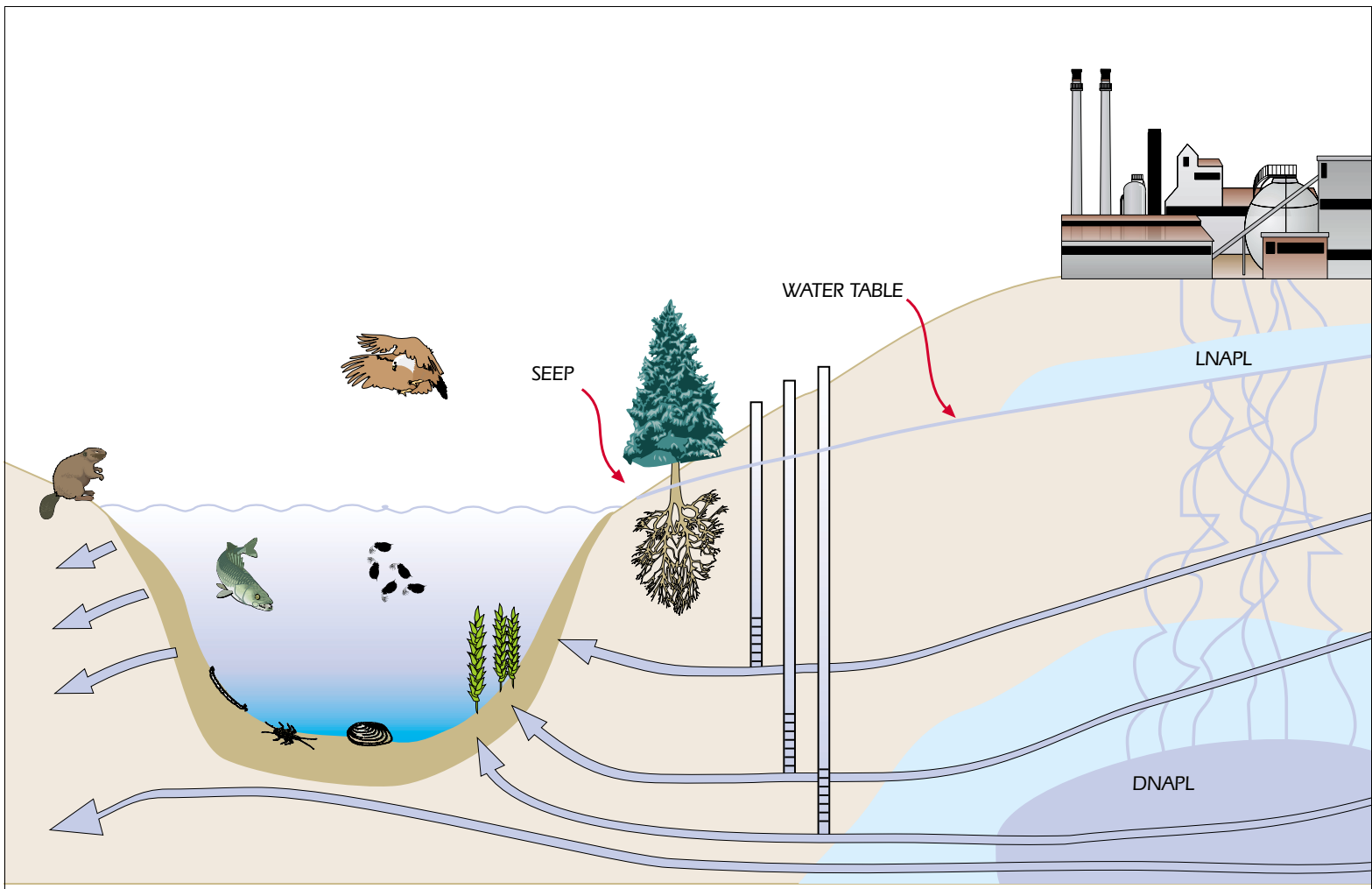




# Proceedings of the Ground-Water/ Surface-Water Interactions Workshop



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## **EXECUTIVE SUMMARY**

## **INTRODUCTION**

Although ground water and surface water are usually evaluated as separate water masses, they are connected by the ground-water/surface-water transition zone<sup>1</sup> in a hydrologic continuum. Understanding contaminant fate and transport in this zone is important to the U.S. Environmental Protection Agency's (EPA's) hazardous waste site cleanup programs across the nation because about 75% of RCRA and Superfund sites are located within a half mile of a surface water body, and almost half of all Superfund sites have impacted surface water. Investigations of ground water and surface water need to be integrated and incorporate recent advances in investigative techniques.

Ecological risk assessments for surface water bodies have all too often focused on the water column (where the ground-water contaminant plumes become extremely diluted), or on the sediments. Typically there has been little or no evaluation of contaminated ground-water discharges. Impacts from the discharge of contaminated ground water on the transition zone ecosystem have been ignored, even though this ecosystem provides important ecological services and is the most exposed to ground-water contaminants. Based on these considerations, the need to evaluate the transition zone is clear.

To address the technical concerns related to ecological impacts in the transition zone, the EPA's Office of Solid Waste and Emergency Response (OSWER) sponsored a workshop in January 1999, which was planned jointly by the Ecological Risk Assessment Forum and the Ground Water Forum.<sup>2</sup> The workshop was organized around answering two fundamental questions:

- How important is the transition zone ecologically?
- How can we measure hydrogeological, chemical, and biological conditions and changes in this zone?

There was a consensus among workshop participants that protecting this zone is important, and that there is a need for studies by interdisciplinary teams to ensure that valid data are obtained from the correct locations and at the right times so that valid conclusions are reached. Both forums plan to use the workshop information to submit research recommendations to EPA's Office of Research and Development, develop a list of suggested tools for investigating hydrogeological fate and transport and ecological effects at contaminated sites, develop Agency guidance, and conduct a pilot study using this methodology. The workshop and these proceedings provide a first step to understanding the fundamentals of evaluating the effects of contaminated ground water discharging through the transition zone.

## **WORKSHOP GOALS**

The overall goal of the workshop was to provide an opportunity for individuals from various scientific and technical backgrounds to discuss the importance of the ground-water/surface-water transition zone and help regulators better understand environmental issues relating to the connections

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<sup>1</sup> In these proceedings, the authors may use terms other than "ground-water/surface-water transition zone" to indicate this zone of transition. These terms may be equivalent (e.g., ground-water/surface water interface) or more restrictive (e.g., hyporheic zone, which refers to the interface between ground water and lotic (moving) surface waters.)

<sup>2</sup> The Ecological Risk Assessment Forum and Ground Water Forum comprise ecological risk assessment and ground-water specialists, respectively, from EPA's Regional Offices, Headquarters, and Office of Research and Development. These forums help the EPA maintain consistency and develop national program guidance.

between ground water and surface water. Within this broad goal, the Ecological Risk Assessment Forum and Ground Water Forum had the following additional specific goals:

**Ecological Risk Assessment Forum Goals:**

- Develop a conceptual model for use in ecological risk assessment at sites where contaminated ground water discharges to surface water.
- Integrate structural, functional, and hydrogeological components and methods for evaluating changes to the ecosystem.

**Ground Water Forum Goals:**

- Increase awareness of new tools used to evaluate fate and transport within the transition zone.
- Identify and understand geological, hydrological, and chemical factors that might influence transition zone dynamics.

## **WORKSHOP DESIGN**

A planning committee from the two forums designed the workshop to promote multidisciplinary interaction on a set of focus issues and questions. The workshop included invited platform speakers, a poster session, discussion groups, and an overall report-out from the groups and subsequent discussion. This approach worked well, resulting in fairly uniform agreement on concepts and recommendations regarding integration and use of investigatory tools.

### **Multidisciplinary Approach**

Invited workshop participants included ecologists, geochemists, and hydrogeologists who work with the ground-water/surface-water transition zone (Appendix A).

### **Conceptual Model**

A draft illustration of the conceptual model representing the forums' current understanding of ground-water/surface-water interactions for a river was presented and explained at the beginning of the workshop. The participants were asked to review the conceptual model and improve it as greater understanding was gained during the course of the workshop. Workshop participants also identified but did not address the need for research into other transition zone environments, such as those for lakes, estuaries, and wetlands.

### **Platform Speakers**

The planning committee invited seven platform speakers to present topics representing a cross-section of information on ground-water/surface-water interactions; the presentations helped workshop participants address focus issues and questions in subsequent discussion groups. The abstracts of the speakers' presentations are included in this report:

- A Federal Statutory/Regulatory/Policy Perspective on Remedial Decision-making with Respect to Ground-Water/Surface Water Interaction (Guy Tomassoni, EPA's Office of Solid Waste)
- Interaction of Ground Water and Surface Water (Tom Winter, U.S. Geological Survey)
- Hydrogeology and Biogeochemistry of the Surface Water and Ground Water Interface of a Mountain Stream (Cliff Dahm, University of New Mexico)

- Ground-Water Plume Behavior Near the Ground-Water/Surface-Water Interface of a River (Brewster Conant, University of Waterloo)
- Assessment Approaches and Issues in Ecological Characterizations (Allen Burton, Wright State University),
- Delineation, Quantification, and Mitigation of Discharging Plumes (David Lee , AECL Chalk River, Ontario), and
- Field Technology and Ecological Characterization of the Hyporheic Zone (Dudley Williams, University of Toronto)

### **Poster Session**

A poster session during the workshop allowed related papers to be presented outside of the formal discussion agenda. Abstracts of the posters are included in this report.

### **Discussion Groups**

The topics of the three discussion groups were hydrogeology, chemistry, and biology as they relate to ground-water/surface-water interactions. Three of the platform speakers, Tom Winter, Allen Burton, and Cliff Dahm, and three members of EPA, Joseph Dlugosz, Ned Black, and Bruce Duncan, served as discussion group co-chairs to guide discussions along the focus issues listed in Appendix B. To focus the discussions further, participants were asked to consider first the scenario of ground water discharging to a river.

Each workshop participant was assigned to two of the three discussion groups, and each group was organized with a balance of hydrogeologists, geochemists, ecologists, and microbiologists to encourage dialogue among people with different academic backgrounds. When the groups rotated for the afternoon session, the co-chairs remained to provide continuity and briefly explain what the morning session had covered. Some of the focus group issues were not fully addressed due to lack of information or time, however. Discussion group summaries are included in this report.

