tracer injections in 1994 and 1995. The basin-scale estimates (3-km scale) were computed by averaging the mean rate constant from the four subreaches in 1994 with the mean for the five subreaches in 1995. Laboratory rate constants estimates were computed using data from the subset of unpoisoned experiments conducted between pH 6 and 6.9, which matches the range of pH's that were measured *in situ*. We chose the coefficient of variation (standard deviation divided by the mean) as a measure of uncertainty.

The mean rate constant for the three field estimates (e.g. *in situ*, sub-reach, and basin-scale) was approximately 2.3×10^{-4} per second. The mean rate constant determined in the laboratory was approximately 30% lower. An average rate constant of 2.3×10^{-4} per second for removal of manganese corresponds to a time constant (inverse of rate constant) of approximately 1.3 hours, which is comparatively fast in a drainage basin where the hydrologic residence time in surface water of Pinal Creek is approximately 1 day. Although the mean estimates for each field technique varied little (4% coefficient of variation), standard deviations varied by approximately a factor of four. The *in situ* estimate of the removal-rate constant was most uncertain with a coefficient of variation of 107%. Estimates made at the kilometer-scale based using the stream-tracer approach were least uncertain, with a coefficient of variation equal to 26%. The coefficient of variation for laboratory and sub-reaches had intermediate values of 84% and 56%, respectively.

DISCUSSION

Rate constants for removal of manganese differed little between laboratory experiments, *in-situ* field measurements, and measurements based on stream-tracer experimentation. The advantage of laboratory experiments was the isolation of the effects of microbial colonies and pH. Marble and others (1999) discuss pH and other factors affecting Mn-oxidation reactions. One problem of the batch-laboratory experiments is extrapolating results to sediment-water ratios that more accurately approximate field conditions. Following Harvey and Fuller (1998), we scaled laboratory-rate constants by multiplying them times the ratio between the average sediment concentration (grams/liter) in the streambed at Pinal Creek and the sediment concentration used in laboratory experiments. That adjustment assumes that grain-size variations, which are likely to affect sediment-surface area available for oxidation of manganese, are the same in laboratory experiments and in the streambed. Another possible problem of the laboratory experiments is controlling for variation in activity levels of microbial colonies. For example, Marble and others (this volume) report a significant time lag before removal in Mn begins in sediment samples that were stored before usage in experiments. Either of those possible problems might explain the lower Mn removal-rate constant compared with in-situ and stream-tracer estimates

In situ sampling within hyporheic flow paths addresses the problem of realistic field conditions by quantifying rates of removal without disturbing the sediments or natural hydrologic fluxes. But this method has practical limitations, however. *In situ* sampling has the disadvantage that the measurements are difficult and time consuming to make in the field, which limits sample sizes. In addition there is also the problem that ancillary physical and chemical factors cannot be varied except though careful site selection. The principal advantage of *in-situ* field measurements is that interactions between flow and biogeochemical processes are preserved, which potentially could reveal findings that would be difficult to detect in a laboratory setting.

Stream-tracer experiments provided the most reliable reach-averaged rate constants for modeling the basin-scale consequences of enhanced chemical reactions in hyporheic zones. Nevertheless, there remains a major disadvantage of the stream-tracer approach for quantifying hyporheic-zone processes. On the basis of stream-tracer experiments alone, we cannot be sure that the removal of reactive solutes actually occurs in hyporheic-zones, or on the leaves of aquatic vegetation in slowly-moving surface water at channel margins or behind channel obstructions. Another problem with stream-tracer methods is that the detection sensitivity for hyporheic zones is not equal across the multiple types of hyporheic zones that may be present in a given system (Harvey and others, 1996). Only direct sampling of hyporheic zones using *in-situ* methods can provide the independent confirmation needed to support physical interpretations at larger spatial scales.

SUMMARY AND CONCLUSION

Mean rate constants for the removal of dissolved manganese agreed closely between three scales of resolution in the field, ranging from centimeter-scale field measurements acquired *in situ* in hyporheic zones to kilometer-scale estimates determined using stream tracers. The laboratory estimate of the Mn removal-rate constant was approximately 30% lower than field estimates. *In situ* and laboratory rate constants had relatively large coefficients of variation (107% and 84%, respectively), which may be too large to be used reliably in transport simulations. Stream-tracer experiments provided estimates of the rate constant with lower uncertainties; 56% when averaged at the reach-scale (approximately 500 meters) and 26% when averaged at the basin-scale (3 kilometers). Our experience at Pinal Creek basin leads us to conclude that a multi-scale approach is a necessity for characterizing enhanced biogeochemical reactions in hyporheic zones.

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Bioassessment of Hyporheic Microbial Communities Using a Specially-designed Sediment Colonization Chamber

By Susan P. Hendricks

Streambed sediments are often very heterogeneous in particle size distribution and permeability, creating mosaics of hyporheic habitats and biotic communities. Biotic patchiness and difficulties sampling the physical environment present challenges for researchers investigating hyporheic microbial transformation processes. Heterogeneous sediments may not be conducive to conventional sampling techniques (Fraser and Williams 1997, Mauclaire, et al. 1998). For example, streambeds composed of large gravel and cobble are prohibitive to mechanical or hand-coring of sediments. Freeze-core sampling techniques often used in heterogeneous sediments for invertebrates are not appropriate because freezing alters microbial activity (Humpesch and Niederreiter 1993, Claret 1998a, 1998b).

Some sampling difficulties may be overcome using artificial chambers. Many investigators have designed chambers for various specific monitoring purposes, including water chemistry, macroinvertebrates, and *in situ* microbial metabolism measurements (Danielopol and Niederreiter 1987, Dodds, et al. 1996, Shati, et al. 1997). There also have been several site- and/or question-specific chamber designs, particularly for sediment microbial studies (e.g., Fischer, et al. 1996, Frazer, et al. 1996, Eisenmann, et al. 1997, Claret 1998a, 1998b). The purpose of this paper is to describe a multi-purpose sediment microbial colonization chamber that combines attributes of several previous designs. The chamber has been used successfully in heterogeneous cherty western Kentucky and Tennessee streams and can be used not only for chemical and microbial monitoring, but also for experimental manipulations *in situ*.

DESIGN CONCEPT

Gravel bars are conspicuous geomorphic features of many mid-reach streams (Figure 1). Conservative tracer experiments in the study streams have shown that both gravel bars and the hyporheic zone are important transient storage zones where dissolved organic matter, nutrients and contaminants may be retained for periods of time and transformed before re-entering the surface stream environment. Microbial activity within these subsurface regions is important in mediating nutrient and carbon cycling (Hendricks and White 1991, 1995; Hendricks 1993, 1996) and potentially important in transforming contaminants.

The chamber was designed for maximum flexibility in placement and function within both the hyporheic zone and within gravel bars lateral to the stream (Figure 1). The design (Figure 2) has allowed us to 1) collect interstitial water samples for nutrient chemistry and dissolved oxygen, 2) sub-sample sediments for various microbial assays (e.g., bacterial productivity, phosphatase activity), and 3) carry out time-course *in situ* experiments for determining transformation rates of various substances (e.g., respiration rates, nitrification rates). Additionally, the sediment volume within the chamber enables 1) collection of small test-tube sized cores from each of the depth intervals for further laboratory microbial analyses (e.g., microbial diversity studies using amplified rDNA restriction analysis, fatty acid analysis, perfusion experiments) and 2) transplant experiments between sites and streams and monitor subsequent changes in activities and other effects. Our initial experiments have been comparisons between an agriculturally impacted third-order stream (Ledbetter Creek) and a pristine third-order stream (Panther Creek) with similar sediment heterogeneities and watershed characteristics.

METHODS

Sediments collected from each stream were sieved (£ 3 mm size fraction), autoclaved, and placed into chamber baskets (Figure 2). The baskets were stacked such that each represented a hyporheic depth interval (0-10 cm, 15-25 cm, and 30-40 cm). Chambers were placed just below the top of the water table along previously determined subsurface flow-paths within the gravel bars and below the sediment-water interface within hyporheic regions (Figure 1). Ports between inner and outer cylinders were aligned in the open position to allow interstitial flow and colonization with microflora for approximately 8-10 weeks.

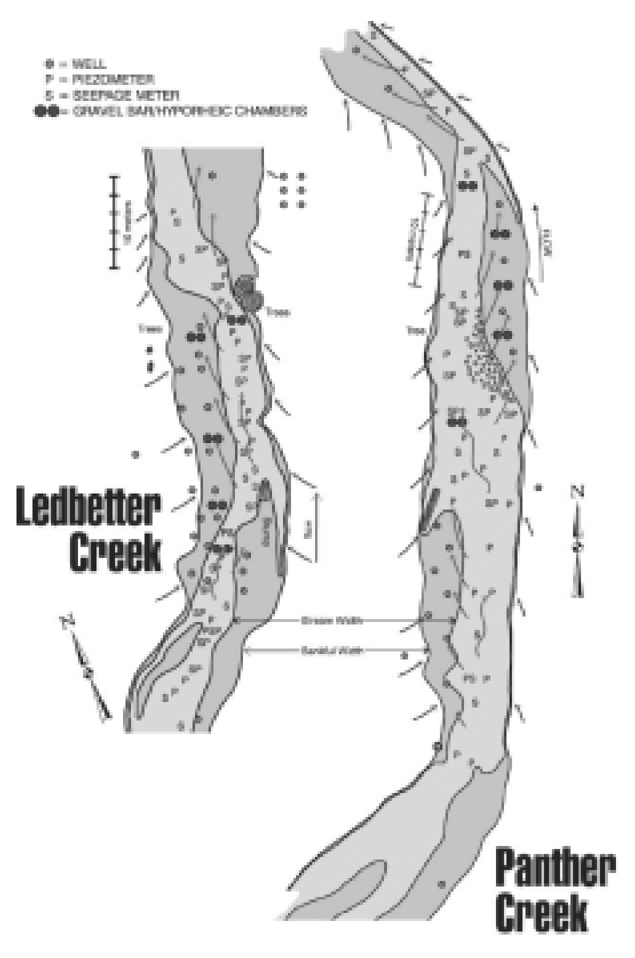

Figure 1. Study sites at Ledbetter and Panther Creeks. Black arrows indicate groundwater inflow: Gray arrows indicate flowpaths of surface water into gravel bars and hyporheic zone beneath stream.

Following colonization, the chamber caps were removed and interstitial water was withdrawn for dissolved O_2, nutrients, and DOC from each of the stacked sediment baskets by attaching a syringe to the tubing embedded in the basket (Figure 2). Baskets were then retrieved from the inner cylinder by pulling up on the central stem. Sediment sub-samples were collected from each basket, placed into sterile containers, and transported to the laboratory for phosphatase activity, bacterial productivity and microbial diversity assays.

In situ experiments also were conducted. For example, interstitial dissolved O_2 and NO_3-N samples were collected from each depth interval within the chamber as pre-incubation references (i.e., ports on both cylinders aligned in the open position). Twisting the inner cylinder in the opposite direction resulted in closing of the ports and isolation of sediments from interstitial flow. Following incubation in the closed position for a chosen period of time (e.g., 24-72 hours), interstitial water was re-sampled. Oxygen consumption (respiration rate) and NO_3-N accumulation (nitrification rate) were estimated as the difference between dissolved O_2 or NO_3-N concentrations before and after incubation over time and expressed as change in concentration g^{-1} wet weight or L^{-1} sediment h^{-1}.

RESULTS

Some examples of subsurface microbial activities important in P, N and C cycles are summarized in Tables 1-3. The tabulated data are means calculated from all depths (3) within replicate chambers (2) within a site (gravel bar=3, hyporheic=2) for each stream. Alkaline phosphatase activity (Sayler, et al. 1979) was higher in the gravel bar than in the hyporheic zone at Ledbetter Creek during both summer and spring sampling periods, and higher in general than in Panther Creek (Table 1), indicating differences in phosphorus demand by the microbial community between the two streams and among sites within the streams.

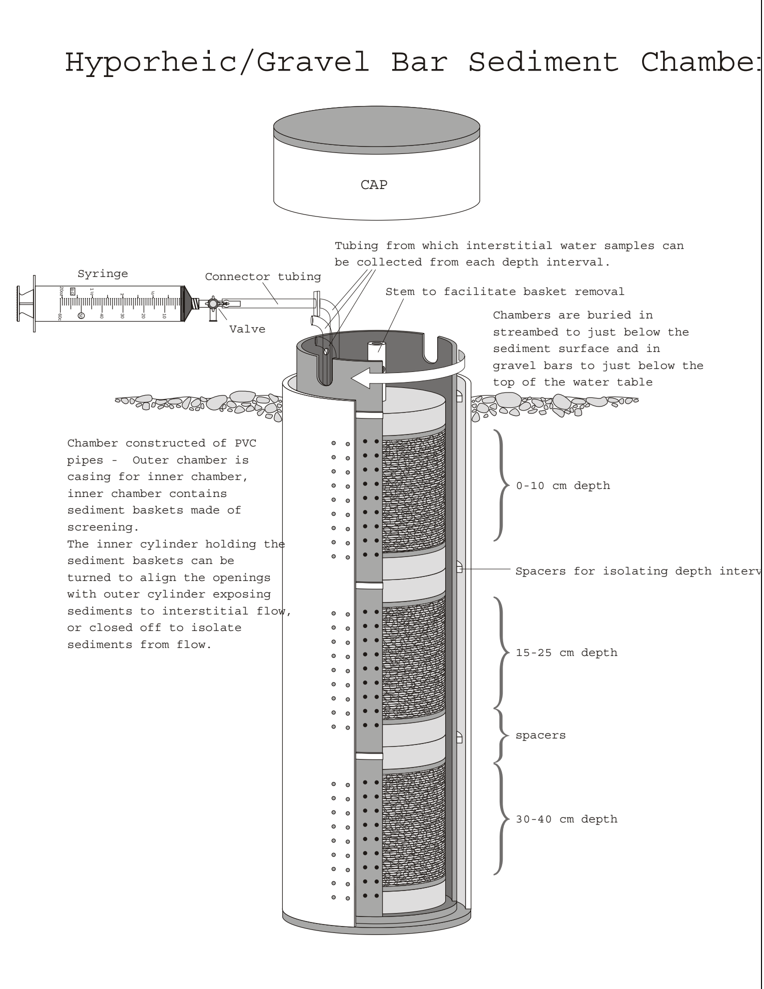

Figure 2. Schematic of gravel bar/hyporheic chamber design.

The Ledbetter Creek gravel bar generally showed higher bacterial productivity (methods modified from Findlay 1993) than the Panther Creek gravel bar (Table 2). Bacterial productivity was highest where interaction between the subsurface gravel bar and stream surface water was greatest as indicated by dissolved O_2 gradients in both gravel bars (data not shown) along subsurface flow-paths (Figure 1).

Nitrification rate (methods of Jones, et al. 1995), reported as the increase in µg NO_3+NO_2 L^{-1} sediment h^{-1}, was higher in Ledbetter Creek than in Panther Creek (Table 3). The Ledbetter Creek sediment bacterial community is composted of taxa, which appear adapted to high levels of NH_4NO_3 fertilizer applications.

Table 1. Alkaline phosphatase activity (APA = µm nitro-phenylphosphate reduced g^{-1} sediment dry wt.) in hyporheic and gravel bar chambers at Ledbetter and Panther Creeks. AG = agriculturally impacted, P = pristine.

Stream	Site	Spring	Summer
Ledbetter (AG)	Gravel Bar	1020.5	1942.9
	Hyporheic	700.9	205.4
Panther (P)	Gravel Bar	687.7	370.9
	Hyporheic	no data	no data

Table 2. Subsurface gravel bar bacterial productivity (µg C m^{-2} h^{-1}) at Ledbetter and Panther Creek as estimated from incorporation of ^{3}H-thymidine into bacterial DNA. AG = agriculturally impacted, P = pristine.

		Gravel Bar Position		
Stream	Month	Upstream	Mid-Bar	Downstream
Ledbetter (AG)	Jan	3.13	11.7	32.3
	Jun	64.5	73.6	225.9
	Sep	37.7	67.1	67.1
Panther (P)	May	72.1	58.6	44.9
	Aug	147.0	51.6	48.0

Table 3. Nitrification rates measured as the increase in NO_3+NO_2 in sediments (µg NO_3+NO_2 produced L^{-1} sediment h^{-1}) in Ledbetter and Panther Creek chambers. AG = agriculturally impacted, P = pristine.