### **Report Out and Overall Discussion**

The information from the three discussion groups was summarized by the co-chairs and presented to all of the participants at the close of the workshop. This in turn led to a general group discussion of topics and future needs for research.

### **WORKSHOP RESULTS**

The workshop brought together representatives from a variety of technical disciplines to focus on the ground-water/surface-water transition zone. Chemists, microbiologists, hydrogeologists, and ecologists from EPA, the U.S. Geological Survey (USGS), the National Oceanic and Atmospheric Administration (NOAA), state environmental agencies, other government agencies, academia, and industry discussed the hydrological, chemical, and biological processes that occur in this transition zone and how to measure and interpret changes in these processes. Discussions highlighted the need to revise the existing conceptual model for ecological risk assessment to evaluate the important structural and functional aspects of the transition zone. Information was provided about many tools used to



evaluate the hydrological, chemical, and ecological aspects of this zone and the spatial and temporal scales at which measurements are needed.

The following is a summary of the key points drawn from the presentations by platform speakers, discussion group dialogues, and revisions to the conceptual model.

### **Platform Speakers**

While providing a common multidisciplinary focus on transition zones, the speakers emphasized the following facets of transition zone hydrogeology, chemistry, and ecology:

- Physiography and climate affect the interaction of ground water and surface water across diverse landscapes. For example, movement of water through the transition zone is influenced by the position of surface water bodies within ground-water flow systems, small-scale geologic features beneath surface water, climate, and hyporheic exchange (the exchange of moving surface water with ground water). These seemingly diverse systems may be studied, analyzed, and managed under a unifying framework based on “hydrologic landscapes.” Transition zones are particularly important ecologically because they store and retain nutrients (and potentially contaminants), transform compounds biologically and chemically, provide refuge to benthic invertebrates, and are a base of the aquatic food web. Virtually no research has been conducted on the effects of contaminants on hyporheic communities. Research should evaluate indigenous microbial activity, organic matter/nutrient cycling, invertebrate community indices, tissue residues of dominant species, in situ toxicity, and in situ physicochemical profiles. Very site-specific research could include novel tools such as ecological food web modeling, semi-permeable membrane devices to evaluate bioaccumulation, toxicity identification evaluations to determine the classes of chemicals (e.g., metals or organic compounds) responsible for observed toxicity, and identification and evaluation of in situ stressors including physical stressors (e.g., flow or suspended solids). It also will be critical to establish appropriate uncontaminated reference sites for comparison with contaminated sites.
- The hydrogeology of the ground-water/surface-water transition zone strongly influences the spatial and temporal distribution of both aerobic and anaerobic microbial processes as well as the chemical form and concentration of nutrients, trace metals, and contaminants in surface and ground waters. Major hydrologic events such as spring snowmelt affect biochemical components. Studies that integrate hydrogeology, biogeochemistry, and aquatic ecology are needed to understand fully the dynamics and importance of the transition zone.
- Determining the location and magnitude of contaminant discharges to surface waters from ground-water plumes is a complex hydrogeological and biogeochemical problem. Although measurements of hydraulic gradient may be sufficient to delineate large discharge areas, numerous seepage studies have shown that areas of significant discharge can be small and easily missed. Even in relatively homogeneous terrain, flows may be highly focused at shorelines, and solute transport may be rapid. Geochemical conditions and contaminant concentrations may change drastically over intervals of a few centimeters. Closely spaced measurements can be used to determine contaminant concentrations in and flux from the streambed and to distinguish areas of high attenuation from areas of poor attenuation (e.g., sand stringers, interconnected zones of higher permeability, or other preferential flow paths).
- Physical and numerical model studies, like seepage studies, indicate surface-water head differences of a few centimeters between riffles, and pools in streams can produce surface-water exchange

flows within permeable alluvial sediments despite net discharge of ground water to the stream. Modeling can be used to reveal interactions between surface water and ground water that are overlooked by larger scale models but have important chemical and biological consequences for the ground-water systems, the stream, and the biota.

## **Discussion Group Summaries**

Each discussion group agreed on the importance of the ground-water/surface-water transition zone and emphasized the need for multidisciplinary approaches to evaluating fate, transport, and effects of contaminants in this zone. The main differences among the groups were in discussion of the tools used by each discipline.

### **Hydrogeology**

The hydrogeology discussion group focused on using a tiered approach to determine the movement of ground water to surface water. The group recommended starting with a general reconnaissance of observable indicators of ground-water discharge and evolve to very detailed and focused sampling of hydraulics, chemistry, and biology. They recommended the following tiers:

- Use field methods that indicate ground-water discharge to surface water either indirectly (by observations of qualitative indicators or by chemical data) or directly (by using physical data to directly measure stage and calculate flow).
- Collect ground-water and surface-water samples over time and during different flow conditions.
- Adjust the field sampling strategy to account for different hydrologic landscapes.

The hydrogeology discussion group also suggested using a generic field design for investigating the ground-water/surface-water transition zone that includes use of piezometer nests, wells screened across the water table, and devices to measure or calculate the flow of water and chemicals through the transition zone. To address the interaction of ground water and surface water, the larger-scale (relative position of the surface water body within the ground-water flow system) hydrogeologic landscape processes and the smaller-scale (transition zone) processes should be evaluated.

The group recommended selecting field demonstration sites for research of ground-water/surface-water interaction in different geographic regimes that account for variation in hydrogeologic landscapes and climate. The design and effectiveness of site-characterization methods should be tested and evaluated, and based on the results, the conceptual model and tools for ground-water/surface-water transition zone characterization should be improved.

### **Chemistry**

The chemistry discussion group emphasized that chemical information is used to evaluate contaminant chemistry and fate, biological processes, and flow paths. The group recommended the following:

- Develop initial estimates of actual or potential risks to receptors. Collect information on site geochemistry and contaminant flow paths—although this might be deferred until after an initial evaluation.

- Develop one or more standard conceptual models to identify important questions to ask and the data to collect at different types and scales of sites. Sampling efforts in the transition zone may be more costly than standard sampling of surface water or shallow ground water.
- Determine chemical variations in time and space. In the transition zone, chemical and biological processes occur over many different time scales such as daily cycles (e.g., temperature and transpiration), short-term weather events, invertebrate and fish life cycles, seasonal changes, and long-term climatic changes and events (such as extreme weather events). Characterizing the spatial extent of contaminant discharge to surface water is just as important as determining the concentration distribution in a ground-water plume. In a screening or predictive risk assessment, contaminant concentrations are used for comparisons to toxicity benchmarks. However, the mass flux or loading of contaminants is also important and influences both the impact of contaminants on habitats and the physical, chemical, and biological transformations of the contaminants at the transition zone. The flux of contaminants can change in magnitude and direction with changes in surface water temperature and stage.

## **Biology**

The biology discussion group concluded that the transition zone is ecologically important. Some surface organisms have a life stage within this zone, and their productivity could be affected by contaminants in the zone. Less is known of the unique species that permanently inhabit the transition zone, and many have not been described. Transition zones often provide high quality habitats and are sites of contaminant reduction and nutrient and carbon cycling. Transition zones also can provide preferred habitat, refugia, sites of high biodiversity, habitat for the macrofaunal food base, microbial production, and energy transfer.

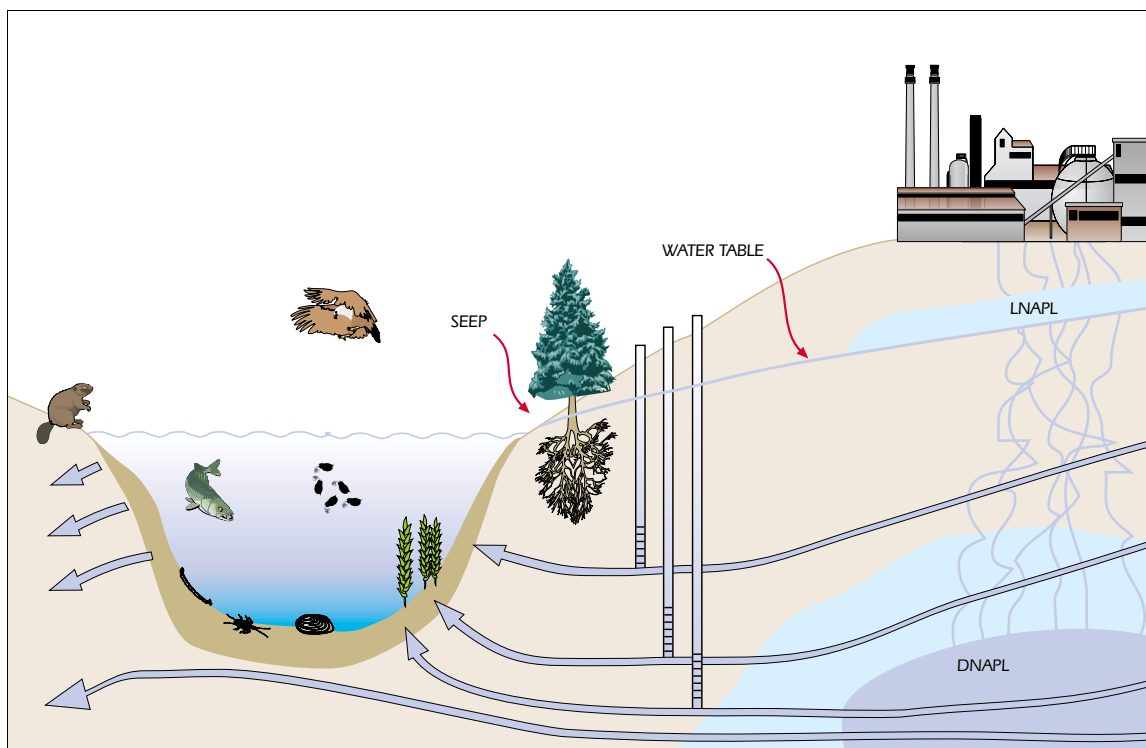
The group agreed that techniques and methods are available to evaluate the structure and function of the macrobiota and meiofauna. Methods also exist to sample organisms in the transition zone; however, many of these methods are neither standardized nor well-developed. In particular, there is no standard method to determine microbial community structure or activity/function. The group made the following recommendations:

- Use standard metrics, such as community composition, density, and species richness, to compare sample results regardless of the specific collection method. Evaluate functional feeding groups.
- Conduct bioaccumulation studies and stable isotope analyses to evaluate food chain relationships.
- Understand the basics of community structure and function at all levels before developing more methods to conduct toxicity testing.
- Coordinate ecologically related sampling in the transition zone with hydrogeological and chemical surveys at ground-water discharge sites. Use these surveys to help define the biological zones likely to be affected.