Stream	Site	ΔNO_3 (µg L^{-1})	% Increase	Rate (µg NO_3 L^{-1} sediment h^{-1})
Ledbetter(AG)	Gravel Bar	801.2	+340	11.13
	Hyporheic	238	+260	3.30
Panther (P)	Gravel Bar	4.5	+5	0.06
	Hyporheic	8.0	+8	0.11

DISCUSSION

It is well known that agricultural practices increase sedimentation and greatly alter the chemistry of surface waters. However, land-use effects on microbial and biogeochemical processes at the groundwater-surface water interface (hyporheic zone) mediated by increased nutrient, carbon, and sediment loads are largely unknown. Contaminants reaching streams from subsurface sources such as groundwater are expected to be processed/transformed at the groundwater-surface water interface depending on heterogeneity and permeability of sediments and subsurface flow-path complexity. Methods and data presented here have focused primarily on delineating differences in hyporheic zone function that mediate agricultural and suburban runoff between and within streams. Results presented above are limited examples of data which might be obtained from colonization chambers. It is feasible to examine other processes which indicate disturbance or alteration of function by other contaminants entering streams from either point or non-point sources (e.g., contaminated groundwaters).

CONCLUSIONS

The sediment microbial colonization chamber described in this paper appears to be a reasonable device for examining microbial activities and biogeochemical transformations within the hyporheic zone or at the groundwater-surface water interface within streambeds.

Advantages of using the sediment colonization chamber described here are 1) construction materials are inexpensive and the design is flexible for a variety of streambed types, 2) chambers are multi-purpose in that both interstitial water chemistry and sediment sampling can be done, 3) time course incubations can be carried out, 4) transplanting of chambers for inter- and intra-site comparisons may be carried out, and 5) either natural sediments or more homogeneous artificial particles (e.g., glass or ceramic beads) may be used in the chambers, 6) replication is quite good and data are consistent between replicate chambers.

Some disadvantages may include 1) installation that may require 2 or more people, 2) colonization periods may be long (6 weeks minimum, 8-10 weeks preferred), 3) chamber sediments may not reflect actual particle size distributions found in streambeds, 4) chambers may prohibit infiltration of natural CPOM (microbial fuel), and 5) chambers may alter local subsurface hydraulics. Continued monitoring of the chambers over time and space will help evaluate their ultimate usefulness in stream ecosystems.

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Fundamentals of SPMD Sampling, Performance, and Comparability to Biomonitoring Organisms

By J.N. Huckins, J.D. Petty, H.F. Prest, J.A. Lebo, C.E. Orazio, J. Eidelberg, W.L. Cranor, R.W. Gale, and R.C. Clark

INTRODUCTION

Passive monitoring devices have long been used by the chemical industry and governmental agencies to ensure compliance to OSHA standards for time-weighted-average (TWA) concentrations of organic vapors in the work environment. With the recent development of lipid-containing semipermeable membrane devices (SPMDs) and samplers based on diffusive gradients across thin polymeric films (DGTs), the passive *in situ* monitoring approach can now be applied to determining TWA concentrations of both hydrophobic organics (SPMDs) and heavy metals (DGTs) in aquatic environments (1-3). In this work, we focus on the fundamentals of SPMD technology, and the potential utility of the approach for monitoring organic contaminants in groundwater (includes the hyporheic zone).

SPMD SOURCE, DESIGN AND THEORY

The SPMD technology is the subject of two government patents and the devices are commercially available from Environmental Sampling Technologies, 1717 Commercial Drive, St. Joseph, MO 64503. A standard SPMD consists of a thin walled (75-95 m) layflat tube of low density polyethylene (LDPE) containing a thin film of 95% pure triolein (Figure 1). The ends of the LDPE, are welded by heat-sealing. The length or size of the standard device can be customized to fit an investigator's sampling needs. The membrane surface area-to-lipid-volume ratio of a standard SPMD is 450 cm^2/mℓ triolein. Because the LDPE membrane is nonporous (i.e., fixed pores do not constitute a significant portion of the polymer free volume) and transient cavities in the membranes are generally < 10 in diameter, only dissolved or readily bioavailable compounds are sampled.

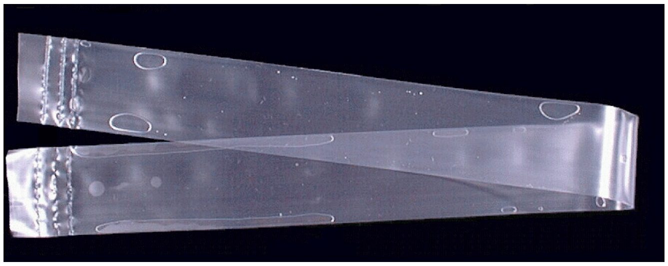

Figure 1. A standard lipid-containing SPMD with three molecular welds near each end. Note that low interfacial tension causes intimate contact (i.e., the present of a lipid film on the membrane interior surface) between the triolein and the membrane even where air bubbles exists.

A fundamental characteristic of passive monitors used to estimate TWAs of contaminants is the proportionality of sampler concentrations to ambient environmental concentrations. Also, such monitors are typically designed to be an infinite sink for target analytes. This characteristic results in a constant volume of air or water extracted per unit time (i.e., linear uptake of analytes at constant ambient concentrations), and the following equation applies

$$C_w = C_{SPMD}\, V_{SPMD}/R_s\, t \quad (1)$$

where C_w is the TWA analyte concentration in water (ng/ℓ), C_{SPMD} is the concentration in the whole device (membrane + lipid) in ng/ℓ, V_{SPMD} is the volume of the SPMD (L), R_s is the sampling rate for a chemical in L/d, and t is exposure time in days (d).

Huckins et. al. (4) have shown that R_s values for PAHs and OCs ranged from 1 to 8 L/d (exposure conditions: 10-26°C, water velocity < 1cm/sec), when using a standard SPMD with V_{SPMD} = 5mL. Thus, in the linear region of analyte uptake, an SPMD with V_{SPMD} = 1 mℓ will daily extract dissolved contaminants from 200 to 1,600 mℓ of water. If the target compounds have relatively low octanol-water partition coefficients (i.e., log $K_{ow} < 4$), such as VOCs, equilibrium between the device and the surrounding water is often achieved in < 1 week. In that case, the following simple model can be used for water concentration estimates:

$$C_w = C_{SPMD}/\, K_{SPMD} \quad (2)$$

where K_{SPMD} is the equilibrium SPMD-water partition coefficient. For compounds with log K_{ow} of 4.0 and > 4.0, K_{SPMD} is 0.75 K_{ow} and 0.3 K_{ow}, respectively.

APPLICABILITY OF THE APPROACH

Standard SPMDs are designed to sample nonionic hydrophobic compounds. The total volume of water extracted by an SPMD at equilibrium is estimated by 0.75 K_{ow} V_{SPMD} (log K_{ow}s 4.0) and 0.3 K_{ow} V_{SPMD} (log K_{ow}s > 4.0). For example, if the target analyte has a K_{ow} of 300 the maximum (equilibrium) volume of water extracted by a standard 1 mℓ triolein SPMD (V_{SPMD} 5 mL) is only a little more (i.e., 1.1L) than a 1L grab sample. Thus, standard SPMDs are useful only for sampling compounds with K_{ow}s > 300, unless an adsorbent is dispersed in the triolein (4).

Trace levels of a variety of classes of organic contaminants have been successfully determined in aquatic systems using SPMDs. These include but are not limited to the following: polycyclic aromatic hydrocarbons, polychlorinated -biphenyls and -terphenyls, organochlorine pesticides, polychlorinated-dibenzodioxins and -dibenzofurans, chlorinated and brominated diphenyl ethers, chlorinated -benzenes, -anisoles and -veratroles, certain alkylated and chlorinated phenols, heterocyclic aromatics, pyrethroid and nonpolar to moderately polar organophosphate pesticides, and nonionic organometals.

DEPLOYMENT CONSIDERATIONS

Because SPMDs readily sample a broad spectrum of chemicals from air, exposure to organic vapors is minimized by transport to and from the sampling site in clean gas-tight metal cans. Other precautions are similar to those used for standard grab sampling methods.

The appropriate exposure duration is dependent on the physicochemical properties (e.g., K_{ow}s) of the target analytes, analytical sensitivity needed, choice of sampling approach (i.e., integrative or equilibrium), environmental conditions, and the potential for vandalism. When calibration data are available (4,6) or can be estimated for contaminants of concern, the following model can be used to determine the time required to reach half of the SPMD equilibrium concentration ($t_{1/2}$):

$$t_{1/2} = \ln 0.5\ K_{SPMD}\ V_{SPMD}/R_s \qquad (3)$$

Knowledge of these half-times or half-lives is useful because the uptakes of analytes are linear during 1 $t_{1/2}$.

Thus, within 1 $t_{1/2}$ equation 1 can be used for water concentration estimates. If an equilibrium sampling approach is used, exposure time should be > 4 $t_{1/2}$s and equation 2 is applicable. SPMD sampling rates are affected by temperature, water velocity, and biofouling. Fortunately, temperature, and to a lesser extent hydraulic conductivity (velocity), are generally more constant in ground water systems than in surface waters. In surface waters, biofouling impedes analyte uptake, often limiting the utility of long exposure times. However, biofouling is much reduced in groundwater, thereby permitting significantly longer exposures (months instead of weeks) for compounds with high K_{ow}s (i.e., 6.0).

Even with the effects of the aforementioned environmental variables on sampling rates, Ellis et. al. (5) have shown that river water concentrations (dissolved phase) of trace organic contaminants can be estimated from SPMD concentrations within two-fold accuracy. Huckins, et al. (1,4) have suggested that the use of permeability reference compounds (PRCs) may further reduce errors in water concentration estimates. PRCs are analytically noninterfering compounds, such as deuterated PAHs with log K_{ow}s < 5.0, that are added to SPMD lipid before deployment. By determining PRC loss rates ($R_s/K_{SPMD}\ V_{SPMD}$ or k_2) from SPMDs during an environmental exposure and comparing them to PRC k_2s measured during the experimental determination of sampling rates (R_ss), the laboratory derived R_ss of analytes can be adjusted to account for the effects of field exposure conditions.

COMPARABILITY TO BIOMONITORING ORGANISMS

The accumulations of organic contaminants by SPMDs and aquatic organisms have been compared in a number of studies (2,4-6). Some studies have shown that the concentration patterns and uptake rates of several classes of chemicals by SPMDs and fishes are similar (6,7). However, it is unrealistic to expect SPMDs to mimic the uptake of all organic contaminants by all aquatic species because large differences exist among species in regard to diet/source of energy, metabolic activities (xenobiotics), and lipid composition and percentages. For example, few aquatic organisms contain 20% lipid by weight as SPMDs do. Thus, the capacities of most aquatic organisms to retain accumulated residues are nearly always less than SPMDs (i.e., organism k_2>>SPMD k_2), which suggests that organisms used as biomonitors may not retain detectable levels of some residues several days after an episodic contaminant release.

GROUNDWATER APPLICATION

Although SPMDs are used extensively in surface waters (2,4) and in the atmosphere (8), their application to ground water systems has been limited to a few studies. This is surprising because laboratory studies performed to determine SPMD sampling rates (4) more closely simulate the relatively constant conditions existing in some ground water systems.

Herein, we highlight a pilot study on the use of SPMDs by EPA Region 9 personnel for sampling dieldrin in groundwater at the George Air Force Base, California. The devices were deployed in two ground water monitoring wells where dieldrin residues were previously determined. The exposure period was 29 days. Based on laboratory calibration studies (4), each standard SPMD sampled a total volume of 58 ℓ of groundwater during the 29-day exposure. Figure 2 illustrates the results of the analysis (high resolution gas chromatography-electron capture detection [ECD]) of SPMD extracts from well water at one of the sites, and of an associated SPMD control. Microgram quantities of dieldrin were concentrated in each of two replicate SPMDs and the SPMD-derived TWA water concentration was estimated at 69 ng/ℓ (recovery-corrected). Earlier, a grab sample at the same site was found to contain 110 ng/ℓ of dieldrin (includes sorbed fraction). Much lower levels (140 to 2,800-fold less) of fifteen other chlorinated pesticides (e.g., chlordane components, endrin, endosulfan II and sulfate, etc.) were also detected in the SPMDs. These trace contaminants were not detected using EPA’s (CLP) low-level pesticide method. In summary, SPMDs appear to be well suited for monitoring trace hydrophobic organics in ground water systems.

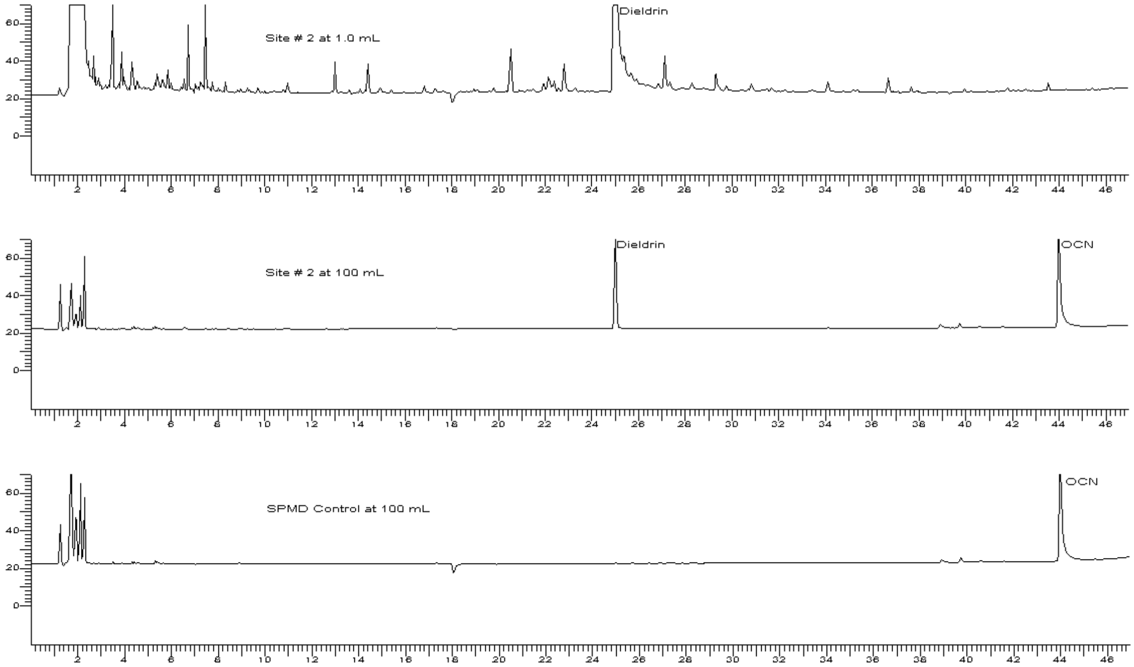

Figure 2. ECD Chromatograms of an SPMD sample extract and a control SPMD. SPMDs were deployed for 29 days in a ground water monitoring well at George Air Force Base, CA. Dieldrin and 15 other organochlorine pesticides were detected in the sample. The bottom two chromatograms were diluted 100-fold to keep dieldrin on scale, and octachloronaphthalene (OCN) was used as an instrumental internal standard.

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Acid Mine Drainage—The Role of Science

By Briant Kimball

Thousands of abandoned and inactive mines are located in environmentally sensitive mountain watersheds. Cost-effective remediation of the effects of metals from mining in these watersheds requires knowledge of the most significant sources of metals. The significance of a given source not only depends on the concentration of a toxic metal, but also on the total mass of metal added to the stream. This discussion deals with accounting for the mass of metal that enters the stream, which is called the mass loading. It is calculated as the product of metal concentration and stream discharge.

Without discharge measurements, the overall effect of high metal concentrations on streams and aquatic organisms is unclear. A traditional discharge measurement is obtained by dividing a stream into small sections and measuring cross-sectional area and average water velocity in each section. Because the channel bottom in mountain streams is not smooth and much of the flow is among the streambed cobbles, accurate discharge measurements are difficult to obtain, even under the best conditions.

AN APPROACH FOR MOUNTAIN STREAMS

A recent study by the U.S. Geological Survey Toxic Substances Hydrology Program illustrates a practical approach to obtaining and using discharge measurements in mountain streams. Chalk Creek, a tributary of the Arkansas River in Colorado, receives mine drainage from the Golf Tunnel adit. Metal-rich mine drainage from the Golf Tunnel is routed around waste rock and a capped tailings pile into a constructed wetland. From the wetland, the mine drainage enters Chalk Creek from small springs and seeps along the stream. Regulatory and land management agencies have asked three basic questions about Chalk Creek. First, is there more than one source of mine drainage that affects the stream? Second, does a remediation plan need to account for drainage from more than one source? Finally, have past remediation efforts been successful? To address these questions, we employed a tracer-dilution study to determine discharge and synoptic sampling to obtain detailed chemical composition from many locations. The synoptic samples are collected during a short period of time, typically a few hours, providing a “snapshot” of the changes along a stream at a given point in time.

ADDING A TRACER: DISCHARGE BY DILUTION

Discharge in mountain streams can be measured precisely by adding a dye or salt tracer to a stream, measuring the dilution of the tracer as it moves downstream, and calculating discharge from the amount of dilution. Because we know the concentration of the injected tracer and the rate at which it is added to the stream, we know the mass added to the stream. By measuring the concentration of the tracer upstream and downstream from the injection point, we can calculate the discharge by dilution of the tracer in the stream. To define discharge in Chalk Creek, a sodium chloride tracer was added at a constant rate for 24 hours at a point upstream from the mine drainage. The chloride injection was monitored at several sites downstream from the injection point, documenting the incremental increase of discharge due to water entering the stream. The difference in discharge between two stream sites gives the total amount of inflow from surface- and ground-water sources in that small reach.

SYNOPTIC SAMPLING: A "SNAPSHOT" IN TIME TO COMPARE METAL LOADING OF SOURCES

Synoptic samples provided metal concentrations, giving a detailed profile of zinc concentrations in both the stream and inflows along the stream reach. To evaluate these concentrations, a mass-loading profile was calculated from the concentrations and the discharge values. The concentrations and the mass-loading profile help answer the basic questions about the sources of metals and the effectiveness of remediation. First, there appears to be more than one source of mine drainage, because the high concentration at 252 meters could not be from the Golf Tunnel. Second, despite the higher concentration of zinc in water from the second source, the loading profile shows that the high-concentration water only contributes about 8 percent of the zinc load and would not require a separate remediation plan. Finally, there are still effects on metals in the stream where old tailings were removed downstream from 300 meters; these effects will likely decrease with time. The example of Chalk Creek shows that the highest inflow concentrations do not always result in the most significant sources of metal loading. Our results show that a site can be investigated in great detail to help make decisions by using tracer injections and synoptic sampling.

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(Mr. Kimball's article is adapted, by permission, from an article published by the USGS. in January 1997. More information on the Toxic Substances Hydrology Program can be obtained at http://toxics.usgs.gov/toxics.)

Temporal and Spatial Trends in Biogeochemical Conditions at a Groundwater-Surfacewater Interface

By John M. Lendvay and Peter Adriaens

BACKGROUND

The Bendix, Allied Signal National Priority List (NPL) site at St. Joseph, Michigan, has been extensively characterized for contaminant distribution and biogeochemical conditions between the contaminant source and zone of emergence in Lake Michigan [Tiedeman and Gorelick, 1993; Semprini, et al., 1995; Lendvay, et al., 1998a; Lendvay, et al., 1998b]. The source of the contaminant plume at the site consists of trichloroethene (TCE) and minor contamination with hydrocarbons. Contaminant hydrocarbons and natural organic matter have stimulated sufficient indigenous microbial activity in the groundwater to result in anaerobic conditions, predominantly sulfate-reducing and methanogenic. Under these terminal electron accepting processes (TEAPs), TCE has been reductively dechlorinated to predominantly *cis*-1,2-DCE, chloroethene, and ethene with minor production of 1,1-DCE, *trans*-1,2-DCE, and ethane.

Since the source of contamination is located approximately 750m up-gradient of Lake Michigan, the flow of groundwater toward the lake raised concern about the potential contamination of Lake Michigan with reductive dechlorination products, particularly chloroethene. Between 1994 and 1996, three transects of temporary bore-holes were established on the beach and approximately 100 meters from shore under the lake bottom to monitor the contaminant distribution and oxidation-reduction conditions at the GSI [Lendvay, et al., 1998a]. This study of the GSI suggested that the predominant TEAPS under Lake Michigan and in the zone along the beach was sulfate-reduction interspersed with methanogenic conditions. Furthermore, reductive dechlorination was the predominant contaminant transformation where these TEAPs predominated. However, in shallow regions of the contaminant plume near the lake shoreline, iron-reducing conditions predominated, which are conducive to either dechlorination [McCormick and Adriaens, 1998] or oxidation [Bradley and Chapelle, 1996] reactions. The more oxidized iron-reducing zone along the top of the GSI was hypothesized to result from re-oxygenation of the plume by surface water run-up, infiltration, and wave activity. Furthermore, it was hypothesized that re-oxygenation of the aquifer to hypoxic conditions resulting from wave activity might provide a suitable environment for aerobic commensalic or cometabolic biodegradation processes in the shallow zone along the beach.

The goals of this current study were to: *i*) evaluate the temporal effects of increased wave activity on the TEAPs and contaminant distribution; *ii*) determine the most likely microbial processes affecting intrinsic remediation of the contaminants at the GSI; *iii*) present laboratory data to corroborate field observations; and *iv*) determine field oxidative flux of chloroethene at the GSI.

METHODS

Multi-level arrays were placed to capture spatial variations in contaminant distribution and predominant TEAPs, seasonal changes and effect of wave activity, and spatial infiltration of lake water into the GSI [Lendvay, et al., 1998b; Lendvay, et al., 1999b]. The arrays were semi-permanent to evaluate temporal effects of lake-activity on contaminant distribution and TEAPs during a six month period (July – December) encompassing seasonal changes in weather and lake activity. Seasonal changes were evidenced by changes in Lake Michigan wave height, as measured by National Oceanographic and Atmospheric Administration (NOAA) buoy 45007, averaged 0.53m for August and September and 1.17 m for November and December with height increasing steadily between June and December (Figure 1) [Lendvay, et al., 1998b].

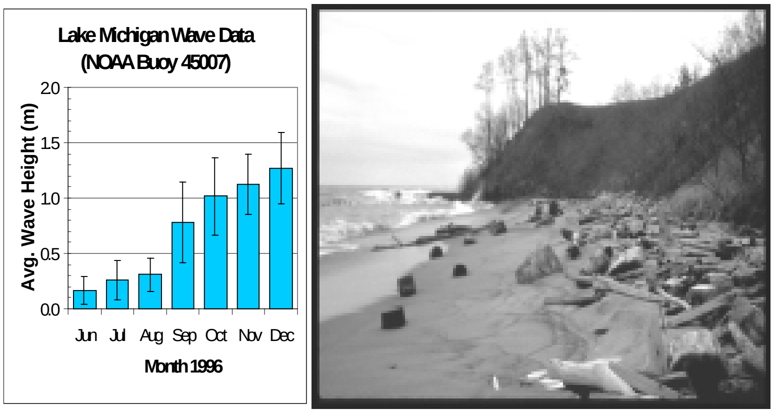

Figure 1: Average wave height for Lake Michigan as measured by NOAA buoy 45007 during the sample time study (left). Error bars represent one standard deviation. Picture of GSI after a major storm event (right). Notice the scatering of large debris, not present prior to the storm.

Groundwater was sampled five times, in four to six week intervals, from each sample point between July and December [Lendvay, et al., 1998b]. Specifically, temperature, pH, reduction potential (redox), specific conductance, and dissolved oxygen were measured using a QED flow cell [Ann Arbor, MI]. Dissolved oxygen, aqueous ferrous iron, and aqueous sulfide were determined colorimetrically using a Chemetrics [Calverton, VA] field sampling kit. Dissolved hydrogen gas in the groundwater was determined as previously described [Lovley, et al., 1994]. Samples for contaminants, methane, sulfate, and short chain organic acids were collected, preserved, and analyzed using headspace gas chromatography, ion chromatography, or HPLC as previously described [Lendvay, et al., 1998b].

Biomass was separated from aquifer solids to evaluate transformation potential by indigenous methane-oxidizing microorganisms as previously described [Lendvay and Adriaens, 1999a]. The resulting liquid suspension was plated and grown in an atmosphere of 50% methane and 50% air at ambient temperature (22° ± 1°C). Methane-oxidizing colonies were washed off the plates and grown in liquid culture. Finally, cells were harvested by centrifugation and washing then resuspended in liquid culture to obtain a cell density of 2.89 mg of cells/mℓ of suspension. Aqueous batch transformation experiments were conducted at ambient temperature to evaluate transformation kinetics of *cis*-DCE, chloroethene and ethene by resting cells.

To evaluate the impact of oxidation on the flux of chloroethene into Lake Michigan, laboratory and field results were transformed to an aquifer oxidative flux (Equation 1) as previously described [Lendvay and Adriaens, 1999a].

$$\frac{dC}{dt} \approx \frac{\Delta[VC]_{Field}}{day} = \lambda C_0 \tag{1}$$

The temporal change in field concentration of chloroethene (dC/dt) was assumed to equal the observed rate of change for chloroethene concentration in the field, and the initial concentration of chloroethene (C_0) was assumed to be the average chloroethene concentration upgradient of the GSI [Weaver, et al., 1995]. The first order decay constant (λ) was then determined. For this calculation, only the sample points that provided evidence of chloroethene oxidation were considered to contribute to the field oxidative flux.

To evaluate the impact of oxidation on the flux of chloroethene into Lake Michigan, laboratory and field first order decay constants were transformed to an aquifer oxidative flux at the GSI using Equation 2 [Lendvay and Adriaens, 1999a]. The porosity (n) was assumed to be 0.32, a nominal value for sandy aquifers. The horizontal distance of the zone where chloroethene is oxidized (x) is the horizontal coverage of ML-2 and ML-3. The vertical coverage of the oxidative zone ($z_{shallow}$) is ratioed to the total depth (z_{total}) of 6.3 meters to only consider the oxidative zone. Finally, the storm activity of the lake is assumed to be sufficient to oxidize chloroethene for only 180 days/year.

$$\frac{dC}{dt} \approx \frac{\Delta[\mathrm{VC}]_{\mathrm{Field}}}{\mathrm{day}} = \lambda C_0 \qquad (2)$$

RESULTS AND DISCUSSION

Vertical profiles of contaminants, geochemically relevant species, specific conductance, reduction potential, and dissolved hydrogen gas concentrations were previously reported [Lendvay, et al., 1998b] with vertical profiles for chloroethene, oxygen and methane presented here (Figure 2). In addition to these profiles, a lack of quantifiable contaminant concentration, high dissolved oxygen, and specific conductance measurements corresponding to typical lake water values provided direct evidence of lake water infiltration at the shallowest sample point as wave activity increased suggesting that lake water penetrated the top 4 meters of the aquifer. Products of electron acceptor reduction, ferrous iron and sulfide, provided evidence for iron-reducing conditions in the shallow zone and iron- and sulfate-reducing conditions in the deep zone of the plume. The methane concentration profile decreased with time in the shallow zone as was noticeable for the December sampling (Figure 2C).

Reduction potential measurements increased in value with time at all elevations suggesting re-oxidation occurred across the entire depth profile between August and December [Lendvay, et al., 1998b]. With the caveat that reduction potential measurements are biased towards the iron couple [Barcelona, et al., 1989; Barcelona and Holm, 1991], observed values were indicative of denitrifying to iron-reducing conditions. Dissolved hydrogen values were indicative for iron-reducing to sulfate-reducing conditions in the shallow zone, and iron-reducing to methanogenic in the deep zone [Lendvay et al., 1998b]. Furthermore, a temporal decrease in dissolved hydrogen concentrations (less reducing TEAPs) corroborated temporal trends in redox measurements.

To be able to discern temporal effects in the contaminant plume, selected contaminant and methane concentrations were compared at the same location in the plume over the time period of interest, using quantile-quantile plots (Figure 3) [Lendvay, et al., 1998b]. These plots show that the concentration of methane was lower for the November and December data compared to the August and September data (Figure 3A). Additionally, these plots showed that chloroethene concentrations decrease with time only in the shallow zone, and slightly increased in the deep zones of the plume (Figure 3C). In contrast, the concentration of *cis*-DCE increased in both the shallow and deep zones of the contaminant plume with time

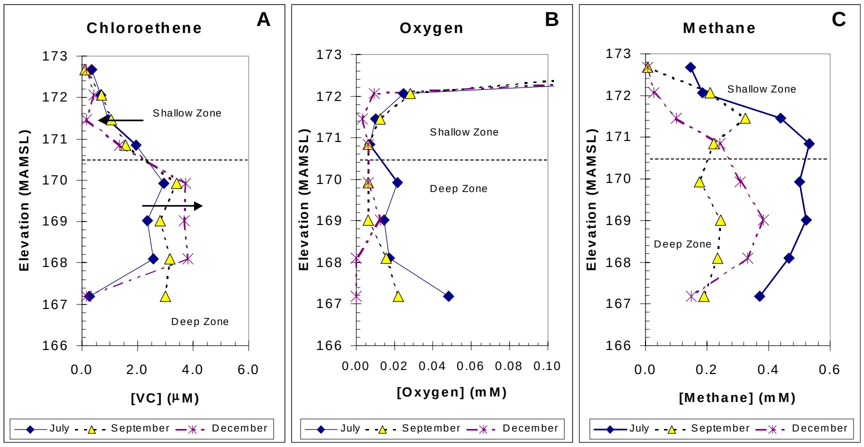

Figure 2: Vertical concentration profiles for chloroethene (A), oxygen (B), and methane (C) at ML-3 for three different time periods.

(Figure 3B). Combining the results for chloroethene and *cis*-DCE suggests the decrease in chloroethene concentration in the shallow zone was not a result of dilution by infiltration of lake water.

To elucidate specific field microbial processes responsible for chloroethene transformation, scattergrams comparing chloroethene or methane with oxygen in the shallow zone were evaluated for statistical correlations [Lendvay, et al., 1998a]. In the case of both chloroethene and methane, peak concentrations occurred at low oxygen concentrations and low chloroethene and methane concentrations occurred at high oxygen concentrations. Combined, these trends suggest that chloroethene may be co-oxidized by methane-oxidizing microorganisms in the shallow zone of the GSI as lake activity increases.

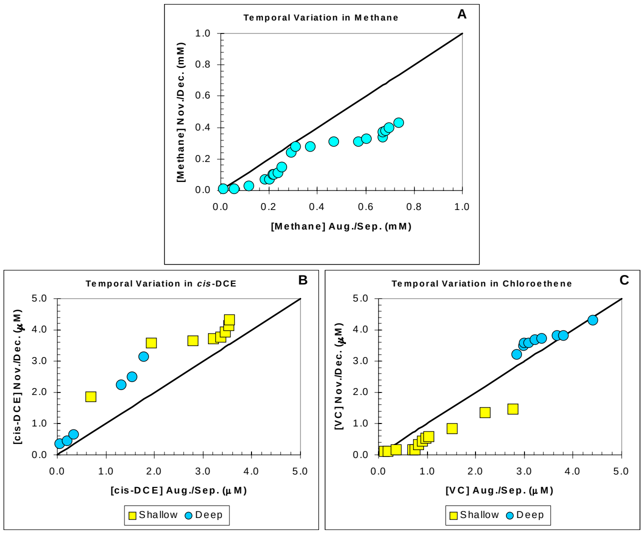

Figure 3: Quantile-quantile plots for the data indicated. For each case, all data (ML-2 and ML-3) are considered for November and December samples on the ordinate, and August and September samples on the abscissa.