## **Conceptual Model**

To produce the conceptual model shown in Figure 1, the workshop planning committee presented a draft model at the workshop and revised it from the comments received from participants. This model, drawn for a river, can be adapted to other sites (lake, tidal, estuaries, marshes, etc.). It combines

ecological and hydrogeological concepts to focus on ecological processes in the transition zone and tools used to investigate fate, transport, and effects of contaminants in discharging ground water.



**Figure 1.** Conceptual model for contaminated ground water discharging to a river illustrating the need to look beyond surface water and benthic ecological receptors and hydrogeological fate and transport. Such a model should consider receptor exposure in the transition zone and account for finer-scale fate, transport, and effects from the discharge of contaminated ground water within this zone.

## CONCLUSIONS

General consensus was reached that protecting the transition zone is important, and there is a need for interdisciplinary studies to understand and document the changes that occur in it. Conclusions related to the two fundamental organizing questions are discussed below.

### How Important is the Transition Zone Ecologically?

The ground-water/surface-water transition zone is an ecological community with important ecosystem functions affecting several trophic levels from microbes to fish. As an ecotone (i.e., a transition from the ground-water ecosystem to the surface-water ecosystem), this zone provides key ecological services to the surface water ecosystem:

- Provides food for benthic macroinvertebrates. The microbial community serves as the food base to the small organisms within the zone that in turn are food for the benthic macroinvertebrates.
- Provides and maintains unique habitats or refugia, particularly in upwelling zones.
- Cycles nutrients and carbon in aquatic ecosystems.

The microbial and biological activity within this zone also may be important for natural attenuation, because large gradients can be created, which can result in subsurface conditions that change from anaerobic to aerobic over short distances. Biodegradation can cause organic contaminant concentrations to change over several orders of magnitude within this zone.

### **How Can We Measure Hydrogeological, Chemical, and Biological Conditions and Changes in this Zone?**

Despite many unanswered questions (see next section) there are many tools from each of the disciplines that can be used to evaluate fate, transport, and effects in the transition zone. It was recognized that the types, locations, and times of measurements required to characterize this zone can vary depending on the questions being asked. Hydrogeologists and ecologists must work together to obtain information that is useful to both and to efficiently and properly evaluate this zone.

### **KEY RECOMMENDATIONS FOR RESEARCH**

The recommendations presented below were identified during the various phases of the workshop, particularly within the discussion groups and during the report-out discussions on the final day.

#### **Common Key Areas**

The major recommendation common to all three discussion groups is that EPA should create a series of regional study areas of contaminated transition zone sites. Hydrogeologists, chemists, and biologists together should determine how, where, and what to sample and how to interpret the results. These scientists are obligated to integrate their objectives into a single conceptual model to evaluate transition zones.

#### **Hydrogeology**

EPA should encourage research in areas that increase the basic understanding of the influences of nearby surface-water bodies on contaminant plume migration. Delineation of plumes can be improved by more widespread application of the hydrologic landscape concepts in site characterization. Specifically, the following are needed: (1) improved techniques for measuring hydraulic heads, in stream and on-shore; (2) improved estimation methods of ground-water flow rates near the surface water boundary; and (3) improved methods for delineating plume concentrations near discharge zones. Increased use of tracers to help document and quantify the rate of ground-water discharges (or recharges) is needed. Better gradient quantitation methods are needed, especially in zones of rapidly fluctuating surface water stage. Also, there is a need for better assessment and evaluation of the heterogeneity of the ground-water zones adjacent to the surface-water bodies.

#### **Chemistry**

EPA should identify a number of regionally representative sites with contaminated transition zones—along with appropriate uncontaminated reference sites—to be studied by EPA's regional and Office of Research and Development (ORD) laboratories and academic grantees. The sites should reflect the scales and contaminant problems typical of each region because the transition zone chemistry, biology, and hydrology of small mountain streams impacted by mines in Region 8, for example, may be very different from those of a zone where chlorinated solvent plumes discharge to one of the Great Lakes in Region 5. The study of ground-water discharge and transition zone flow in estuaries will be further complicated by tidal fluctuations. Members of the chemistry discussion group

felt strongly that extrapolating data from small streams to large rivers and lakes is unacceptable. Also, some investigations techniques work well in small streams, but not in areas of high flow. As with any landscape approach, the chemical species and the dominant chemical and physical processes vary for different landscapes, but some basic processes may be common to some or all of these sites.

## **Biology**

Biological investigations rely heavily on hydrogeological and chemical investigations, particularly for identifying discharge zones. The regional study sites recommended by the other two groups should be used to fulfill several biological research needs. The greatest need is for basic biological research, such as life histories, faunal surveys, and organism activity, so that the full importance of the transition zone can be determined and changes related to contaminants can be quantified. Sampling and evaluation tools for both contaminated and uncontaminated substrates need to be developed and standardized to determine contaminant effects on species richness, trophic structure, and organism growth for macrobiota, meiofauna, and microorganisms in the transition zone ecosystem. Quantitative links are needed between site-specific chemical, hydrogeological, and ecological factors and the valued functions of the transition zone (e.g., contaminant degradation, food base for benthic organisms, role as a refuge, and high quality habitat).

## **NEXT STEPS**

This workshop was the first step in creating a multidisciplinary foundation for investigating, monitoring, and evaluating effects in the transition zone from the discharge of contaminated ground water. Future efforts building on this foundation should take many paths. For example, the conceptual model of the transition zone presented here is continually evolving. Conceptual models representing discharges to water bodies other than rivers need to be considered so that approaches and tools appropriate to wetlands, estuaries, and lakes—including those influenced by tides—can be identified and developed. Similarly, other pathways need to be identified and addressed, such as contaminated sediments as sources of contamination to ground water and to the transition zone where infiltration of surface water occurs.

Based on the workshop, the Ground Water Forum and the Ecological Risk Assessment Forum intend to:

- Submit research recommendations to ORD.
- Develop a list of suggested tools for investigating hydrogeological fate and transport and ecological effects at contaminated sites.
- Develop Agency guidance for incorporating the transition zone into risk assessments.
- Conduct a pilot study.

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## **PRESENTATION ABSTRACTS**



# **A Federal Statutory/Regulatory/Policy Perspective on Remedial Decision-making with Respect to Ground-Water/Surface-Water Interaction**

by Guy Tomassoni

The ground water/surface water interaction zone is important because 75% of Superfund and RCRA sites are located within a half mile of a surface water body. Forty-seven percent of Superfund sites have recorded impacts to surface water. Most RCRA sites are located adjacent to or near surface water (presumably for ease of transportation and manufacturing). Within the last 25 years, the Clean Water Act has succeeded in cleaning up point sources in the United States, and EPA now needs to consider non-point sources.

“Risk-based decision making” (RBDM) has received a bad reputation within EPA because it has been equated to “risk-based corrective action” (RBCA). A goal of this workshop is to provide the scientific basis to convince policy-makers to allow RBDM. EPA supports RBDM, but places more emphasis on site-specific evaluations based on sound science. RBDM generally requires a multidisciplinary approach, an understanding of requirements, and flexibility in applicable statutes, regulations, and policies.

There are many technical and policy issues regarding ground-water/surface-water interactions. Good policy is flexible, and good policy comes from good technical information. This workshop therefore may influence future policy. Superfund and RCRA remediation (“corrective action”) programs. These laws mandate protection of human health and environment. The Superfund National Contingency Plan offers greater detail; RCRA relies more on program guidance.

**Highlights from “Rules of Thumb for Superfund Remedy Selection” (<http://www.epa.gov/superfund/resources/rules/index.htm>)**

Superfund’s goal is to return usable ground water to beneficial uses (current and future) where practical. When this is not practical, Superfund strives to prevent further migration and exposure, and to evaluate opportunities for further risk reduction. Ground water generally is considered “potable” if it is so designated by the state, or considered so under federal drinking water guidelines. Preliminary remedial goals are set at levels that protect resources—including surface waters—that receive contaminated ground water, taking into account Clean Water Act requirements or state standards, if they are more stringent. Attaining drinking water standards in contaminated ground water is not always enough to protect sensitive ecological receptors. Final clean-up levels should be attained throughout the plume and beyond the edge of any wastes left in place. The “point of compliance” for a surface water body is where the release enters the surface water. Alternate concentration limits (ACLs) may be considered where contaminated ground-water discharges to surface water, where contaminated ground water does not lead to increased contaminants in surface water, where enforceable measures are available to prevent exposure to ground water, or where restoring ground water is “not practicable.” There are about 23 Superfund ACLs nationwide. EPA expects to use treatment to address “principal threats” posed by site where practical.

**RCRA Setting, Based Upon the May 1, 1996, Advance Notice of Proposed Rulemaking (<http://www.epa.gov/correctiveaction>)**

RCRA has similar requirements to Superfund with respect to: returning usable ground water to beneficial uses; points of compliance for ground water and surface water; protection of surface water from contaminated ground water; provisions for ACLs (but without an explicit link to “practicability”); and treatment of principal threats. If current human exposures are under control and no further migration of contaminated ground water is expected, primary near-term goals are established using two environmental indicators. Surface water becomes the boundary if the discharge of contaminated ground water is within “protective” limits.

The OSWER Policy Directive on Monitored Natural Attenuation (MNA) was issued in final form, and is pertinent to the ground water/surface water issue. It addresses dilution, dispersion, absorption, and degradation—all of which occur in ground water/surface water interaction. The directive requires controlling sources and monitoring; it stresses the need to look beyond obvious contaminants.

In summary, the majority of contaminated sites have serious potential to affect surface waters. The federal framework allows for RBDM with respect to ground water/surface water interaction, but we must still achieve the expectation of restoring ground water to beneficial use and ensure discharges of ground water to surface water are protective. Key policy issues to ponder—and to pass to senior managers—include:

- how to achieve short- and long-term protection;
- where, how, and how often to measure compliance;
- whether to restore ground water; even if it has no impact to surface water;
- the diversity of surface bodies;
- the relation of cleanup goals to the Clean Water Act’s National Pollutant Discharge Elimination System (NPDES) approach; and
- how to account for, track, and communicate total loads in watersheds.