To test this field-derived hypothesis and corroborate the field measurements, laboratory studies were conducted using groundwater and aquifer solids collected from the GSI. The mixed cultures were grown on methane as a sole source of carbon and energy under aerobic conditions. A resting cell oxidation experiment was conducted for *cis*-DCE, chloroethene, and ethene in triplicate (Figure 4). Separate controls of either 220 mg/ℓ sodium azide or 0.3% (vol./vol. gas phase) ethyne were effective at suppressing all transformation of contaminants. Considering Figure 4, transformation of both chloroethene and ethene is evident relative to controls, with the rate of chloroethene oxidation being 2.9 nmoles/(day-mg protein) and ethene oxidation being 0.9 nmoles/(day-mg protein). No transformation of *cis*-DCE was observed relative to controls. These results support the field findings, that chloroethene and possibly ethene are co-oxidized by methane-oxidizing microorganisms while *cis*-DCE is not.

To evaluate the impact of chloroethene oxidation on the flux of chloroethene into Lake Michigan,

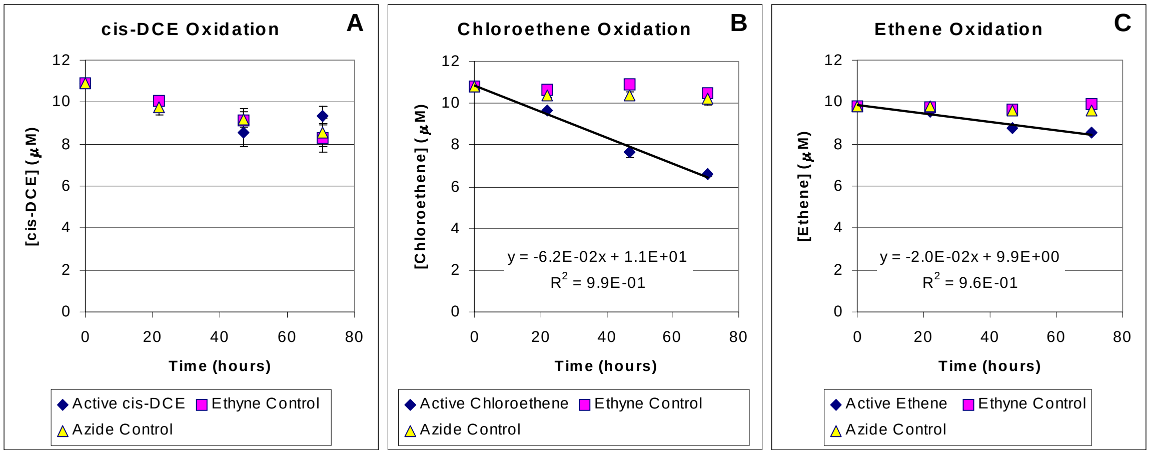

Figure 4: Resting Cell Oxidation of cis-DCE (A), chloroethene (B), and ethene (C) by methane oxidizing microorganisms.

Table 1: Reported value for chloroethene flux at transect-5 (upgradient transect) using a MOD-FLOW model [Weaver, et al., 1995], and values for chloroethene flux at the GSI using calculated field and laboratory rates. Percent values represent the percent of chloroethene flux at transect-5 that is oxidized by the reported value.

Defined Value	Flux (g/(year-m^2))
Chloroethene Flux at Transect-5	0.86
Oxidative Flux of Chloroethene by Field Measurement	0.063 (~7%)
Oxidative Flux of Chloroethene by Laboratory Measurement	0.0007 (~0.1% of 0.86 or ~1% of Field Flux)

laboratory and field results were transformed to a field oxidative flux [Lendvay and Adriaens, 1999a]. Using the calculated field and laboratory chloroethene oxidation rates, field flux calculations were possible (Equation 2). The calculated oxidation fluxes were compared to the chloroethene flux upgradient as calculated by a MOD-FLOW model (Table 1) [Wilson, et al., 1994].

Field calculations of the oxidative flux for chloroethene suggest that only about 7% of the annual chloroethene flux into Lake Michigan is mitigated by measurable biogeochemical processes at the GSI as a result of increased storm activity. Of this observed field flux, only 1% could be associated with a particular microbial culture namely methane-oxidizing microorganisms. The remaining catalytic activity affecting the contaminant plume may be due to other physiological types in the aquifer solids such as non-culturable methane-oxidizing, heterotrophic [Wackett, et al., 1989; Davis and Carpenter, 1990], autotrophic [Vannelli et al, 1990], ethene oxidizing [Freedman and Herz, 1996], iron-reducing [Bradley and Chapelle, 1996], or fermentative microorganisms [Bradley, et al., 1998]. This study has contributed to our understanding of the dynamics of GSIs with respect to microbial activity and geochemistry, and points towards a possible role of methane-oxidizers in mitigating chloroethene imparted toxicity.

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Natural Attenuation of Chlorinated Solvents in a Freshwater Tidal Wetland, Aberdeen Proving Ground, Maryland

By Michelle M. Lorah and Lisa D. Olsen

Ground-water contaminant plumes that are flowing toward or currently discharging into wetland areas present unique remediation problems because of the hydrologic connections between ground water and surface water and the sensitive habitats in wetlands. Because wetland sediments typically have a large diversity of microorganisms and redox conditions that could enhance biodegradation, they are ideal environments for natural attenuation of organic contaminants. “Natural attenuation” is a general term that includes all naturally occurring physical, chemical, and biological processes that can reduce contaminant concentrations or toxicity without human intervention. Biodegradation generally is considered the most important of these processes for ground-water remediation purposes because it is a destructive process, unlike sorption, dilution, or volatilization. Natural attenuation is a treatment method that would leave the ecosystem largely undisturbed and be cost-effective. In this research, the natural attenuation of chlorinated volatile organic compounds (VOCs) was studied in a contaminant plume that discharges from a sand aquifer to a freshwater tidal wetland at Aberdeen Proving Ground, Maryland (Lorah, et al., 1997).

Biodegradation processes of two of the major contaminants, trichloroethylene (TCE) and 1,1,2,2-tetrachloroethane (PCA), are the focus of this combined field and laboratory study. The fate of PCA in the wetland is particularly emphasized in this research because the occurrence and dominant pathways of PCA degradation in ground water or soil were largely unknown. The few previous studies on PCA degradation were laboratory experiments that were constructed with anaerobic mineral medium or glass beads and seeded with mixed cultures from municipal sludge waste, or with abiotic aqueous mixtures of transition-metal coenzymes (Lorah, et al., 1997). The general field approach used in this study included (1) installing nested drive-point piezometers to characterize the ground-water chemistry and contaminant distribution along two transects through the wetland (one shown in Figure 1), and (2) using porous membrane sampling devices (peepers) to obtain centimeter-scale resolution of contaminant distribution in the wetland porewater. The general laboratory approach included conducting batch microcosm experiments with wetland sediment and porewater under methanogenic, sulfate-reducing, and aerobic conditions to confirm field evidence of biodegradation pathways, investigate potential controlling factors on biodegradation, and estimate biodegradation rates.

Field evidence collected along the two ground-water flowpaths shows that anaerobic biodegradation of TCE and PCA is enhanced in the wetland compared to the aquifer sediments (Lorah, et al., 1997; Lorah and Olsen, in press). The enhanced biodegradation is associated with the natural increase in dissolved organic carbon concentrations and decrease in redox state of the ground water along the upward flow direction in the wetland sediments. The aquifer typically is aerobic. Iron-reducing conditions are predominant in the lower wetland sediment unit composed of clayey sand and silt, and methanogenesis was predominant in an upper unit composed of peat (Figure 2). A decrease in concentrations of TCE and PCA and a concomitant increase in concentrations of anaerobic daughter products occurs along upward flowpaths through the wetland sediments (Figures 1 and 2). The daughter products 1,2-dichloroethylene (1,2-DCE), vinyl chloride (VC), 1,1,2-trichloroethane (1,1,2-TCA), and 1,2-dichloroethane (1,2-DCA) are produced from hydrogenolysis of TCE and from PCA

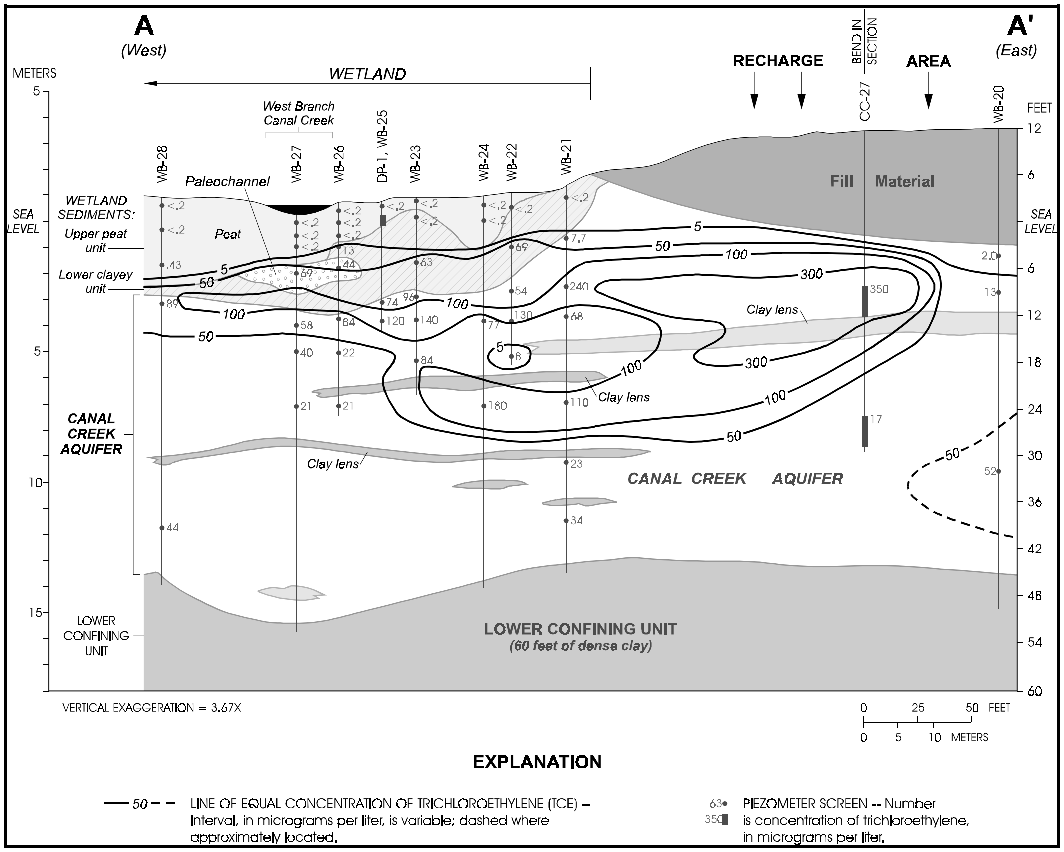

Figure 1. Concentrations of TCE in ground water along section A-A′, June-October 1995.

degradation through hydrogenolysis and dichloroelimination pathways. Total concentrations of TCE, PCA, and their degradation products, however, decrease to below detection levels (generally less than 0.5 µg/ℓ) within 0.15 to 0.30 m of land surface. Natural attenuation in the wetland sediments seems to be effective even where relatively high concentrations of VOCs are discharging upward through very thin (less than 2 m) layers of wetland sediment and when microbial activity probably decreases during cooler seasons (Lorah, et al., 1997; Lorah and Olsen, in press). Field evidence indicates that highly reducing conditions are not necessary for dichloroelimination of PCA to 1,2-DCE, or for hydrogenolysis of PCA to 1,1,2-TCA and then to 1,2-DCA. Maximum concentrations of VC, however,

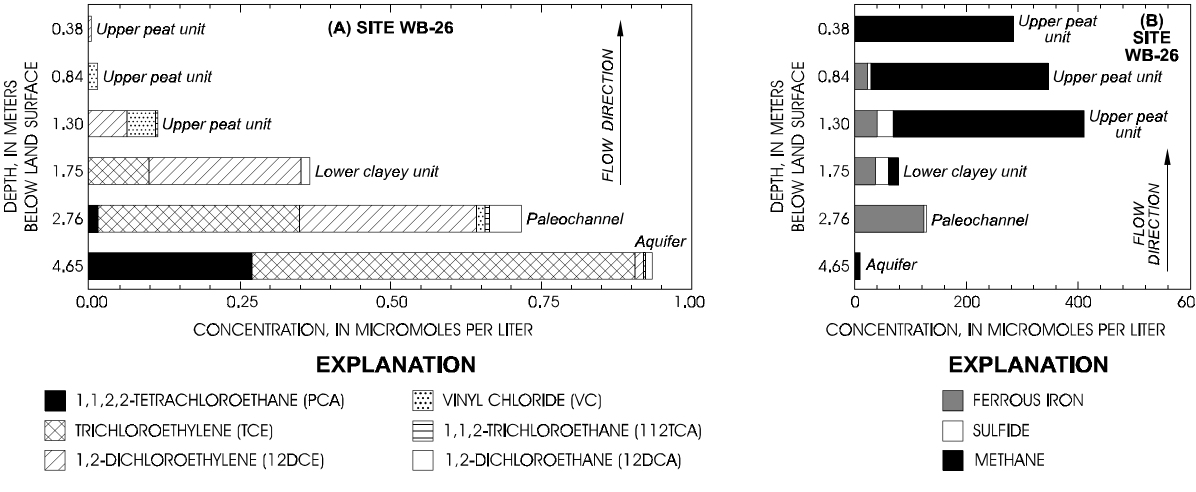

Figure 2. Vertical distribution of **(A)** the parent contaminants TCE and PCA and possible anaerobic daughter products and **(B)** selected redox-sensitive constituents at site WB-26, June-October 1995.

coincided with the highest concentrations of methane in the wetland porewater, indicating that continued anaerobic degradation of 1,2-DCE to VC and of VC to the non-toxic end-product of ethylene may require the highly reducing conditions of methanogenesis.

Laboratory microcosms that were prepared using wetland sediment and ground water from the site confirmed field evidence of biodegradation pathways and allowed estimation of biodegradation rates (Lorah, et al., 1997). TCE biodegradation occurred through hydrogenolysis to 1,2-DCE (predominately the *cis* isomer) and VC under methanogenic (Figure 3) and sulfate-reducing conditions. For PCA degradation under methanogenic conditions, the *cis* and *trans* isomers of 1,2-DCE and VC were the predominant persistent daughter products in one set of microcosm experiments (Lorah and Olsen, 1999) (Figure 3). In two sets of later experiments, however, 1,2-DCA was the predominant persistent daughter product from PCA and 1,1,2-TCA degradation under methanogenic conditions. The differences between the experiments seemed to result from differing pathways of 1,1,2-TCA degradation, rather than from differences in the initial PCA degradation pathway. 1,1,2-TCA was produced simultaneously with 1,2-DCE early in the time course in all experiments. The 1,1,2-TCA produced from hydrogenolysis of PCA was degraded by dichloroelimination to VC in the first experiment, whereas it was degraded by continued hydrogenolysis to 1,2-DCA in the second and third experiments. Natural temporal or spatial variations in the microbial populations in the wetland sediments may have caused the differing degradation pathways in these experiments.

In all PCA-amended microcosms, 1,1,2-TCA occurred simultaneously with 1,2-DCE early in the time course, indicating that hydrogenolysis and dichloroelimination of PCA can occur simultaneously (Lorah and Olsen, 1999). Significantly lower ratios of *cis*-1,2-DCE to *trans*-1,2-DCE were produced by dihaloelimination of PCA than by hydrogenolysis of TCE (Figure 3). Only one other study, which was conducted in the laboratory using anaerobic municipal sludge, has reported evidence for both of

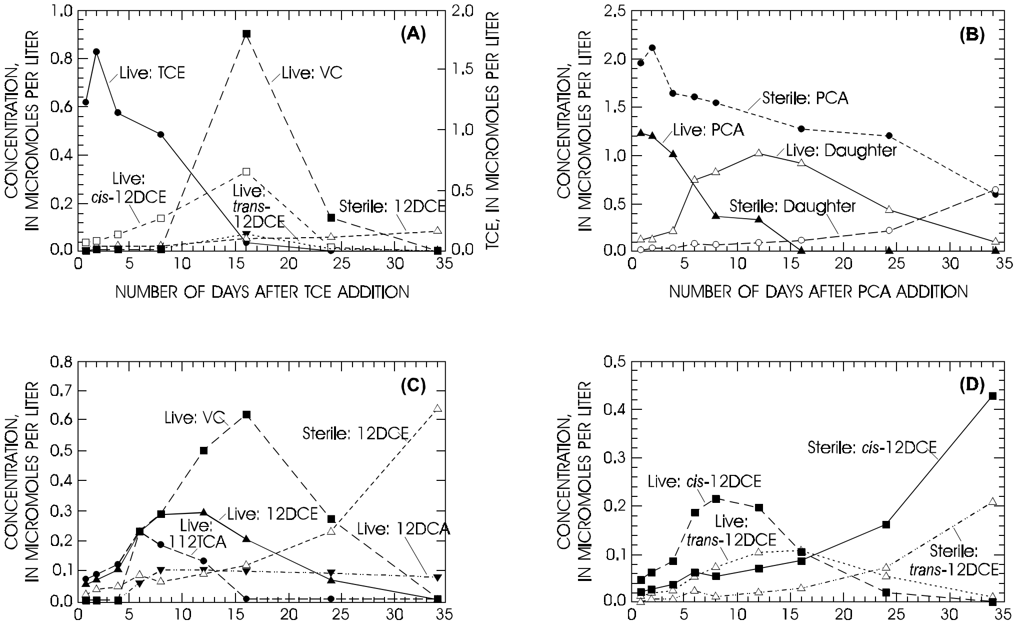

Figure 3. Degradation under methanogenic conditions in microcosms amended with 3.0 µmol/L of TCE or 2.9 µmol/L of PCA at day 0: **(A)** TCE and the daughter products *cis*-12DCE, *trans*-12DCE, and VC in the TCE-amended microcosms; **(B)** PCA and the sum of daughter products in the live PCA-amended microcosms and formalin-amended controls; **(C)** daughter products 12DCE (total of the *cis* and *trans* isomers), VC, 112TCA, and 12DCA in the PCA-amended microcosms; and **(D)** *cis*-12DCE and *trans*-12DCE in the PCA-amended microcosms. [The concentrations shown are the average measured in duplicate microcosms sacrificed at each time step.]

these PCA degradation pathways (Chen, et al., 1996). Recognition of the dichloroelimination pathway for PCA is important because TCE is a common co-contaminant with PCA at this site and other hazardous-waste sites. The 1,2-DCE isomer distribution potentially could assist in determining whether PCA degradation is occurring at sites where TCE is a co-contaminant. In the PCA-amended microcosms with the wetland sediment, TCE production commonly was less than 5 % of the initial PCA concentration in the live and sterile microcosms, showing that abiotic dehydrochlorination is not a significant degradation pathway for PCA in this environment.

Under methanogenic conditions, first-order biodegradation rates of TCE ranged from 0.30 to 0.37 day^{-1} (half-life of about 2 days), showing extremely rapid biodegradation in these organic-rich wetland sediments. Although the TCE biodegradation rate was an order of magnitude slower under sulfate-reducing conditions (0.032 day^{-1}) than methanogenic conditions, the rate was still two orders of magnitude higher than those reported in the literature for anaerobic TCE biodegradation in microcosms constructed with sandy aquifer sediments (Rifai, et al., 1995). The slow production and degradation of 1,2-DCE and VC in TCE-amended microcosms that were incubated under sulfate-reducing conditions or with the addition of an inhibitor of methanogenic activity confirmed field evidence that methanogenic activity is important in continued anaerobic degradation of these daughter products.

First-order rate constants for anaerobic degradation of PCA and 1,1,2-TCA ranged from 0.15 to 0.58 day^{-1} (half-lives of 1.2 to 4.6 days), again showing that biodegradation of highly chlorinated VOCs is extremely rapid in the wetland sediments. Similar PCA degradation rates were observed under methanogenic and sulfate-reducing conditions, although methane production and sulfate reduction occurred simultaneously during the first 15 days of incubation in the microcosms that were amended with sulfate to stimulate sulfate-reducing conditions. The addition of an inhibitor of methanogenic activity to PCA-amended microcosms decreased the methane production rates by a factor of 10 and caused a nearly 50% decrease in the PCA degradation rate compared to microcosms without the inhibitor. In addition, the production and subsequent degradation of the daughter products 1,2-DCA, 1,2-DCE, and VC were slower when methanogenic activity was inhibited in the PCA-amended microcosms. Both the TCE-amended and PCA-amended microcosm experiments, therefore, indicate that complete anaerobic degradation of the chlorinated VOCs is most rapid when methanogenic activity is high.

Although the wetland sediments have predominantly anaerobic conditions, aerobic conditions may be present in surficial sediments near the air-water interface and in subsurface sediments near plant roots, providing a suitable environment for methanotrophs that can degrade chlorinated VOCs through cometabolic oxidation (Lorah, et al., 1997). Although coupling of anaerobic and aerobic degradation processes has been suggested as the best possible bioremediation method for chlorinated VOCs such as TCE, few studies have investigated the degradation of TCE under both anaerobic and aerobic conditions for a natural subsurface setting. In aerobic microcosm experiments with the wetland sediment, biodegradation of *cis*-1,2-DCE, *trans*-1,2-DCE, and VC only occurred if methane consumption occurred, indicating that methanotrophs were involved. Aerobic biodegradation rates for *cis*-1,2-DCE, *trans*-1,2-DCE, and VC were in the same range as those measured for TCE and PCA under anaerobic conditions. Production of these anaerobic daughter products of TCE and PCA, therefore, could be balanced by their consumption where methanotrophs are active in the wetland sediment, including near land surface and in the rhizoplane and root tissues of aquatic plants in wetlands (Lorah, et al., 1997).

In summary, biodegradation through both anaerobic and aerobic processes is a significant natural attenuation mechanism for chlorinated hydrocarbons in these wetland sediments, causing a reduction in contaminant concentrations and toxicity before surface-water receptors are reached. This combined field and laboratory study provides a general approach and scientific basis for investigating the feasibility of natural attenuation as a remediation alternative for other sites where ground-water plumes discharge to wetlands and similar organic-rich environments at ground-water/surface-water interfaces. Because conditions in the wetland sediments are naturally conducive to biodegradation of the chlorinated VOCs in the discharging ground water, biodegradation could potentially be sustained indefinitely, unlike many ground-water environments where biodegradation commonly is limited by the supply of organic substrates. The results of this study also increase our understanding of the fate of chlorinated VOCs in the environment, providing information beneficial in characterizing contaminant behavior and in implementing bioremediation systems for other ground-water contaminant plumes.

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Discharge of Contaminated Ground Water to Surface Water: An Ecological Risk Assessment Perspective

By Mary Baker Matta and Tom Dillon

INTRODUCTION/OVERVIEW

The ecological risk associated with the discharge of contaminated ground water to surface water may be difficult to evaluate at complex hazardous waste sites. However, at many sites, groundwater discharges provide a significant pathway for contamination to reach ecological receptors. Although EPA has guidance for generic risk assessment, and has specific guidance for ecological risk assessments at CERCLA sites, specific guidance on how to evaluate ecological risk of groundwater discharges is lacking.

The hyporheic zone connects the ecological communities in ground water, sediment, and surface water. Although benthic macroinvertebrate communities are often considered in ecological risk assessments (and they may be adversely affected by contamination in the hyporheic zone), microbial communities of the hyporheic zone are rarely considered receptors of concern in ecological risk assessments. Because groundwater discharges contribute to sediment and surface water contamination they also have the potential to adversely affect fish and other aquatic species, particularly where bioaccumulative compounds are released or where sensitive life stages are in close proximity to groundwater discharge points.

The nature and extent of the contamination present in groundwater and characteristics of the ecosystem will determine what and where to sample, and what tests should be conducted to evaluate ecological risk and develop protective cleanup levels if risk is significant. Natural attenuation is increasingly considered as a remedial option at many sites. Natural attenuation is influenced by microbial activity and physico-chemical characteristics of the groundwater and its movement. Therefore, if natural attenuation is to be considered as a viable remedial option, the microbial community in the hyporheic zone should be protected, and its role in chemical fate and transformation should be assessed. At sites where ecological risk is significant, more active cleanup measures may be necessary to protect natural resources.

NOAA’s experience in aquatic ecological risk assessment is applied in this poster to provide some recommendations for evaluating ecological risk of groundwater discharge to surface waters. This poster focuses on data needs and how to answer them, structured around the EPA risk assessment process.

RISK ASSESSMENT STEPS 1 AND 2: SCREENING LEVEL ECOLOGICAL RISK ASSESSMENT

NOAA prepares Coastal Hazardous Waste Site Reviews using available information to screen sites based on:

- proximity of the site to the coast or inland water bodies that support anadromous fish populations

- site history, contaminants that are likely to be or have been detected at the site
- potential contaminant migration pathways (including groundwater)
- presence of sensitive habitats or species near the site

This same information is required in screening level risk assessments.

Maximum contaminant concentrations in groundwater are screened by NOAA using a value ten times greater than chronic ambient water quality criteria to account for potential dilution when groundwater enters surface waters and to protect all aquatic species. Therefore, detection limits for chemical analysis of unfiltered groundwater should be less than 10 times chronic ambient water quality criteria to conduct this assessment. The most recent edition of Hazardous Waste Site Reviews (NOAA, 1997) indicates that groundwater discharges are a widespread problem for natural resources:

- At 10 of the 11 sites evaluated, groundwater is a potential pathway for contaminants to reach natural resources.
- At 8 of the 11 sites evaluated, concentrations in groundwater exceed screening levels.

Sites Reviewed in December, 1997

Region 1	Beede Waste Oil, Plaistow, NH
Region 2	V&M/Albaladejo Farms, Vega Baja, Puerto Rico
Region 3	Fort George G. Meade, Anne Arundel Co, MD
	Norfolk Naval Base, Norfolk, VA
	Salford Quarry, Lower Salford Townshp, PA
Region 4	Brunswick Wood Preserving, Brunswick, GA
	MRI Corp, Tampa, FL
	*Terry Creek Dredge Spoil/Hercules, Brunswick, GA
	Tyndall Air Force Base, Bay Co, FL
Region 6	Madisonville Creosote Works, Madisonville, LA
Region 10	Oeser Company, Bellingham, WA

*Groundwater not a significant pathway to natural resources

RISK ASSESSMENT STEP 3: BASELINE RISK ASSESSMENT PROBLEM FORMULATION

Steps**:**

- Refine list of contaminants based on screening
- Summarize toxicological effects
- Consider likely fate and transport of contaminants
- Determine receptors likely to be at risk
- Determine complete exposure pathways
- Develop conceptual site model with risk questions
- Develop assessment endpoints

Considerations specific to sites with groundwater contamination:

- Potential biogeochemical alterations of contaminants.
  - -persistent organic contaminants might be released as an LNAPL or DNAPL and bind to sediments as they are released to surface water.

  - Metals might be released in dissolved form and complex with other compounds at the discharge point, groundwater discharge to marine water may alter solubility of metals.
  - Groundwater discharge may leach metals from sediments.
  - Organic contaminants released in a solvent plume may be more bioavailable

- Conceptual model for the site should include pathways for exposure and mechanisms of toxicity for the contaminants and receptors specific to the site

- Consider characteristics of discharge specific to the regime:
  - groundwater discharge into intertidal zone at marine sites;
  - discharge into tidal creeks in salt marshes;
  - hyporheic zone in alluvial rivers as a function of channel morphology, bed roughness, and permeability (Triska, et al. 1989).

- Consider hyporheos as receptors of concern (macrofauna and microbes)

<u>Assessment Endpoints of General Concern to NOAA (with some specific examples)</u>

- Protection of benthic community structure and function
  (Protection of stonefly populations from direct toxic effects)

- Protection of aquatic community structure and function
  (Protection of fish eggs and larvae from direct toxic effects, including ecologically relevant sub-lethal effects)
  (Protection of hyporheic microbial community from direct toxic effects)

- Protection of fish populations and communities
  (Protection of fish from reproductive effects)
  (Protection of fish from immune system disruption)
  (Protection of fish from reductions in survival and growth)

- Protection of specific habitat functions (for example, nutrient cycling)
  (Protection of hyporheic microbial community from direct toxic effects)

- Protection of fishery resources from contamination
  (Protection of human health from exposure to bioaccumulated contaminants)

RISK ASSESSMENT STEPS 4, 5, AND 6: STUDY DESIGN/DATA QUALITY OBJECTIVES/FIELD VERIFICATIONS/SITE INVESTIGATIONS

<u>Steps</u>

- Evaluate uncertainty in existing data
- Develop measurement endpoints to evaluate assessment endpoints
- Develop work plan to evaluate exposure and effects
  - methods
  - statistical considerations
  - sampling locations, timing, frequency

- Verify sampling design
- Site investigation
- Data analysis

Considerations specific to sites with groundwater contamination:

- Evaluating exposure potential is a major concern; need to determine nature and extent of contamination and factors that may control bioavailability and toxicity:
  - Discharge locations
  - Flux of contaminants
  - Form/speciation of contaminants
  - Presence of non aqueous phase layers (NAPL)
  - Potential contaminant interactions, for example enhanced transport of hydrophobic (biomagnifying) contaminants in a dissolved solvent plume

- NOAA recommends a weight of evidence approach based on:
  - Groundwater models predicting a vector discharge to surface water
  - Remote sensing and geological analysis: identification of paleochannels using ground-penetrating radar; location of surface depressions, abandoned meander channels to locate springbrooks through aerial photography (Stanford and Ward, 1993).
  - Developing a water budget - upstream/downstream gauging, tracer studies
  - Changes in water quality parameters due to groundwater discharge (temperature, pH, conductance, nutrients, DOC, oxygen (Triska, et al., 1989).
  - Direct measurements

- Specific effects measurements will be a function of receptors of concern; contaminants; and exposure pathway
  - Benthic macroinvertebrates-generally a concern for direct toxicity via surface water or sediment contamination as a result of groundwater discharges
  - Microbes-generally a concern for direct toxicity of groundwater, pore water, or surface water
  - Fish- may include a concern for direct toxicity of pore water or surface water to early life stages (for example, where dissolved metals are discharged) or a concern for indirect toxicity after contamination of sediment and food organisms.

- Groundwater and NAPL can contaminate sediments and surface water

- Ecological risk associated with sediment contamination is usually evaluated via
  - chemical analysis of sediment (focus on persistent contaminants)
  - toxicity testing
  - benthic community evaluations
  - chemical analysis of biota for bioaccumulative contaminants
  - comparisons of tissue concentrations to literature effects thresholds
  - food web modeling for persistent bioaccumulative contaminants

- Ecological risk associated with water contamination is usually evaluated via
  - chemical analysis of water (focus on persistent contaminants or continuous releases of less persistent contaminants)

  - -aquatic toxicity tests
  - -comparisons of water concentrations to literature or AWQC benchmarks.

- Sampling and analysis concerns:
  - -number and locations of samples should be adequate to evaluate exposure potential and minimize uncertainty (plumes should be characterized, and locations where sensitive receptors would be exposed should be sampled)
  - -seasonal considerations affecting groundwater flow or the seasonal presence of sensitive receptors may require multiple sampling events
  - -analyze filtered and unfiltered water (organisms are exposed to both)
  - -analyze pore water where appropriate for the receptor (fish eggs, for example)
  - -collect ancillary data that can be used to interpret bioavailability, toxicity, and potential for natural attenuation (sediment grain size, sediment total organic carbon, acid volatile sulfides, dissolved organic carbon, nutrients, alkalinity, dissolved oxygen).
  - -use detection limits low enough to compare to benchmarks
  - -consider metal speciation and effects on bioavailability and toxicity
  - -selection of reference sites is critical in evaluating exposure and effects (reference sites should be similar to the study site, but located away from point sources of contamination)

RISK ASSESSMENT STEP 7: RISK CHARACTERIZATION

<u>Steps</u>**:**

- Interpreting data
- Tracking sources
- Modeling mass flux
- Modeling food web effects
- Reducing and incorporating uncertainty
- Applying protective assumptions
- Interpreting the weight of evidence
- Developing cleanup levels

<u>Considerations specific to sites with groundwater contamination:</u>

- Interpreting data
  - -agree on interpretive methods before collecting data
  - -compare results to benchmarks, control samples, and reference site results
  - -consider normalizing data to nutrients, grain size, or other factors
- Source tracking (relative contribution of groundwater and surface releases) is important to ensure success of the remedy (in terms of reducing risk to ecological receptors). Consider the potential for recontamination through ongoing groundwater discharge.
- Models on groundwater discharge rates and contaminant loading are usually highly uncertain, therefore, to be protective, conservative assumptions must be made until better techniques, data, and models are available.
- Conduct specific studies to determine the potential for natural attenuation, which is driven largely by microbes and their physico-chemical environment (consider the specific types of microbes required to degrade contaminants at the site; some require aerobic).