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# **Interaction of Ground Water and Surface Water**

By Thomas C. Winter

## **INTRODUCTION**

Surface water bodies are hydraulically connected to ground water in most types of landscapes; as a result, surface-water bodies are integral parts of ground-water flow systems. Even if a surface water body is separated from the ground-water system by an unsaturated zone, seepage from the surface water may recharge ground water. Because of the interchange of water between these two components of the hydrologic system, development or contamination of one commonly affects the other. The movement of surface water and ground water is controlled to a large extent by the physiography (land-surface form and geology) of an area. In addition, climate, through the effects of precipitation and evapotranspiration, affects the distribution of water to—and removal from—landscapes. Therefore, it is necessary to understand the effects of physiography and climate on surface water runoff and ground-water flow systems in order to understand the interaction of ground water and surface water.

The purpose of this paper is to: present an overview of how physiography and climate affect the interaction of ground water and surface water and present the concept of hydrologic landscapes as a unifying framework for study, analysis, and management of seemingly diverse landscapes. Specifically discussed are the effects of the following factors on movement of water between ground water and surface water: (a) position of surface water bodies within ground-water flow systems; (b) small-scale geologic features in beds of surface water; (c) climate; and (d) hyporheic exchange.

## **GENERAL HYDROLOGICAL PROCESSES RELATED TO THE INTERACTION OF GROUND WATER AND SURFACE WATER**

### **Position of Surface Water Bodies With Respect to Ground-Water Flow Systems**

Ground water moves along flow paths of varying lengths from areas of recharge to areas of discharge. The source of water to the water table (ground-water recharge) is infiltration of precipitation through the unsaturated zone. Ground-water flow systems can be of greatly different sizes and depths, and they can overlie one another. Local flow systems are recharged at water-table highs and discharge to adjacent lowlands or surface water. Local flow systems are the most dynamic and the shallowest flow systems; therefore, they have the greatest interchange with surface water. Local flow systems can be underlain by intermediate and regional flow systems. Water in these deeper flow systems have longer flow paths, but they also eventually discharge to surface water. Surface water bodies that receive discharge from more than one flow system receive that water through different parts of their bed. Local flow systems discharge in the part nearest shore, and larger-magnitude flow systems discharge to surface water further offshore. Because of the different lengths and travel times of water within flow paths, the chemistry of water discharging into the surface water from different flow paths can be substantially different.

In some landscapes, surface water bodies lie at intermediate altitudes between major recharge and discharge areas. Surface water bodies in such settings commonly receive ground-water inflow on the upgradient side and have seepage to ground water on the downgradient side. Furthermore, depending

on the distribution and magnitude of recharge in the uplands, the hinge line between ground-water inflow and outflow can move back and forth across part of the surface water bed.

The above characteristics of ground-water flow systems with respect to surface water apply in a general regional sense to most landscapes. However, the detailed distribution of seepage to and from surface water is controlled by: (a) the slope of the water table with respect to the slope of the surface water surface; (b) small-scale geologic features in the beds of surface water; and (c) climate.

### **Effect of Local Water-Table Configuration and Geologic Conditions on Seepage Distribution in Surface Water Beds**

Upward breaks-in-slope of the water table result in upward components of ground-water flow beneath the area of lower slope and downward breaks-in-slope of the water table result in downward components of ground-water flow. These flow patterns apply to parts of many landscapes, but they are particularly relevant to the interaction of ground water with surface water because water tables generally have a steeper slope on both the inflow and outflow sides relative to the flat surface of surface water bodies. The ground-water flux through a surface water bed associated with these breaks-in-slope, whether the seepage is to or from the surface water, is not uniformly distributed areally. Where ground water moves to or from a surface water body underlain by isotropic and homogeneous porous media, the flux is greatest near the shoreline, and it decreases approximately exponentially away from the shoreline. Anisotropy of the porous media, which is a function of the orientation of sediment particles in the geologic materials, affects this pattern of seepage by causing the width of areas of equal flux to increase with increasing anisotropy. Yet the decreasing seepage away from the shoreline remains nonlinear.

Geologic heterogeneity of surface water beds also affects seepage patterns. Small-scale variations in sediment type can cause the locations and rates of seepage to vary substantially over small distances. For example, highly conductive sand beds within finer-grained porous media that intersect a surface water bed results in subaqueous springs. The horizontal and vertical hydraulic conductivity of the streambed can vary by several orders of magnitude because of the variability of streambed sediments. The complex distribution of seepage patterns caused by the heterogeneous geology of surface water beds has been documented by field studies in many settings.

### **Effect of Climate on Seepage Distribution in Surface Water Beds**

The most dynamic boundary of most ground-water flow systems is the water table. The configuration of the water table changes continually in response to recharge to and discharge from the ground-water system. Changing meteorological conditions strongly affect seepage patterns in surface water beds, especially near the shoreline. The water table commonly intersects land surface at the shoreline, resulting in no unsaturated zone at this point. Infiltrating precipitation passes rapidly through a thin unsaturated zone adjacent to the shoreline, which causes water-table mounds to form quickly adjacent to the surface water. This process, termed “focused recharge,” can result in increased ground-water inflow to surface water bodies, or it can cause inflow to surface water bodies that normally have seepage to ground water. Each precipitation event has the potential to cause this highly transient flow condition near shorelines as well as at depressions in uplands.

Transpiration by near-shore plants has the opposite effect of focused recharge. Again, because the water table is near the land surface at edges of surface water bodies, plant roots can penetrate into the saturated zone, allowing the plants to transpire water directly from the ground-water system.

Transpiration of ground water commonly results in a drawdown of the water table much like the effect of a pumped well. This highly variable daily and seasonal transpiration of ground water may reduce ground-water discharge to a surface water body significantly or even cause movement of surface water into the subsurface. In many places, it is possible to measure diurnal changes in the direction of flow during seasons of active plant growth: that is, ground water moves into the surface water during the night, and surface water moves into shallow ground water during the day.

These periodic changes in the direction of flow also can take place on longer time scales. Focused recharge from precipitation predominates during wet periods, and drawdown by transpiration predominates during dry periods. As a result, the two processes—together with the geologic controls on seepage distribution—can cause flow conditions at the beds of surface water bodies to be extremely variable. These processes probably affect small surface water bodies more than large surface water bodies because the ratio of edge length to total volume is greater for small water bodies than it is for large ones.

A type of landscape that merits special attention are those areas underlain by limestone and dolomite. These landscapes, which are referred to as karst terrains, commonly have fractures and solution openings that become larger with time because of dissolution of the rocks. Ground-water recharge is very efficient in karst terrain because precipitation readily infiltrates through the rock openings that intersect the land surface. Water moves at greatly different rates through karst aquifers; it moves slowly through fine fractures and pores and rapidly through solution-enlarged fractures and conduits. The paths of water movement in karst terrain are especially unpredictable because of the many paths ground water takes through the maze of fractures and solution openings in the rock. Seeps and springs of all sizes are characteristic features of karst terrains. In addition, the location where the streams emerge can change, depending on the spatial distribution of ground-water recharge in relation to individual precipitation events. Large spring inflows to streams in karst terrain contrast sharply with the generally more-diffuse ground-water inflow characteristic of streams flowing across sand and gravel aquifers.

### **Hyporheic Exchange**

Streambeds and banks are unique environments because they are where ground water that drains much of the subsurface of landscapes interacts with surface water that drains much of the surface of landscapes. “Hyporheic exchange” is the term given to the process of water and solute exchange in both directions across a streambed. The direction of seepage through the bed of streams commonly is related to abrupt changes in the slope of the streambed or to meanders in the stream channel. This process creates subsurface environments that have variable proportions of water from ground water and surface water. Depending on the type of sediment in the streambed and banks, the variability in slope of the streambed, and the hydraulic gradients in the adjacent ground-water system, the hyporheic zone can be as much as several feet in depth and hundreds of feet in width. The dimensions of the hyporheic zone generally increase with increasing width of the stream and permeability of streambed sediments. Because of this mixing between ground water and surface water in the hyporheic zone, the chemical and biological character of the hyporheic zone may differ markedly from adjacent surface water and ground water.

Although most work related to hyporheic-exchange processes has been done on streams, processes similar to hyporheic exchange also can take place in the beds of some lakes and wetlands because of the reversals in flow caused by focused recharge and transpiration from ground water near surface water, discussed above. Therefore, it is not enough to know only the relationship of surface water to

ground-water flow systems and to small-scale seepage patterns in surface water beds, because hyporheic-exchange processes also can be important in some types of landscapes.

### **Hydrologic Landscapes as a Unifying Concept for Diverse Localities and Regions**

As indicated above, many geologic and climatic factors affect the movement of water through a basin. The many different types of landforms, geologic settings, and climate variations that make up many regions of the Earth may make it seem that a unifying conceptual framework is impossible to achieve. Indeed, it is not unusual for scientists and water- and land managers to emphasize the uniqueness and complexity of a given locality rather than the similarities that it might have with other localities. However, with respect to the movement of water and chemicals, many seemingly diverse landscapes have some features in common, and it is these commonalities that need to be identified. Only by evaluating landscapes from a common conceptual framework can processes common to some or all landscapes be distinguished from processes unique to particular landscapes. A common conceptual framework also would lead to development of field designs of data collection programs that could be transferred to other landscapes having similar characteristics.

The concept of hydrologic landscapes is based on the idea that a single, simple physiographic feature is the basic building block of all landscapes. This feature is termed a “fundamental landscape unit,” and is defined as an upland adjacent to a lowland separated by a steeper break in slope. Water moves over the surface of a fundamental landscape unit depending upon the surface slope of the upland, lowland, and intervening steeper slope, and it moves through the subsurface depending upon the hydraulic characteristics of its internal geologic properties.

All landscapes can be conceived of as variations and multiples of fundamental landscape units. Variations and multiples of fundamental landscape units can be used to define a number of general landscape configurations; for example: (1) the width of the lowland, valley side or upland can range from narrow to wide; (2) the slopes of the three surfaces can vary; (3) the height of the valley side can range from small to large—that is, the upland can be only slightly higher than the lowland or it can be much higher; or (4) small fundamental landscape units can be superimposed on any or all of the surfaces of larger-scale fundamental landscape units.

General landscape configurations such as these can be used to define general landscape types that describe major physiographic features of the Earth. For example:

- (1) A landscape consisting of narrow lowlands and uplands separated by high and steep valley sides is characteristic of mountainous terrain. This general configuration can be nested into multiples at different scales within mountainous terrain as one moves from high mountain basins to larger and larger valleys within a mountain range complex.
- A landscape consisting of very wide lowlands separated from much narrower uplands by steep valley sides is characteristic of basin and range physiography and basins of interior drainage. In this type of terrain, the uplands may range from being slightly higher to much higher than the lowlands.
- A landscape consisting of narrow lowlands separated from very broad uplands by valley sides of various slopes and heights is characteristic of plateaus and high plains.
- A landscape consisting of one or more small fundamental landscape units (terraces) nested within a larger lowland is characteristic of riverine valleys and coastal terrain. A landscape consisting of

numerous small fundamental landscape units superimposed on both the uplands and lowlands of larger fundamental landscape units is characteristic of hummocky glacial and dune terrain.

### **Common Hydrologic Characteristics of Generalized Hydrologic Landscapes**

The movement of water over the surface and through the subsurface of generalized landscapes is controlled by common physical principles regardless of the geographic location of the landscapes. For example, if a landscape has low land slope and low-permeability soils, surface runoff will be slow and recharge to ground water will be limited. In contrast, if the soils are permeable in a region of low land slope, surface runoff may be limited but ground-water recharge will be high. In landscapes that have a shallow water table, transpiration directly from ground water may have a substantial effect on ground-water flow systems, and on the movement of ground water to and from surface water.

Landscapes characterized by multiples of fundamental landscape units can have complex ground-water flow systems because small-scale local flow systems associated with each topographic break in the landscape are superimposed on larger, more regional flow systems associated with larger fundamental landscape units. Two seemingly diverse landscapes, such as riverine and coastal terrain, have many of these types of physiographic characteristics in common, and presumably would have many hydrologic characteristics in common as well. Ground-water flow conditions in hummocky terrain are even more complex than riverine and coastal terrain because of the numerous small fundamental landscape units superimposed somewhat randomly on larger and larger fundamental landscape units. Indeed, in glacial and dune terrain, many multiples of fundamental-landscape-unit scale can be present. Furthermore, generally shallow water tables characteristic of coastal, riverine, and hummocky terrain result in the opportunity for highly transient local ground-water flow systems caused by focused recharge and transpiration directly from ground water.

### **Implications for management of water and remediation of contaminated localities**

Management of water, and remediation of contaminated localities, requires sound understanding of hydrological processes. Contaminated ground water and surface water are common in all types of landscapes. Because of the cost of studies and of remediation, it is nearly impossible to devote adequate resources to the huge number of sites that need attention. Therefore, it is of great practical value to seek transferability of study design, study results, and remediation techniques. It is suggested that the concept of hydrologic landscapes can serve as a foundation for determining the commonalities of diverse localities, and sharpen the perspective of their differences. If this can be accomplished, the transfer value of study designs and remediation methods should substantially reduce the cost of site remediation.

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# **Hydrogeology and Biogeochemistry of the Surface Water and Ground Water Interface of a Mountain Stream**

By Cliff Dahm

Our interdisciplinary research group has been studying the hydrogeology, biogeochemistry, and ecology of the surface water and ground water interface of the Rio Calaveras in the Jemez Mountains of northern New Mexico since 1991. Snowmelt is a prominent factor in the hydrogeology of both surface discharge and the alluvial ground water of the site. Strong interannual variability in the strength of the snowmelt signal affects both the biogeochemistry and ecology of the surface water and ground water. Water table variation in drought years is small, and upwelling and downwelling zones through the bed of the channel show a complex spatial pattern, with distinct losing and gaining sections of stream over a 150-meter reach throughout most of the year. Water table variation in wet years with good snow pack ranges between 40 to >100 centimeters in the alluvial flood plain, and most of the reach is gaining (upwelling) from March through May. Flow lines are directed towards the stream with both ground water and saturated overland flow contributing to increased stream discharge. Drought years are characterized by discharge increases as little as three times base flow while discharge increases during wet years exceed two orders of magnitude above base flow.

Biogeochemical characteristics of the surface water and ground water are strongly influenced by the hydrogeology. Snowmelt generates water that is rich in nitrate, dissolved organic carbon (DOC), and oxygen. Much of the increase in dissolved organic matter and nutrients is derived from the region of seasonal saturation (ROSS) that is inundated during snowmelt. Studies on the DOC leached from the ROSS have shown that half of this DOC is labile and metabolized within one month. Alluvial ground water shows strong vertical structure from the snowmelt inputs with peaks in oxygen, nitrate, DOC, and low molecular weight organic acids in the upper 50 centimeters in the first few weeks following snowmelt. As water table elevations drop, concentrations of oxygen, nitrate, sulfate, DOC, and organic acids decrease, while byproducts of anaerobic metabolism such as ferrous iron, manganous manganese, and methane increase. Surface water inputs of organic matter and nutrients also reflect the changing hydrology that occurs from snowmelt to base flow conditions. For example, nitrate and DOC levels are highest during the early stages of snowmelt and low during base flow conditions. Algal primary production shows a nitrogen limitation during low-flow conditions but not during times of increased stream discharge.

Interactions between surface waters and ground waters at this site also affect the biological communities of the stream benthos. High discharge during periods of snowmelt scours benthic algae and reduces chlorophyll concentrations and algal biomass throughout the reach. As snowmelt discharge decreases, a diatom-dominated benthic algal bloom commonly occurs over much of the stream bottom. As flows return to base flow conditions, a spatially heterogeneous pattern of algal community structure and biomass emerges. Persistent upwelling zones at base flow, where ground water discharges into surface water, are generally more productive reaches and composed of a complex mix of diatoms, green algae, and cyanobacteria. More focused benthic invertebrate activity appears to occur in these reaches. Persistent downwelling zones, where surface water recharges the ground water, commonly have lower rates of algal primary production and contain a higher proportion of

cyanobacteria in the algal community. Hydrogeology, nutrient availability, and interactions between grazers and primary producers all play important roles in structuring the benthic algal community.

Integrative studies that combine hydrogeology, biogeochemistry, and aquatic ecology are needed to fully understand the dynamics and importance of the ground water/surface water interface. Research at Rio Calaveras in northern New Mexico has been designed to bring these disciplines together in a multidisciplinary study of a well-instrumented 150-meter reach of mountain stream. This research has shown the importance of major hydrologic events such as spring snowmelt in the overall hydrology, biogeochemistry, and ecology of this ecosystem. In addition, the distribution of aerobic and anaerobic microbial processes in the alluvial ground water system and the chemical form and concentration of nutrients and trace metals in the surface waters and ground waters are strongly affected by the hydrogeology of the ground water/surface water interface.

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# **Ground-water Plume Behavior Near The Ground-Water/Surface Water Interface of a River**

By Brewster Conant, Jr.

## **INTRODUCTION**

What happens to ground-water contaminant plumes as they discharge through river beds and the ground water/surface water interface (GWSI) is not well understood. Relatively few published studies address this issue, even though an estimated 51 percent of National Priority List sites are thought to impact surface water (U.S. EPA, 1991) and the most common route for the contaminants to migrate into the surface water was via ground-water transport (U.S. EPA, 1989). Understanding processes occurring beneath and near rivers becomes particularly relevant when making remediation decisions that are risk-based or involve natural attenuation. Such decisions could benefit greatly by identifying important plume transport and fate processes and by conducting detailed hydrogeological studies of plumes to characterize the spatial and temporal variations of contaminant discharges to rivers.

## **GROUND-WATER PLUME DEVELOPMENT**

Many factors influence the transport and fate of contaminants in the subsurface prior to a ground-water plume discharging to the surface water of a river. To understand the significance of these factors, it is useful to consider the fundamentals of how dissolved-phase contaminant ground-water plumes are created. Several factors play important roles in plume development:

- Physical and chemical characteristics of the contaminants
- Geometry and temporal variations in the contaminant source zone
- Transport mechanisms (advection and dispersion)
- Reactions (destructive and non-destructive)

Many of these factors are just as applicable to contaminant behavior near and beneath rivers as they are away from the river. Knowing the behavior and concentration distribution of plumes, before they enter the complex conditions near and beneath a river, allows better assessment of what modifying effects near river processes have on the plume.

## **Contaminant Characteristics**

A contaminant's physical and chemical characteristics play an important role in how the contaminant is transported and redistributed in the subsurface and the hazard it poses to aquatic life. Many types of contaminants are found in the subsurface including; synthetic organics, hydrocarbons, metals, other inorganics (e.g., nitrate), radionuclides, and pathogens (e.g., viruses and bacteria). Contaminants can be present as solids, liquids (e.g., non-aqueous phase liquids [NAPL]), dissolved in water, or present as gasses. Each contaminant has a different propensity to solubilize, sorb, bioconcentrate, volatilize, or react, and these characteristics affect both their mobility and toxicity. With respect to organic compounds, the strongly hydrophobic organic compounds (e.g., PCBs, pesticides, and PAHs) have higher bioconcentration factors and tend to be more toxic to aquatic life than less hydrophobic organics such as chlorinated volatile organic compounds (CVOCs). The strongly hydrophobic compounds generally have low aqueous solubilities and, when dissolved in water, move

much more slowly than ground water (i.e., adsorb and are retarded), whereas, the CVOCs have higher solubilities and are less retarded. Consequently, many of the longer and higher concentration dissolved-phase organic plumes in ground water are dominated by the more mobile CVOCs, which are generally thought to be “less toxic” to aquatic life. However, aquatic biota located in the streambed and at the GWSI (i.e., not in the surface water) may still be adversely affected by CVOCs because they may be exposed to high concentrations in the discharging ground water prior to any dilution by surface water. If ground-water concentrations are higher than freshwater aquatic life standards or guidelines, the locations of these discharge zones may represent a hazard to both the benthic and hyporheic aquatic life in the streambed, regardless of how these contaminants might later attenuate in the surface waters of the open river channel.