- Water quality and sediment goals for receptors can be empirically derived from toxicity tests but back calculating for groundwater quality goals requires a good model

Examples:

At the Metal Bank of America site in Philadelphia, PA, the primary pathway for contaminants to reach natural resources was through discharge of contaminated groundwater and non-aqueous phase layer. PCBs accumulated in sediment, clams, and fish near the site to concentrations that were determined to pose significant risk.

RISK ASSESSMENT STEP 8: RISK MANAGEMENT

Considerations specific to sites with groundwater contamination:

- Potential for recontamination- uncontrolled groundwater discharges have the potential to interfere with a sediment remedy
- Monitoring-the effects that drove the selection of the remedy should be incorporated into monitoring, significant ongoing exposures should be monitored over time and re-evaluated

CONCLUSIONS/RECOMMENDATIONS

- Potential for groundwater to provide a contaminant pathway to aquatic species should be considered, it seems to be a problem throughout the country in all regions examined.
- NOAA screens GW for potential concern using 10 times chronic AWQC values
- Detection limits for unfiltered groundwater should be low enough to conduct this screening
- Consider potential biogeochemical alterations and complex interactions between contaminants.
- Consider characteristics of discharge specific to the regime:
- Consider hyporheos as receptors of concern (macrofauna and microbes)
- Use multiple methods and a weight of evidence to evaluate exposure potential (discharge locations and contaminant fluxes)
- Evaluate potential for bioaccumulation and food web effects

- Specific sampling and analysis methods will depend on characteristics of contaminants and receptors at the site (but consider seasonal variations and sample in such a way as to provide information relevant for the behavior of the organisms at the site)

- **A critical need is to reduce uncertainty in risk conclusions: better methods are needed to locate and quantify contaminant flux from groundwater to surface water**

- Until better data is available, protective assumptions should be used to evaluate risk to natural resources

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Defining Groundwater Outcrops in West Neck Bay, Shelter Island, New York Using Direct Contact Resistivity Measurements and Transient Underflow Measurements

By Ronald Paulsen

ABSTRACT

Mapping out groundwater discharge zones can be a formidable task due to the highly variable nature of the discharge zone, temporal and spatial variability of seepage rates within the zone, and complications from tidal loading. An integrated approach incorporating direct contact resistivity logging and transient seepage rate measurements was undertaken to delineate the seepage zone and monitor discharge on a bay-wide scale. Conductivity values for the saturated sediments ranged from 280 S/cm in freshwater zones to 12,800 S/cm in zones with high salinity. The discharge zone at West Neck Bay, Shelter Island was observed to extend to 10-75 feet offshore. The groundwater seepage within the discharge zone was measured using a time transient seepage meter that was developed with ultrasonic technology. Seepage velocities in the study area ranged from 1.27×10^{-3} cm/s to 3.94×10^{-5} cm/s, equivalent to a mean value of 16 ℓ/m^2/d. Integrating over the horizontal extent of the seepage zone, the total daily discharge was estimated to be 1.72×10^{6} ℓ/day for the north-east section of West Neck Bay. This estimate of the total discharge due to underflow is comparable to the recharge in the contributing area, estimated to be 1.50×10^{6} ℓ/day for this section of the bay.

DIRECT CONTACT RESISTIVITY MEASUREMENTS

To characterize near-shore sediments in a simple and rapid manner, we used geophysical logging to determine the electrical resistivity of surface sediments off-shore. Electrical measurements have been used for some time to characterize the lithology and hydraulic characteristics of geological structures. The basic concept of resistivity logging dates back to 1927 when C.M. Schlumberger made the first well log near Paris (Goldberg, 1997). Conductivity generally increases with increasing porosity (Gueguen and Palciauskas, 1994). Archie (1942) invoked laboratory measurement of conductivity to infer amounts of water and hydrocarbons in the pore space. The electrical conductivity of saturated sediment is commonly analyzed in terms of the formation factor F as a function of the porosity where $_s$ is the electrical conductivity of the saturated bulk sediment, $_w$ is that of the interstitial solution, and the Archie exponent $n \sim 1\text{-}2$. Archie's law is applicable when the conductivity of the interstitial solution is much higher than that of the sediment particles, so those surface conduction phenomena are insignificant.

At off-shore locations where groundwater discharge is negligible, resistivity measurements of the sea water and sediments saturated by water of identical salinity can be used to determine the formation factor and infer the porosity from Archie's law (Aller 1982). In sediments where freshening of the pore spaces has occurred due to groundwater discharge, the measurements usually show a decrease of electrical resistivity with depth, which provides important qualitative constraints on the increase of salinity in the pore fluid and the depth range over which the transition from fresh to sea water occurs.

Several different electrode configurations are commonly used to measure electrical resistivity. Our project employs a direct contact probe (Figure 1) arranged in a Wenner array, which is a non-linear array with the potential electrodes placed close together and evenly spaced. This configuration provides discrete measurements even if good contact is not always maintained. Electrode *A* and *B* are the positive and negative electrodes that measure the current *I*, and *M* and *N* are the electrodes that measure the voltage drop *V* (Figure 2).

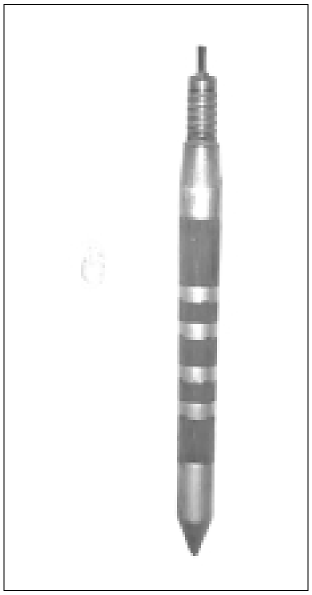

Figure 1.

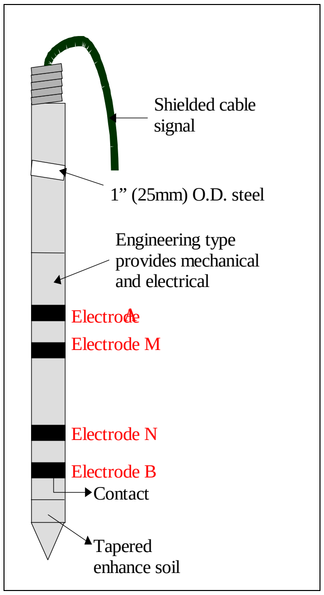

Figure 2.

The off-shore horizontal extent of the interface was delineated by direct contact resistivity measurements. The resistivity probe was driven manually into the bay bottom by scuba divers at six-inch increments. The unit’s string pot (that was originally designed for use with a Geoprobe percussion drill keeps track of the depth measurement automatically and also trigger the electrical measurement) had to be modified accordingly. The string pot was mounted on a jig and manually moved along a displacement that would coincide with the depth that the probe was being driven into the bottom sediments. Resistivity measurements were also simultaneously triggered manually. After the resistivity was logged, the diver then drove the probe to the next six-inch level. This continued until a freshwater zone was contacted or the probe had been driven to a maximum depth of 4 ft. The diver then moved on to the next off-shore position at a horizontal spacing of ~30 feet, and the manual probing and logging operations were repeated.

Cross-sectional plots as shown in Figure 3 where prepared from the field measured resistivity of bay bottom sediments off shore. The blue (dark) areas indicate the location of fresh water outcrops off-shore and the red (light) areas indicate only saltwater is present.

DESCRIPTION OF GROUNDWATER UNDERFLOW DEVICE

In recent years ultrasonic flow meters have been developed and used to measure relatively low flow rates in a variety of water and wastewater industries. In this study we take advantage of this advancement in ultrasonic technology to develop a seepage meter for continuous measurement of submarine groundwater discharge.

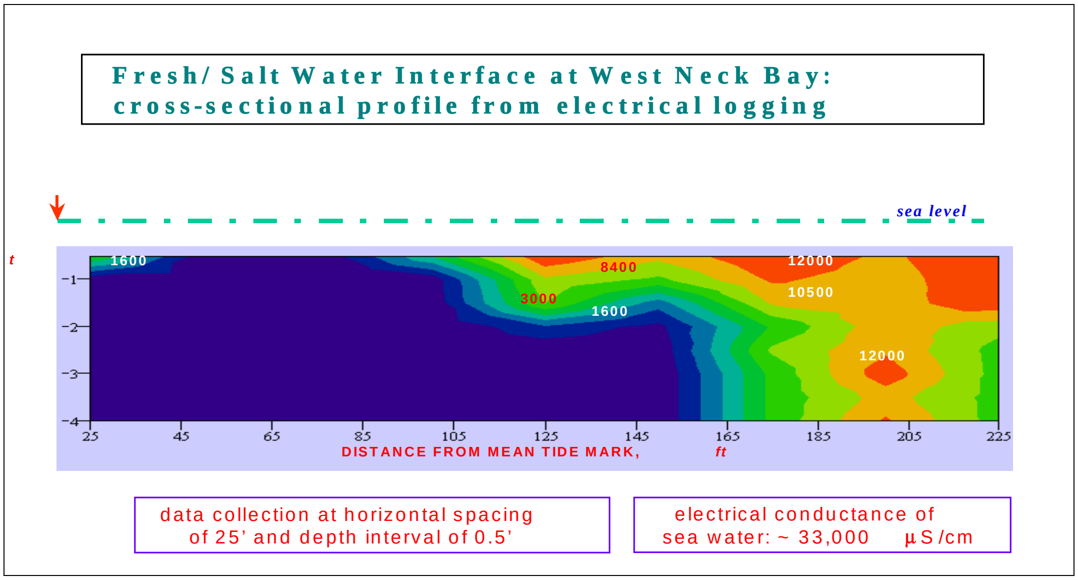

Figure 3.

A transient-time flow meter uses the effect of the flow on the travel time of an ultrasonic signal as the bases for determining the flow rate. Figure 4 shows a cross section of the meter with the path of the flow tube sonic beam and non-intrusive transducers. A multi-pulse sonic signal is transmitted through the flow tube in both directions by transducers located at opposite ends. When there is no flow the signal will arrive at each transducer at the same time. However, when there is flow in the tube the upstream flow will cause the signal to arrive ahead of the signal traveling downstream. The difference in transit times (t) between the two signals is proportional to the liquid's flow velocity V_f. The constant of proportionality depends on the average of the upstream and downstream transit times and length L of the tube. The specific discharge from the seepage surface q is inferred from the flow velocity by multiplying V_f by the ratio between the areas of the flow tube and the collection funnel.

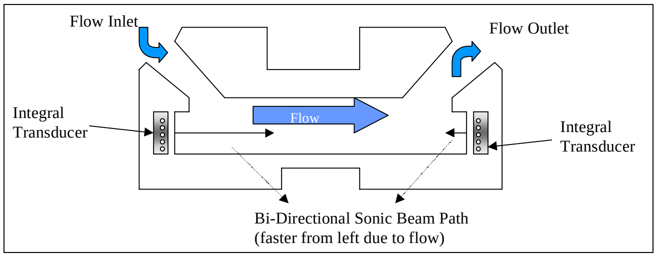

Figure 4.

Our seepage meter system is based on the widely used technique of placing a funnel (24" x 24") into the seepage surface on the seabed to capture submarine groundwater discharge (Figure 5). This seepage flow is then directed via tubing through the ultrasonic meter, which is connected to a data logger. The sampling frequency and duration are programmed into the logger by the investigator. This meter can resolve seepage rates on the order of 10^{-6} cm/s, detect reversals in flow, and it includes a totalizer which acquires data on cumulative volume of water passing through the meter which (when after normalized by the collection funnel area) provides the specific discharge.

CONCLUSION

This study has demonstrated the feasibility of using a methodology that integrates geophysical logging and transient seepage measurement to map out the spatial distribution of seepage and measure the underflow discharge in real time. Conductivity values for the saturated sediments were observed to range from 280 µS/cm in freshwater zones to 12,800 µS/cm in zones with high salinity. The discharge zone at West Neck Bay, Shelter Island was observed to extend to 10-75 feet offshore. Electrical conductivity profiles of the coastal system obtained by direct-contact resistivity logging delineates in cross-section the subset of pore water that has been subjected to significant freshening, and in turn they provide important constraints on the geometry of the fresh/salt water interface and the mechanisms of mixing.

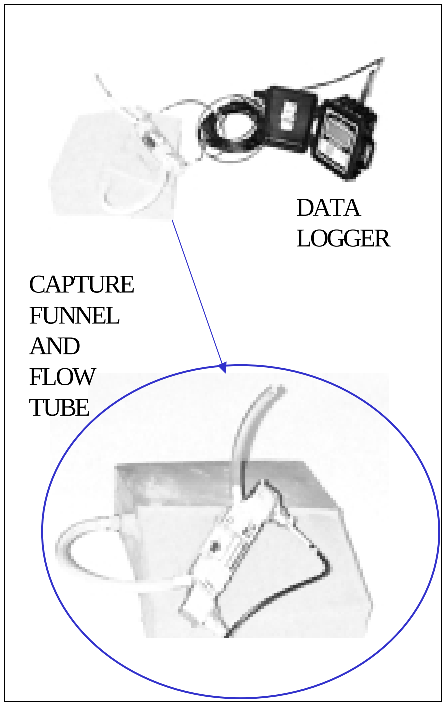

Figure 5.

While the resistivity logging is very effective in identifying key areas with pronounced seepage, continuous measurements using the ultrasonic seepage meter provide high-resolution data on the discharge in real time. Relatively high seepage velocities ranging from 1.27 x 10^{-3} cm/s to 3.94 x 10^{-5} cm/s (with a mean value equivalent to 16 ℓ/m^2/d) were measured in the study area (Figure 6). The input of underflow to the hydrological budget was evaluated. Integrating over the projected area of the seepage zone, the total daily discharge was estimated to be 1.72 x 10^6 ℓ/day for the northeast section of West Neck Bay. This estimate of underflow discharge is comparable to the recharge in the contributing area, estimated to be 1.50 x 10^6 ℓ/day for this section of the bay (Schubert,1998).

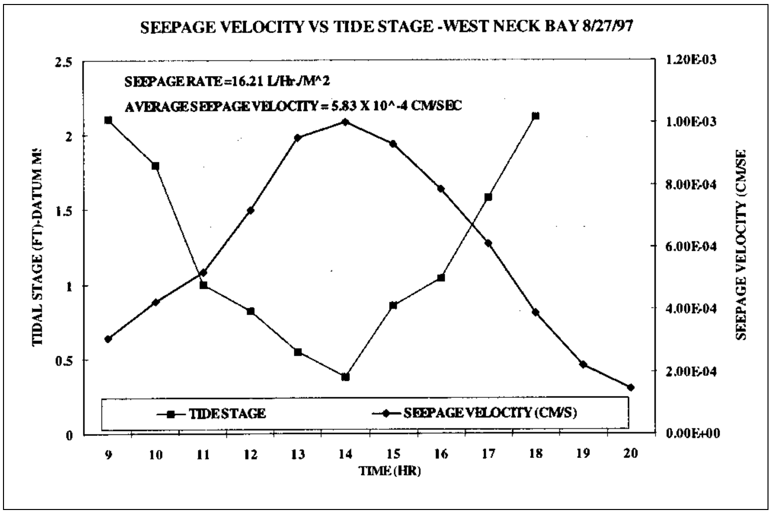

Figure 6.

The techniques used for this investigation were effective in defining the spatial extent of the off shore groundwater seepage zone and in measuring the flux within that zone (Shaw and Prepas, 1989). The investigator working within this dynamic and spatially variable zone are advised to use extreme caution in their interpretation of any field measurements. Adequate numbers and replications of groundwater seepage measurements need to be taken in order to in order to address the spatial variability of the bay bottom and changes in near shore hydraulic gradients associated with tidal flux and precipitation.