### **Contaminant Source Zone**

At many Superfund and RCRA sites, considerable effort is spent trying to delineate the source of contaminants impacting the ground water. These sites, particularly those involving CVOCs, typically involve so-called “point sources” of ground-water contamination resulting from spills or releases limited over relatively discrete release areas. This paper does not address “non-point” sources of contamination, such as nitrate and pesticide contamination from large-scale agricultural applications, even though such “source areas” cover more of the watershed area contributing water to the stream.

Each individual contaminant source zone has a particular distribution in the subsurface. The location, mass, and type of contaminants in the subsurface, along with characteristics of the subsurface geology and ground-water flow, will influence whether the source produces a ground-water plume with a continuous, variable, or a “slug” input. A source below the water table consisting of dense non-aqueous phase liquid (DNAPL) results in continuous dissolved-phase plumes that can persist for tens to hundreds of years if left to naturally dissolve (Feenstra, et al., 1996). Variable source plumes may be caused by variations in waste stream inputs, or by preferential dissolution and depletion of multi-component contaminant sources over time (Feenstra and Guiguer, 1996). Slug inputs are “instantaneous” or short duration releases that do not persist at the initial release location and move through the flow system as a localized mass. Of particular concern for impacts on surface water are the continuous and variable sources which represent long term sources of contaminants to a river. Continuous-source plumes may result in areas of the streambed being constantly exposed to high concentrations of contaminated ground water. Because contaminants enter streambed from the ground water below, the sediments become contaminated at ground water discharge locations. Even if those sediments are eroded away and transported down stream, the clean materials redeposited in their place will be subsequently contaminated by further ground water discharge.

## **TRANSPORT**

### **Ground-Water Flow**

The primary mechanism by which contaminants are transported away from source zones and toward ultimate points of discharge, such as rivers, is advection (i.e., dissolved phase contaminants moving with the ground water). Therefore, the ground-water flow system plays a fundamental role in determining where a dissolved phase plume from a contaminant source zone will go and whether a given surface water body may be affected. Many factors affect ground water flow including; climate (particularly precipitation recharge), watershed characteristics, geology, hydraulic conditions (water table slope and ground-water potential), and hydrogeologic boundary conditions (such as discharge or “no-flow” locations). Characterizing the ground-water flow system at a site can be more large scale or regional when initially conceptualizing potential contaminant plume flow paths. However, when

investigating point-source plumes that reach rivers, the focus needs to be on smaller scale flow characteristics in order to accurately determine specific locations of contaminated ground water discharge to the river.

Several types of significant vertical ground-water flow behavior can occur both on a regional scale and on a more local scale in the vicinity of streams. Depending on the depth and location of a source zone, the plume may be transported through what Toth (1963) termed local, intermediate, regional, ground water flow systems. If the ground water plume develops in a shallow local flow system, it may discharge to the nearest surface water body. If the plume develops from a deeper source zone (e.g., DNAPL) or is located within a regional or intermediate flow system, it may travel beneath several lakes or streams before ultimately discharging to one of them. Winter (1999) shows some examples of vertical cross-sectional views of ground water interactions for streams, lakes, and wetlands. Different types of ground water/river interactions are also shown in Bear (1979, p. 52).

The lateral component ground water flow (i.e., in plan-view) near rivers exhibits a variety of behaviors. In a study of rivers in large alluvial aquifers by Larkin and Sharp (1992) showed that ground water flow could be base flow, under flow, or mixed flow, depending on the slope, sinuosity, and depth of penetration of the river in the aquifer. Base flow occurs when ground water flows essentially perpendicular to the river and discharges to it. Under flow occurs when ground-water flow near the river is parallel to the river and does not discharge to the river channel (at least not for some great distance). Mixed flow is a combination of base flow and under flow where ground water near the river flows at an angle to the river and discharges to it some distance downstream. Woessner (1998) presents some other variations in this behavior. One consequence of these possible behaviors is that plumes entering alluvial valleys may not necessarily travel straight across the flood plain toward the river but instead may travel down valley large distances before discharging through the stream bottom and into the stream. In such regimes, simply trying to determine the path of a plume near a river becomes a challenge and finding the exact areas of discharge may be very difficult.

### **Defining and Locating The Ground-Water/Surface-Water Interface**

As ground water travels through the subsurface, it eventually reaches the GWSI near the stream or river. At the GWSI, a transition occurs between the hydraulic, biochemical, thermal, and ecological conditions of the surface water and those associated with the ground water. Because changes in these parameters may be gradational, defining the location of the GWSI is not simple. The location of the GWSI is not static and may change as a result of daily or seasonal fluctuations in river stage and ground water flow. The GWSI can be defined as the location where water having some portion of surface water is in contact with 100 percent ground water. This contact may occur right at the streambed-water column interface, or it may exist at some depth within the streambed or stream banks. The contact between the contrasting waters may be reasonably sharp or transitional. The primary reason that the GWSI may exist within the streambed materials, as opposed to the upper surface of them, is due to topographic variations in the streambed and changes in the slope of the river (i.e., hydraulic potential). Surface water may enter the sediments at downwelling zones and reenter the river at upwelling zones (Vaux, 1968, and Boulton, 1993). Downwelling generally occurs at the head of riffles and upwelling (along with ground water discharge) occurs at the upstream edge and base of pools. Figure 1 is a schematic depicting downwelling and upwelling zones (in vertical cross section) and the effect on the location of the GWSI and a discharging ground water plume. The surface water can also leave the channel laterally and travel several meters or more into the streambanks and eventually reenter the channel down stream (Harvey and Bencala, 1993). Where surface water leaves the stream channel, ground water can not directly enter the channel; therefore, the GWSI and ground

water plume will be pushed away from those locations and the plume may ultimately discharge elsewhere (Figure 1).

The GWSI is not synonymous with the term “hyporheic zone.” The hyporheic zone is an ecological term that generally refers to an ecotone where both ground water and surface water are present in a streambed along with a specific set of biota (i.e., the hyporheos). Hyporheic zones occur as a result of flowing waters (e.g., streams) and so the term is not applicable to quiet waters (e.g., lakes) even though they have GWSIs too. A broader definition of the hyporheic zone has been proposed by White (1993) that includes any area impacted by channel (i.e., surface) water, but one set of specific criteria defining this zone has not yet been agreed upon. Delineating both the GWSI and the hyporheic zone is important when considering ecotoxicological impacts because a unique set of benthic and hyporheic aquatic life have adapted to the stream environment. The hyporheic zone may represent an ecological resource needing protection. Other work suggests the GWSI may also be an important natural attenuation zone for contaminated ground water discharge.

## Dispersion

Dispersion of contaminants in ground water refers to a process by which dissolved phase concentrations are reduced by the spreading out of the plume and hydrodynamic mixing of the water with cleaner surrounding ground water. Reductions in plume concentrations by dispersion in ground water flowing in aquifer sands and gravels is a very, very weak process compared to the turbulent mixing processes that occur in the open channel flow of rivers. Because of low lateral dispersion, plumes emanating from discrete source zones (e.g., DNAPL) are generally long thin “snake” like plumes (Rivett, et al., 1994) rather than wide “fan” shaped plumes. One important implication of low dispersion is that high concentration “cores” of ground water plumes (Cherry 1996), measured a short distance downgradient of the source, may not diminish much before reaching the river. Therefore, it is possible for very high concentration portions of the plume to reach discharge areas unless other reactions (e.g., biodegradation) occur along those flow paths to reduce the concentrations.

In locations where surface water enters the streambed, a hyporheic zone “mixing” of surface water with ground water may occur. This mixing process will result in what may appear to be quite substantial reductions in plume concentrations. The mechanisms causing this type of mixing are not well understood and result in “apparent” dispersion. Some of the uncertainty may stem from the fact that the hyporheic zone represents primarily a “surface water” flow path as opposed to a “ground water” flow path. For instance, the “mixing” that supposedly occurs in the hyporheic zone may actually be the result of ground water mixing with surface water at the base of the water column which then reenters the subsurface at a nearby downwelling zone (see the downstream downwelling zone in Figure 1).

## Reactions

Two types of reactions can occur in the subsurface, destructive and non-destructive. Destructive reactions destroy or irreversibly transform the contaminant into other compounds. These reactions include biodegradation, abiotic

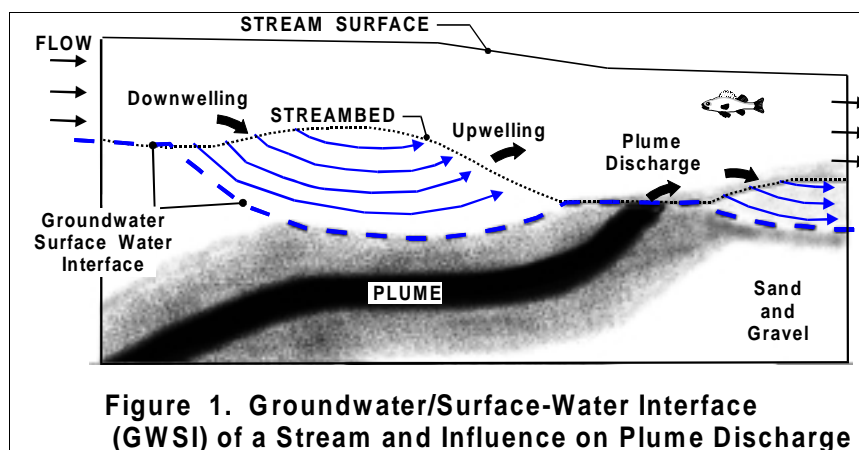


Figure 1. Groundwater/Surface-Water Interface (GWSI) of a Stream and Influence on Plume Discharge

reactions, and radioactive decay. Non-destructive reactions are reversible processes that may result in changes in contaminant concentrations in the ground water but do not destroy or transform the compound. These reactions include such things as adsorption, precipitation and dissolution, and ion exchange. A good discussion of these types of reactions as they apply to natural attenuation of chlorinated solvents can be found in U.S. EPA (1998). The relative importance of these reactions may be different in the immediate vicinity of the river than in the rest of the aquifer. In the streambed, high organic carbon content deposits contribute to higher adsorption than is typical for the surrounding aquifer. Adsorption of contaminants slows down (retards the movement of the contaminants relative to ground water flow) and sequesters them for later release. Adsorption results in contaminant loading of the sediments and in delayed breakthrough of contaminants flowing into the stream channel. Moreover, the high organic carbon and nutrient cycling also sustains a microbiological community that contributes to a greater potential for biodegradation. Biodegradation may greatly reduce contaminant concentrations. In some cases these reactions may be beneficial but in others the transformation products may be more toxic than the parent compound. In some instances (particularly petroleum product plumes), reactions that transform organic contaminants may also consume all the dissolved phase oxygen in the ground water and cause the ground water plume to become anaerobic. The adverse effect of this anaerobic water on the hyporheic and benthic aquatic life (that require oxygen to live) may be even greater than the toxic effects of the contaminants.