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Influence of Stream Orientation on Contaminated Ground-Water Discharge

By Don A. Vroblesky

The discharge zones of contaminated ground water are often beneath surface-water bodies. Such discharge zones have been identified by using analyses of bottom-sediment gas bubbles (Vroblesky and Lorah, 1991) and have been mapped using diffusion samplers in shallow Coastal Plain aquifers (Vroblesky and others, 1991; 1992) and in a fractured-rock aquifer (Vroblesky and others, 1996). In this paper, analyses of diffusion samplers buried beneath a gaining stream were used to investigate the relation between stream orientation and ground-water contaminant discharge.

Many environmental factors have the potential to influence the locations of contaminant discharge to surface water. These factors include preferential ground-water flow from one side of the creek, channeling of contaminants by fractures or other permeability heterogeneities, or capture of contaminants by vegetation near the stream. The purpose of this report is to present preliminary data suggesting that stream-channel orientation relative to the ground-water flow direction also is an influential factor affecting contaminant discharge from ground water to surface water.

The approach used to delineate areas of contaminated ground-water discharge to surface water involved the installation of diffusion samplers in the bottom sediment of Huntington Downs Creek, in Greenville, South Carolina. The diffusion samplers consisted of 40-mℓ (milliliter) glass vials enclosed in sealable polyethylene bags. Preparation, burial, recovery, and analysis of the diffusion samplers is described in an earlier study (Vroblesky and others, 1996). Samplers were buried approximately 1 ft (0.3 m) deep in the creek-bottom sediment, which consisted of sand or weathered rock. The origin point of the diffusion-sampler array in Huntington Downs Creek was a spring at the origin of the creek (Figure 1). The total length of the array was approximately 400 ft (122 m), ending at the discharge culvert to Huntington Downs Pond. The distance between samplers in each line was approximately 10 ft (3.048 m). The site identification numbers for the diffusion-sampler locations were the distance, in feet, along the creek channel downstream from the spring at the origin of the creek.

The diffusion samplers were installed in the creek bottom sediment on May 25, 1994, and recovered on June 1, 1994. Immediately upon removal of each diffusion sampler from the bottom sediment, the outer polyethylene membrane covering the vial opening was cut open, leaving the inner polyethylene membrane intact. A cap was screwed onto the diffusion sampler over the inner polyethylene membrane (the polyethylene was between the glass vial and the Teflon[1] septum of the cap). The samples were analyzed for volatile organic compound (VOC) content within 48 hours of sample collection. A 50-µL vapor sample was slowly withdrawn and immediately analyzed on a Photovac[1] 10S55 field gas chromatograph (GC), equipped with a capillary and a packed column. The total VOC analysis was accomplished by calibrating the GC against a 10-ppm vapor standard of trichloroethene (TCE). In this investigation, the difference between total VOC concentrations detected in diffusion samplers and their respective replicates ranged from 5 to 21 percent.

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[1] The use of tradenames does not imply endorsement by the U.S. Geological Survey.

Water-level measurements from an observation well near the source of the creek and an observation well downgradient from Huntington Downs Pond, and extrapolation of water-table contours based on measurements made in wells approximately 350 to 550 ft south of the creek (Rust Environment and Infrastructure, 1995) show that ground water near the creek moves generally north to northwestwardly, discharging to ponds and streams (Figure 1). The water-table distribution derived from these measurements is used in this investigation to show the probable dominant directions of ground-water flow in the vicinity of Huntington Downs Creek (Figure 2).

The shallow aquifer is composed of a silty clay saprolite containing relict metamorphic structures and rock fabrics. Estimates of hydraulic conductivity in the saprolite aquifer in the study area range from less than 2 ft/d (Rust Environment and Infrastructure, 1995) to about 3.2 ft/d Kubal-Furr and Associates, 1996). The estimated rate of ground-water flow in the saprolite aquifer (average thickness of approximately 40 ft) is about 76 ft/yr (Kubal-Furr and Associates, 1996). Steeply dipping relict fractures and foliation planes are present in the saprolite and appear to influence the direction of contaminant transport (Rust Environment and Infrastructure, 1995). Based on lithologic observations made during an excavation of the spring in August 1994, the spring appears to be the discharge zone of water-bearing relict fractures in the saprolite.

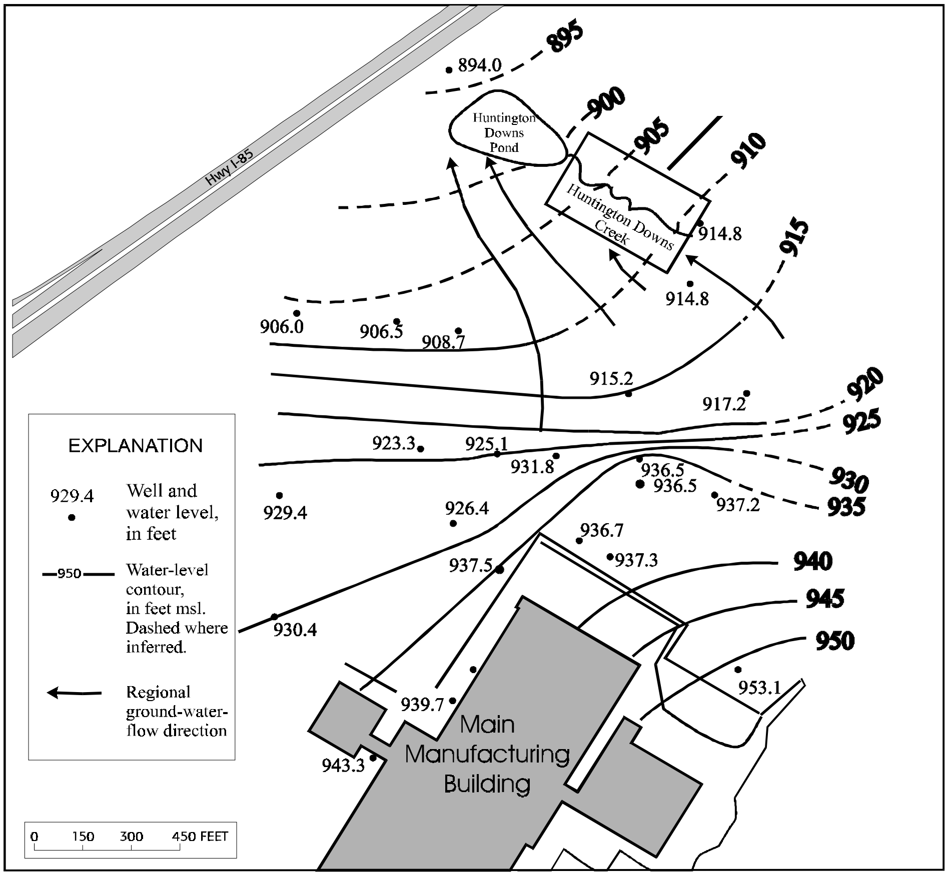

Figure 1. Ground-water flow directions near Huntington Downs Creek (Modified from Rust Environment and Infrastructure, 1995).

Analysis of the vapor in the diffusion samplers for total VOCs showed that the concentrations, as vapor, ranged from 0.3 to 21.2 ppm relative to TCE. Analysis of the vapor in diffusion samplers from

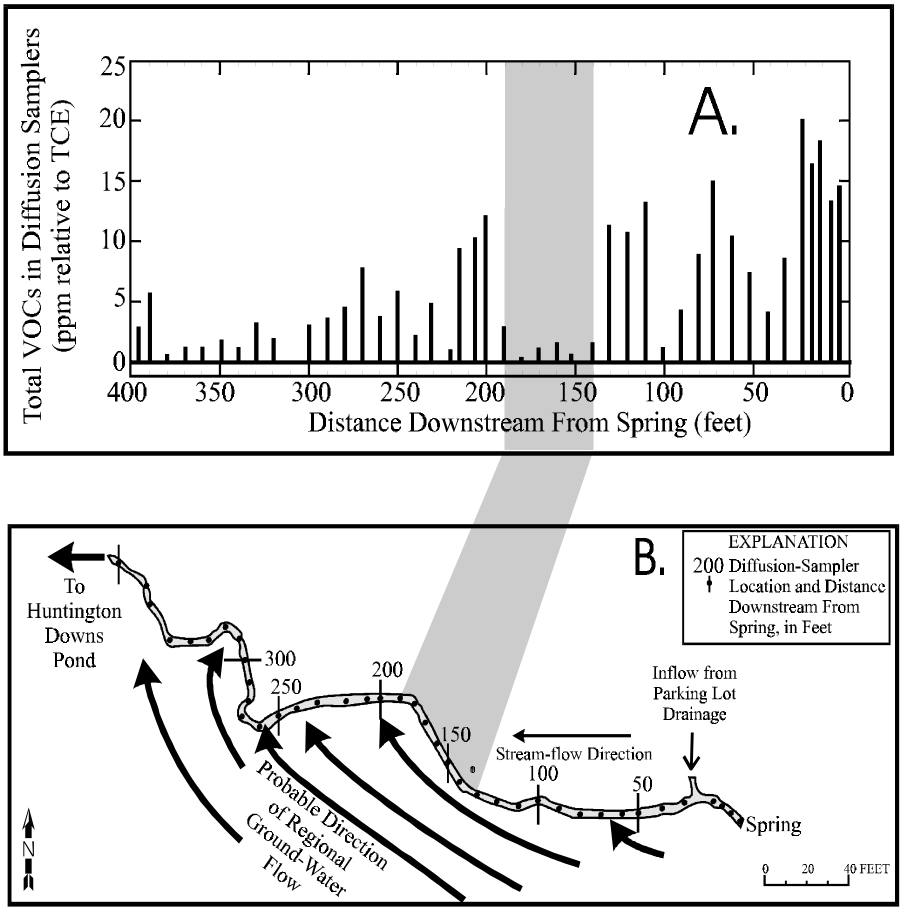

Figure 2. Concentrations of volatile organic compounds (VOCs) detected in vapor diffusion samplers beneath Huntington Downs Creek (A), and locations of samplers in creek (B), June 1994.

locations 21, 72, 110, 200, and 270 ft downstream from the spring, using the gas chromatograph coupled to a capillary column, indicated the presence of TCE and tetrachloroethene (PCE). A similar analysis on the vapor in the diffusion sampler from 349 ft downstream from the spring showed no detectable concentrations of TCE or PCE. Because the only known source for VOC contamination is south of the creek, the TCE and PCE detected in the diffusion samplers are considered to represent contaminated ground-water discharge from the southern side of the stream.

The highest concentrations of VOCs (16.6 to 21.2 ppm) detected in the diffusion samplers beneath the stream were found near the origin of the creek, approximately 16 ft downstream from the spring (Figure 2). The presence of a spring indicates that there is an upward hydraulic gradient from the ground water into the surface water. Therefore, the relatively high concentration of total VOCs in the ground water beneath the stream immediately downstream from the spring implies that contaminant discharge to the creek involved seepage of contaminated ground water upward through the stream bed as well as movement of contaminants into the stream via the spring.

The distribution of VOC concentrations in the diffusion samplers beneath the stream showed a general downstream decrease in the maximum concentrations detected (Figure 2). The concentrations of TCE and PCE in diffusion samplers also decreased downstream. Thus, the downstream decrease in maximum detected concentrations of total VOCs probably reflects a decrease in concentrations of ground-water contaminants along a flowpath away from the source. The overall distribution of VOC concentrations in the diffusion samplers, however, showed an irregular pattern, with areas of relatively low concentrations between areas of relatively high concentrations (Figure 2). For example, the concentrations of total VOCs in diffusion samplers in the reach between sampling points 140 and 190 were consistently less than 3 ppm; however, concentrations of total VOCs in diffusion samplers immediately upstream and downstream from that reach were greater than 10 ppm. In fact, concentrations of total VOCs in diffusion samplers between sampling points 140 and 180 were below the apparent background concentration measured at location 349, implying that there was no substantial discharge of chlorinated VOCs to the creek in that reach. A unique feature of the creek reach between sampling points 140 and 180 is that it is oriented approximately parallel to the probable dominant direction of ground-water flow. In contrast, the creek reach encompassing sampling points 50 to 90 and 200 to 250 are oriented at a sharper angle to the probable dominant direction of ground-water flow (Figure 2B). VOC concentrations in most diffusion samplers from those reaches were higher than in the reach encompassing sampling points 140 to 180 (Figure 2A).

A variety of factors potentially affect the distribution of contaminant discharge to a stream. Not all of the factors were identified in this preliminary investigation. For example, potential influences include bed-sediment heterogeneities, relict fractures, vegetation, and hyporheic zones. However, the uniformly low concentrations of total VOCs in the channel reach oriented approximately parallel to the probable dominant direction of ground-water flow (between diffusion samplers 140 and 190) compared to adjacent reaches oriented at a sharper angle to ground-water flow, strongly suggest that orientation of the creek exerts a major influence on contaminant discharge. Reaches of the creek that transect the axis of the contamination plume receive greater contaminant and ground-water discharge than the reach oriented along the axis of contaminant transport.

In conclusion, diffusion samplers placed beneath creek-bed sediments were used to detect the distribution of VOC contamination discharging from ground water to Huntington Downs Creek, in Greenville, South Carolina. The uniformly low concentrations of total VOCs in the channel reach oriented approximately parallel to the probable dominant direction of ground-water flow, between diffusion samplers 140 and 190, compared to adjacent reaches oriented at a sharper angle to ground-water flow, strongly suggest that orientation of the creek is a major influence on contaminant discharge. Reaches of the creek that transect the axis of the contamination plume appear to receive greater contaminant discharge than a reach oriented along the axis of contaminant transport. These data imply that site investigators attempting to locate zones of ground-water contaminant discharge to surface water in meandering streams should put particular emphasis on reaches transecting the dominant direction of contaminated-ground-water transport.

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Factors Controlling Hyporheic Exchange in a Southern Ontario Stream: Modeling Riffle-Scale Patterns in Three Dimensions Using MODFLOW

By R.G. Storey, D.D. Williams, and K.W.F. Howard

INTRODUCTION

The general pattern of exchange flow between stream surface waters and their hyporheic zones (Fig.1) has been observed in numerous field situations (e.g., Valett, et al., 1994), and in laboratory flume studies (e.g., Thibodeaux and Boyle, 1987). These latter studies have shown that the downwelling/upwelling sequence is produced by a rise in hydraulic head of the surface water as it rises over the surface of a riffle, and a rapid drop in head as surface water flows down the downstream slope of the riffle. Thus from a surface water point of view, the forces controlling the riffle-scale pattern of exchange flow have been adequately explained.

However, in the field situation hyporheic zones are subject not only to the forces applied by surface waters, but also to hydraulic gradients associated with the underlying aquifer. Stream reaches are rarely hydraulically neutral, but either receive net ground water inflow or export water to the aquifer. How then do riffle-scale exchange flows persist without being overwhelmed by net ground water movements?

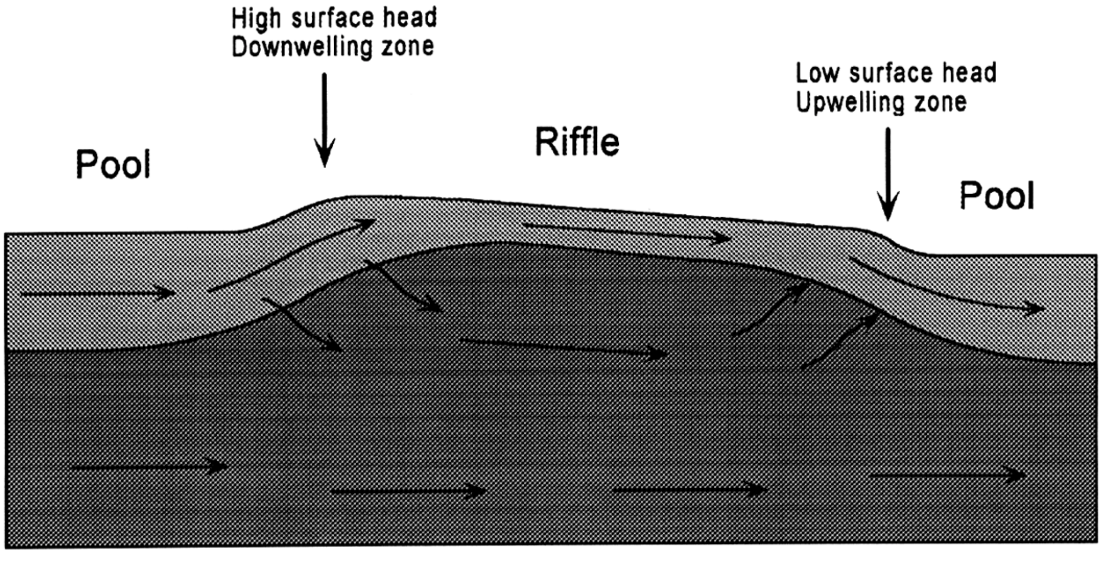

Fig. 1. Subsurface flow paths associated with pool/riffle sequences in rivers.