#### **A TETRACHLOROETHYLENE (PCE) GROUND-WATER PLUME DISCHARGING TO A RIVER**

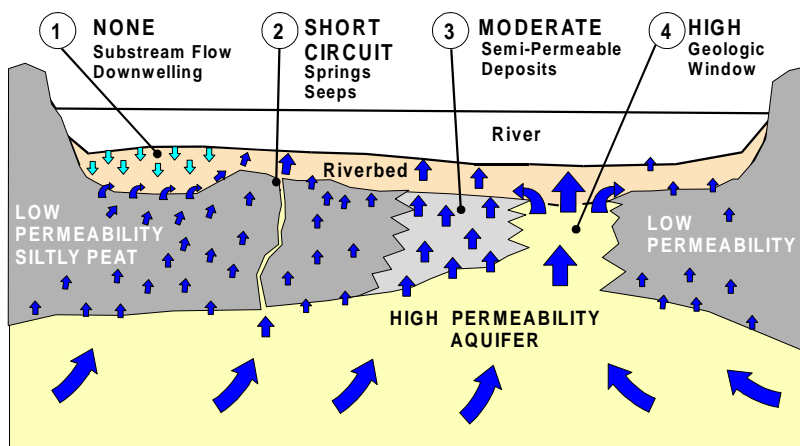
To illustrate the importance of some of the above factors, results of investigations are presented for a site located in Angus Ontario, where a dissolved-phase PCE ground water plume from a dry cleaning facility discharges into the nearby Pine River. Previous subsurface investigations at this site using the Waterloo Profiler (Pitkin, 1994; Writt 1996) and recent work (Conant, unpublished data) have delineated a dissolved phase ground water plume that emanates from a PCE DNAPL source area. The plume travels 205 m laterally through a shallow but locally confined aquifer before discharging upward through a silt and peat semi-confining unit and then the sandy streambed deposits underlying the Pine River. The plume is approximately 50 m wide and has a vertical thickness of 4 to 6 m. Water quality data collected with the Waterloo Profiler show that the peak PCE concentrations in the plume at the bank of the river (<5 m from the river) are about 8000 µg/l. Virtually no PCE degradation products were detected in the aquifer beneath the stream bank. Drivepoint piezometers screened in the aquifer at the river's edge show that there is a strong upward hydraulic gradient at the river. These piezometers have water levels approximately 1 m higher than the river stage. Water quality testing beneath the opposite bank of the river shows that the plume does not pass beyond the opposite bank.

Periodic sampling of the river water where the ground water plume discharges has detected no contamination, or very low PCE concentrations, generally less than 2 µg/l. No PCE degradation products have been detected in the surface water. The river is about 14 m wide and during most of the year is generally less than 0.75 m deep and flows at approximately 1.5 to 2.9 cubic meters per second. The estimated total flux of dissolved PCE contamination traveling within the aquifer ground water toward the river each year (expressed as equivalent pure phase PCE) is approximately 15 to 40 liters (Writt 1996). In the River channel massive dilution of the discharging PCE ground water plume by the surface water occurs and the plume does not appear to significantly impact the surface water quality. However, high concentrations of contaminants within the streambed itself represent locations where adverse ecological impacts may be occurring. At some locations, concentrations in water samples collected from within the streambed were much higher than EPA's Freshwater Aquatic Life Chronic Toxicity Standard for PCE of 840 µg/l and the Canadian Water Quality Guideline of 110 µg/l for the protection of aquatic life.

Plume water traveling through the streambed deposits is subject to a wide range of hydrological and geochemical (redox) conditions which are spatially variable on a scale of centimeters to meters. Streambed temperature surveys have identified areas of the streambed dominated by ground water discharge. Hundreds of water samples have been collected to characterize discharge zones and locate the plume. The Waterloo Profiler, the newly developed “Mini-Waterloo Profiler,” and “driveable multilevel samplers” have been used to collect interstitial water samples from the streambed and underlying shallow aquifer. These samples have been analyzed for both inorganic and organic parameters. Soil coring, ground penetrating radar surveys, and slug testing of streambed mini-piezometers have also been used to help develop a conceptual model of the subsurface system.

Four different types of flow conditions have been observed beneath the river at the site and are associated with varying geochemical conditions. The four types of ground water flow in the streambed include: no flow, short circuit, high flow, and low to moderate flow (see Figure 2). In no flow locations, no ground water is discharging to the stream as a result of geological barriers or hydraulic barriers like downwelling.

Consequently, at those locations the interstitial water in the streambed is geochemically quite similar to surface water and is not contaminated. The “short circuit” condition refers to discharge at springs and seeps where PCE contaminated ground water flows rapidly up through very localized gaps in the semi-confining unit and undergoes little or no attenuation or modification. In high flow areas, more permeable deposits result in areas of higher ground water flux. These areas are reflected in strong temperature anomalies at the streambed surface. More rapid flow and shorter residence times in the streambed deposits results in the discharge of contaminated ground water that has been only briefly exposed to reducing conditions (i.e., anaerobic and nitrate reduction). Consequently, PCE contaminated ground water has undergone very little degradation and attenuation. In the low to moderate ground-water discharge zones, contaminated ground water flows up through moderately permeable geological deposits where sulfate reducing and methanogenic conditions occur and substantial reductive dehalogenation of PCE is indicated by the presence of relatively high concentrations of degradation products (i.e., 100s to 1,000s of  $\mu\text{g}/\text{l}$  of trichloroethylene, *cis*-1,2-dichloroethylene, vinyl chloride, ethene, and ethane). PCE concentrations at one location dropped from about 3700  $\mu\text{g}/\text{l}$  to less than 50  $\mu\text{g}/\text{l}$  within a vertical distance of 15 cm and there was a corresponding increase in the concentrations of degradation products which was primarily *cis*-1,2-dichloroethylene (see Figure 3). In low to moderate ground-water discharge areas PCE concentrations in the streambed are reduced to below the EPA’s Freshwater Aquatic Life Chronic Toxicity Standard. At some of those locations, however, 100s up to a 1800  $\mu\text{g}/\text{l}$  of vinyl chloride (a human carcinogen) has been created. The potential hazard posed by vinyl chloride is unknown because it does not have an aquatic life water quality standard or guideline. In the short circuit and high ground water discharge zones the concentrations in the streambed were observed to be higher than the EPA standard for PCE. At this site the potential impact of the plume is clearly quite spatially variable.



**Figure 2. Types of Groundwater Discharge**

In terms of the overall plume behavior, it is important to note that the only place where substantial degradation and transformation of PCE is observed is in the last 3 m of the plume’s flow path from the source area. Some portions of the plume that have traveled 200 m laterally through the aquifer and



arrive at the streambed as PCE, may end up transforming completely and discharging to the surface water column as vinyl chloride or *cis*-1,2-dichloroethylene instead. At this site, water quality monitoring in the aquifer upgradient and immediately adjacent to the river does not fully characterize the type or concentration of contaminants that ultimately enter the surface water.

## SUMMARY

Determining the location and magnitude of contaminant discharges to rivers from ground-water plumes is a complex hydrogeological and biogeochemical problem. Determining specific ground-water flow paths near a stream and its GWSI is not an easy task. Moreover, the effect of transport and fate processes on the plume near the GWSI and within streambed deposits may be quite different from those observed in the aquifer further away from the stream. Large changes in geochemical conditions and plume concentrations may occur in the streambed over intervals of only centimeters, both vertically and horizontally. Measurements of ground water plume concentrations made adjacent to the stream or in the aquifer underlying the stream banks may not accurately reflect either the concentrations of contaminants in the streambed or the contaminant flux that ultimately reaches the surface water. The Angus study shows that a range of different plume discharge behaviors can occur at a single site and that closely spaced vertical and horizontal water quality sampling is necessary to detect these behaviors. In some places, reactions in the streambed transformed contaminants to daughter products and reduced the overall concentration of contaminants discharging to the river. In other places no attenuation of contaminants occurred and aquatic life in the streambed at these discharge zones had the greatest exposure to the parent compound. Aquatic life in the surface water column is typically less at risk from ground water contamination than benthic organisms because of dilution with clean surface water. The current challenge for hydrogeologists is to assist ecologists in identifying potential problem discharge zones so the toxicological impacts on benthic and hyporheic aquatic life can be assessed.