The aims of this study were first to determine the local geological and hydrogeological conditions necessary to produce riffle-scale exchange flows within a given regional hydrogeological environment.

A secondary aim was to determine how hyporheic exchange flows would be affected by natural changes or artificial disruptions to aspects of the aquifer, stream flow or stream bed.

METHODS

The Speed River, in Southwestern Ontario, is a low-gradient stream, approximately 6 m wide and 0.15-0.35 m deep at the study site. The primary aquifer, a dolomite bedrock, is overlain by 20 m of low permeability glacial kame deposits. The stream itself lies in a bed of modern alluvium 1-1.5 m deep, and extending 30-40 m wide on each side of the stream, which has a very high permeability.

An area of the river catchment, 1,000 m x 500 m, was modeled using MODFLOW (USGS), a three-dimensional finite difference ground water flow model. The two lateral boundaries of the model were defined by the Speed River catchment boundaries, and the upper and lower boundaries followed ground water flowlines. The model focused on a single riffle of the stream, a 10 m long section. Stream stage was defined by constant head boundaries in the top layer of the model, with a rise and fall of a few cm over the length of the riffle site.

RESULTS AND DISCUSSION

Initially the model was run without inserting the high conductivity alluvial deposits. In these runs hyporheic flows everywhere were upwelling, and towards the stream laterally, even when aquifer heads were low in summer.

When the zone of high permeability, representing alluvial deposits, was inserted around the stream, flow patterns changed dramatically. Hydraulic gradients within the near-stream zone became very low (<1 cm per m) and small differences of <3 cm in surface hydraulic head between upstream and downstream ends of the riffle produced downwelling and lateral exchange flows in the subsurface. This occurred even though hydraulic gradients in the material surrounding the alluvium were strongly towards the stream.

These results show that in a low gradient stream system with strong hydraulic gradients from the catchment towards the stream, exchange flows can still occur in a zone of high- permeability alluvium. The essential feature of this alluvium was that it lowered hydraulic gradients within the hyporheic zone to within the range of variation shown by the stream surface heads as they flowed between pools and riffles. Thus these variations were able to alter flow paths up to 1.5 m deep in the stream bed.

In reducing the vertical hydraulic gradient, the alluvium changed the dominant hydraulic gradient beneath the stream bed from almost vertical to almost horizontal. This meant that flows within the alluvium were driven by hydraulic heads downstream rather than by those in the underlying aquifer and surrounding catchment. The large flux of water flowing downstream within the alluvial sediments was able to supply or withdraw sufficient water to support lateral and vertical exchange flows between the stream and alluvial sediments, independently of hydraulic heads beneath and to the sides of the alluvium.

Sensitivity of exchange flows to changes in system conditions

In this simulation, the highly permeable alluvial sediments allowed exchange flows in the hyporheic zone to operate somewhat independently of the heads in the aquifer. Thus exchange flows were relatively insensitive to changes in aquifer heads; however field data showed that a large increase of several meters in aquifer heads from summer to fall did result in loss of exchange flows. Exchange flows are sensitive, however, to a decrease in permeability of the alluvium, as may result from siltation of the river bed.

Importance of alluvial sediments to exchange flows in other stream systems

Do all streams that receive net input of ground water from their catchments, require a zone of high conductivity alluvium in order for exchange flows to occur? This depends on the steepness of the stream, which determines the hydraulic gradient between upstream and downstream ends of a riffle, and the hydraulic gradient in the aquifer. In a steeper stream, or one with weaker hydraulic gradients between aquifer and stream, exchange flows can occur in less permeable near- stream sediments.

CONCLUSIONS

Modeling on a small scale has shown that surface water head differences of a few centimeters between riffles and pools can produce exchange flows within permeable alluvial sediments, despite net discharge of ground water to the stream. This model reveals local interactions between surface water and ground water which would not be predicted by larger scale models, but which have important chemical and biological consequences for the stream and ground water systems.

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Solute and Solid Phase Relationships in the Surface Hyporheic Zone of a Metal Contaminated Stream, Silver Bow Creek, MT

By Johnnie N. Moore and William W. Woessner

INTRODUCTION

Transformations occurring within the hyporheic zone impact the chemistry of both the overlying surface waters and the underlying ground water systems. The hyporheic zone is a key ecological niche crucial to the health of stream biota, as well as a major site of exchange, metabolism, and storage of particulates and solutes in rivers. There is, therefore, a critical need to understand the nature of the geochemistry that governs the transformation of materials through the hyporheic zone, especially metals and metalloids that are toxic to aquatic organisms utilizing the hyporheic zone.

The complexities of the substrate in most streams/rivers make determining the relationships between solute and solid phases difficult. To address this issue we have used ceramic beads as an artificial substrate to examine what solid phases are in equilibrium within the shallow hyporheic zone. Combined with “mini-tube wells,” this inexpensive and rapid method can be used to examine solute and solid phase components in essentially any stream/river.

Site Conditions

Silver Bow Creek , at the headwaters of the Clark Fork River, has received contaminated surface water and sediments from the Butte gold, silver and base metal mining and processing region for over a century (Moore and Luoma, 1991). Over 100 million tons of tailings and mining wastes were released into Silver Bow Creek, a portion of which were deposited at the Miles Crossing Research Site located 18 Km down stream (Figure 1).

At the Miles Crossing Site, Silver Bow Creek has an average discharge of 850 L/s. Its water is near neutral, high in dissolved oxygen and relative low in dissolved metals (Table 1). The fluvial plan is covered with up to 2 m of metal rich mine tailings highly elevated in arsenic, cadmium, copper, iron, lead, manganese and zinc.

Groundwater flow is generally in the direction of the sloping fluvial plain (Woessner, 1998; Smart, 1995; Shay, 1997) (Figure 1). Groundwater within the fluvial plan is acidic and contaminated (Table 1). On the large scale, groundwater exchange with the creek occurs as the stream stage falls below the fluvial plain water table. In the study area reaches of flow through channel (Site 1 and 3) and zero exchange (parallel flow)(Site 2) were observed.

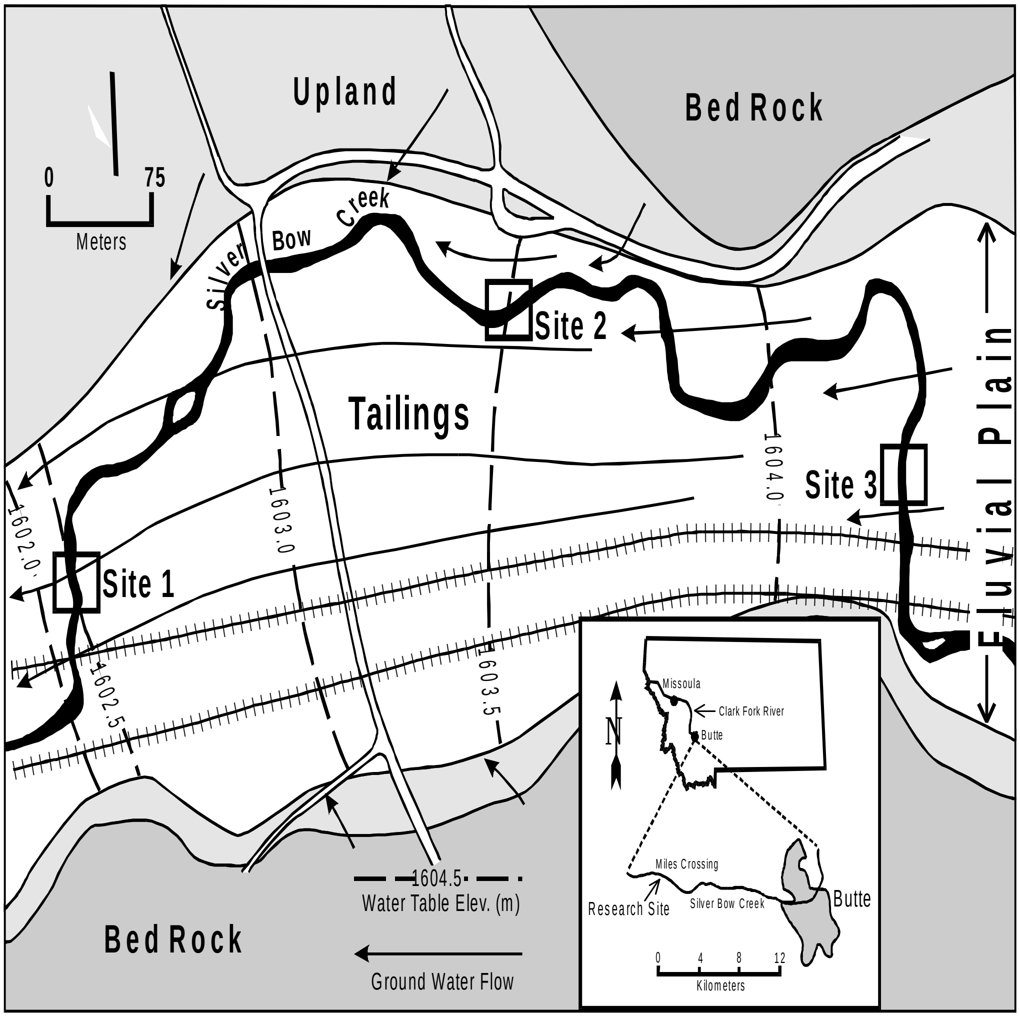

Figure 1. Location map of the Miles Crossing Research Site including Silver Bow Creek and the associated fluvial plain (zone of stream deposited higher hydraulic conductivity sediments. Groundwater flow is parallel to the fluvial plain and down valley. Bed tubes and mini tube wells were installed in three portions of the stream bed, Sites 1, 2 and 3.

Definition of the Hyporheic Zone

The hyporheic zone is generally defined as the saturated zone beneath and associated with the stream channel that shares some biological, chemical or physical characteristics with the surface water Williams, Triska, et al., 1989; Valett, et al., 1990; Hendricks and White, 1991; Valett, 1993). Our work uses geochemistry to define this transition zone between 100 % surface water and 100% groundwater. We further focus part of our effort on the “surface” hyporheic zone defined as the transition zone within 30 cm of the streambed at our site. Benner (1995) and Benner, et al. (1995) described a geochemical transition zone extending to a depth of one or more meters at Site 1. Nagorski (1997) continued work at the Site 1 and two additional sites focusing her effort on conditions within 30 cm of the streambed.

Table 1.

Water Quality	**Silver Bow Creek (Nagorski, 1997)**	**Fluvial Plain Groundwater (Benner, 1995; Shay, 1997)**
Constituent	*Std. Units and mg/ℓ*	*Std. Units and mg/ℓ*
pH	7.7	4.2-4.9
D.O.	7.2	<1
Cond.	0.424	2.0
Alkal.	1.3E+02	0
Cl	14	20
NO_3-N	1.3	1-2
SO_4	78.4	1487
Al	(<0.07)	33
As	0.010	0.010
Ca	47	141
Cd	(<0.01)	0.55
Cu	0.136	19
Fe	0.22	365
Mg	10.4	33
Mn	0.90	28
Na	23	42
Pb	(<0.1)	(<0.06)
Zn	0.645	54

METHODOLOGY

Bead Tube Samplers

Bead tube samplers are 40-175 cm long polycarbonate tubing (1cm OD, 0.6 cm ID) slotted with a 1 mm width ban sawed on two sides at 3 mm intervals were filled with aluminosilicate beads (2 mm average diameter). Plastic dividers were inserted into the columns at 10-cm intervals to minimize vertical migration of water in the samplers. Completed bead tubes were then acid cleaned in 20% reagent grade HCl for two hours and rinsed repeatedly with sterilized deionized water until a pH of 5 was reached.

Bead tube samplers were inserted into the bed by driving a dual tube steel rod into the stream sediments, removing the center solid rod, inserting the bead tube and then removing the outer steel tube. Sediments were allowed to collapse around the sampler. The tubes were installed so that about 10 cm of the sampler extended above the stream bed. Bead tubes were retrieved after 42 to 52 days.

Retrieved tubes were rinsed in the field to remove excess sediment, labeled, photographed, wrapped in plastic and stored. In the laboratory, columns were oven dried at 70 C and sectioned into 4 to 7 segments, depending on the amount of visible coating. Approximately one gram of beads were placed in an acid-washed centrifuge tube to which 10 mℓ of 40% metal-grade HCl was added. The sample was shaken for 1 hour and centrifuged for 10 minutes. Solutions were analyzed for major metals using ICAPES using standard procedures.

"Mini Tube Wells"

Small diameter tube wells were constructed using 0.95 cm diameter polyethylene with 5 cm of the tip slotted and covered with a nylon mesh screen. These groundwater sampling devices were installed as single instruments or nests using the same driven dual tube method used to install the bead tubes.

These small diameter tubes were sampled using a 60 cc acid-washed syringe after purging at lease one tube volume and one syringe volume. Tubes were then tightly capped to keep them full of bed water. The syringe-collected samples were pushed through a 0.45 um acid-washed filter and into two acid washed sample bottle. Bed water samples for cation analyses were preserved with trace metal grade HNO_3 and samples for anion analyses were untreated. Samples were placed on ice and returned to the lab for standard IC and ICAPES analyses. DO, pH, specific conductance and alkalinity were determined in the field.

RESULTS

At Site 1, surface water is alkaline, oxygenated and contains relatively high concentrations of nitrate and low concentrations of sulfate; ground water is acid and has low concentrations of oxygen, and high sulfate. The bead tube data allows for a higher resolution of the complexities of the hyporheic zone (transition zone) than tube wells as interfaces can be resolved by examining the continuous bead tube. Iron is a major control due to the precipitation of Fe-oxyhydroxides at the interfaces between the surface water and ground water with the hyporheic zone. Solute Fe concentrations are relatively low in the surface water and hyporheic zone water, with a concomitant elevation in the solid phase Fe on the beads. Two sets of bead tube sections show that Fe precipitates at the surface water-hyporheic zone boundary and at the ground water-hyporheic zone boundary. High values of solid phase Fe seen in the surface water beads resulted from fine sediment particles attached to the bead surfaces, not from Fe-oxyhydroxides precipitates.

Certain elements (As, Cu, Mo, P, Pb, Sr) are strongly related to Fe precipitation, but others are offset (e.g., Mn and Zn). Surface water and ground water contain relatively low concentrations of As and Fe, however, the surface hyporheic zone has elevated concentrations of As and Fe. We believe these elevated concentrations result from the dissolution of Fe-oxyhydroxides that contain As at the pH and dissolved oxygen levels found only in the surface hyporheic zone. At some sampling points Fe precipitates were either absent of showed a complex interfingering.

CONCLUSIONS

Bead tubes and tube wells provided detailed geochemical data in the near surface hyporheic zone (30 cm). The presence of iron hydroxides and co precipitating As and metals was observed and quantified. The bead tubes provided continuous sampling of the hyporheic zone and were useful in establishing the presence of geochemical interfaces. These instruments are best suited for sampling of groundwater and surface water systems with geochemical contrasts.

We can identify relationships at the 1-2 cm scale in the solid phase and at the 10 cm scale in the solute phase using these methods. We think that improvements in resolution could be obtained by constructing bead samplers with smaller beads and using high-resolution "peepers" (dialysis membrane samplers) for solute sampling. This modification should resolve changes within the hyporheic zone at the cm or possibly the sub-cm scale. However, the use of peepers would increase the cost and complexity of the technique. For many problems the method we present should offer a rapid and relatively easy technique to examine the fine scale relationships within the hyporheic zone.

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