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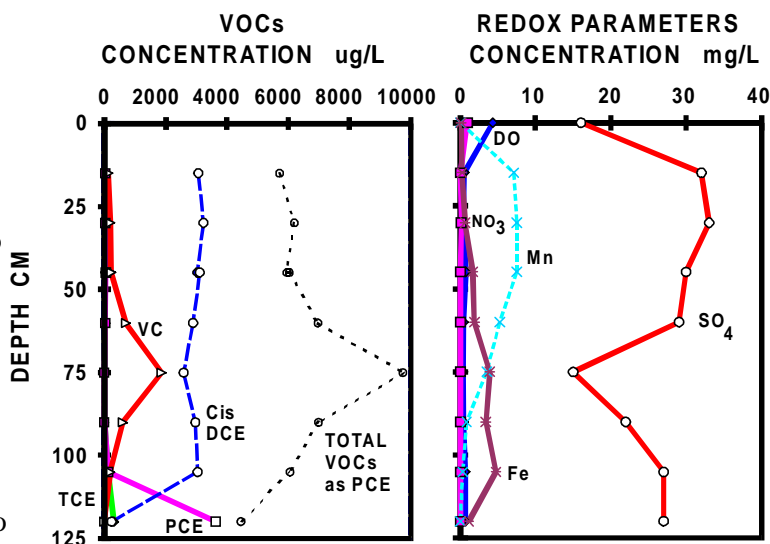


Figure 3. Groundwater Concentrations at a Low to Moderate Discharge Zone

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# Assessment Approaches and Issues in Ecological Characterizations

By G. Allen Burton, Jr. and Marc S. Greenberg

Ecosystems are extremely complex; consisting of a multitude of species that vary widely in the sensitivity to contaminants and who are dependent on each other to varying degrees. Ecosystems are routinely impacted by natural disturbances (e.g., high or low flows, habitat alteration, food availability), some of which can be quite severe and cover over large areas (e.g., hurricanes, flooding, drought, anoxia, temperature shock, invasive species, disease). These natural disturbance events must be considered when trying to ascertain the role of human (anthropogenic) disturbances. Ecosystems are also dynamic and vary through space (spatially) and time (temporally). These variations can be important at the millimeter scale where microenvironments determine nutrient and contaminant availability. However, distances of kilometers may be more significant for biogeographical issues such as forest fragmentation, foraging, and migration. Practical time scale issues vary in importance from minutes to decades. So, when we try and discern whether or not ecosystems are impacted by anthropogenic disturbances, we must do so in the context of these ecosystem complexity issues. The importance of an anthropogenic disturbance, such as exposure to chemicals, follows these natural spatial and temporal processes to a large extent. In other words, the significance of chemical exposure to an organism, population, or community may vary in importance over distances of mm to km and time periods of minutes to years, depending on the organism's behavior and the chemical's fate. However, these somber realities of complexity are not insurmountable. The following discussion will show effective ways of determining whether ecosystems are significantly impacted and which stressors are causing the primary problems.

Traditional water quality assessments typically focus on water quality standards, which assume if a single chemical criteria is exceeded then impairment to the receiving water or its beneficial use designation may exist. A limited number of states, such as Ohio and North Carolina, have also developed biocriteria, which rank indigenous fish and benthic macroinvertebrate communities into classifications ranging from poor to excellent. Toxicity testing of surrogate species, such as the fathead minnow (*Pimephales promelas*) and water flea (*Ceriodaphnia dubia*), have been incorporated into the National Pollutant Discharge Elimination System (NPDES) permit program for wastewater effluents. Toxicity testing requirements are occasionally incorporated into a permit and require testing of upstream water, effluent, and near- and far-field receiving water samples. More recently, sediment toxicity test methods have been developed by the U.S. Environmental Protection Agency (U.S. EPA) (U.S. EPA 1994); however, these have not been incorporated into NPDES permits and have been used to only a limited extent in assessments of aquatic ecosystem contamination. Each of these approaches has associated strengths and weaknesses, describing one aspect of contaminant effects under a certain set of exposure assumptions, which may or may not be realistic. These approaches can be used with confidence in situations where gross contamination exists. However, most of our current environmental concerns are more complex and often of a chronic toxicity nature. Often in remediation projects one must decide to what point or level clean-up should extend. In complex watersheds, there often is a need to decipher to what degree each potential source of pollution is contributing to impairment. It is now well accepted by those in the field of ecotoxicology that an integrated approach that combines several traditional assessment approaches, plus other non-standardized methods is necessary to reduce the uncertainty of whether *significant* ecosystem contamination exists (e.g., Burton

1999, Chapman, et al., 1992). This integrated approach is described below in the context of its application to ground water and surface water transition zones.

All ecosystems and their resident species are stressed at one time or another. We tend to focus on that subset of ecosystems where anthropogenic stressors are at issue. Since natural and anthropogenic stressors can be physical, chemical, or biological, the assessment process must consider all of them. Ecosystems, their interacting components, and the stressors which affect them are dynamic and not in equilibrium. So the assessment process must also consider organism exposures to stressors from a magnitude, frequency, and duration perspective. These realities dictate that an integrated assessment contain the components listed in Table 1.

**Table 1.** Elements of an Integrated Assessment of Aquatic Ecosystems

<i>Component</i>	<i>Sampling Media</i>	<i>Frequency</i>
Habitat	Drainage area, riparian zone, waterway	Seasonal
Chemistry	Drainage area soil, water, sediment, pollutant sources, and tissues of key receptors	Low and high flow
Biota	Benthos, fish, and fish-eating wildlife	Seasonal
Toxicity	Surface water, pore water and sediment (laboratory and <i>in situ</i> )	Low and high flow

Within the four general components of habitat, chemistry, indigenous biota, and toxicity the primary stressors and receptors can be identified with the proper sampling and test design. This approach can follow the ecological risk assessment paradigm whereby there is a problem formulation step, followed by field and laboratory assessments of exposure and effects and finally a risk characterization via a weight-of-evidence approach.

For assessing potential contamination in ground water/surface water transition zones it is critical to team hydrologists, hydrogeologists, aquatic biologists/toxicologists, and environmental chemists in the assessment process. A tiered assessment approach is the most cost effective way to conduct an integrated assessment, eliminating the collection of data which may not be necessary (Table 2). The specific measurement methods that are used in these approaches should be optimized for each study, depending on the problem and questions being asked. For example, in freshwater systems this means optimizing the indicator species used for toxicity testing and response endpoints (e.g., sublethal biomarkers, growth, reproduction, tissue residues, mortality), selecting the appropriate exposure *in situ* (e.g., surficial vs. deep sediments, small mesh to reduce suspended solids, UV blockers to prevent photo-induced toxicity from polycyclic aromatic hydrocarbons), or selecting the appropriate data analysis methods for the benthic invertebrates (e.g., metrics like Invertebrate Community Index, orthogonal comparisons).

Assessing the ecological significance of ground water/surface water transition zones will present some new challenges. Virtually no contaminant effects research has been conducted on biological communities which inhabit the hyporheic zones. It will be critical to establish good reference sites as a point of comparison. These transition zones are particularly important in the storage and retention of nutrients (and possibly contaminants), biological and chemical transformations, as a refugia for invertebrates, and a base of the aquatic food web. Therefore, the measurement endpoints should be focused on determining effects on these traits. Appropriate measurement endpoints could include: indigenous microbial activity, organic matter/nutrient cycling (for more advanced studies), invertebrate

**Table 2.** Tiered Assessment Approach for Characterizing Ground water/Surface Water Transition Zone Contamination\*

Tier 1a: Hydrological characterization of transition zone locations, upwelling vs. downwelling, rates, surface water dynamics.

Tier 1b: Characterization of benthic invertebrates (sediment surface and hyporheous, grabs, colonization, transplants) and habitat quality.

Tier 2: Toxicity testing of indicator species (sediment (laboratory); surface water (high and low flow), surficial sediment and pore water (*in situ*)). Tissue residue analysis of *Lumbriculus variegatus* (*in situ* exposure) and dominant indigenous species.

Tier 3: Site-specific studies to separate physical and chemical stressors with associated chemical analyses, if needed.

\* Assumes initial problem formulation process has identified contamination of ground water or surface water with potential transfer to the other.

community indices (meiofaunal and macrofaunal—grab and colonization), tissue residues of dominant species, *in situ* toxicity, and *in situ* physicochemical profiles (e.g., via peepers, datasondes).

If Tiers 1 and 2 indicate that the surface or ground waters are toxic and/or are impacting the indigenous community then Tier 3 may be necessary to tease out which stressors dominate at the site. These are very site-specific based designs, but can include novel, yet proven, tools such as ecological food web modeling, semi-permeable membrane devices (SPMDs) to look at bioaccumulation potential, toxicity identification evaluations (TIEs) which fractionate chemical classes for toxicity testing, and stressor identification evaluations (SIEs) which are *in situ* based TIEs but incorporate other physical stressor determinations (Burton et al 1996 and 1998; Greenberg et al 1998), and more detailed characterizations of community effects and exposure dynamics.

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# **Delineation, Quantification, and Mitigation of Discharging Plumes**

By David R. Lee

## **INTRODUCTION**

Methods have been developed for locating and sampling ground water and solute discharge areas on the beds of surface waters. In many settings, these can aid in the assessment of natural attenuation or in estimating the direct flux of ground water contaminants to surface waters. Where plumes are not sufficiently attenuated by natural mechanisms before reaching surface waters, passive subsurface treatment methods, as exemplified by the Chalk River wall and curtain, are now demonstrated at full scale. The purpose of this presentation was to highlight the author's approach to these problems.

The concept of monitored, natural attenuation sounds good, but putting it into practice will take careful work. If it has been difficult to monitor natural attenuation in relatively simple, well-characterized hydrogeological settings, then it will be even more difficult to perform such monitoring near the beds of surface water bodies. Transients in flow and changes in water levels are only a part of the difficulty.

Another unappreciated difficulty, is the profound influence of geologic heterogeneity on contaminant migration. Heterogeneity can result in orders of magnitude variations in flow within a relatively small volume of earth. Many people believe that hydraulic conductivities at a site vary by factors of 1.2 to 1.5. However, in actual fact at most sites, hydraulic conductivities vary by factors of 10 to 300! Since one of the controls on attenuation is ground-water residence time, attenuation may vary widely across most sites. Therefore, the technical information on which to base an evaluation of attenuation at real sites depends upon the determination of spatial distributions in flow, particularly on finding the faster flow areas at each site.

Measurements of hydraulic gradient can indicate large discharge areas. However, the results of numerous seepage studies have shown that areas of rapid discharge can be small and easily missed. If not located, zones of contaminant entry will not be assessed. In other words, if flow is focused, as it often is, the impacts of the discharge and the processes or evidence for attenuation may have to be monitored within the relatively small, fast-flow areas, which have the greatest potential for poor attenuation and transport of contaminants to surface. If flow rates exceed the required reaction times, the potential for subsurface attenuation may not be realized. High flow areas occur where there are preferential flow paths, such as sand stringers or interconnected zones of higher permeability. The areas where these flow paths intersect surface waters may be overlooked without thorough field work. Even in relatively homogeneous terrain, flow may be highly focused at the shorelines and transport may be rapid.

## **IS ATTENUATION WISHFUL THINKING OR REALITY?**

While it is reasonable to expect some attenuation for many contaminants at most sites, those who seek to monitor attenuation or to measure impact face many pitfalls. Sampling must include the faster flow areas in order for measurements of flow and contaminant concentrations to be representative. If the act of sampling dilutes the ground-water concentrations, and this is easy to do near the

sediment/water interface, the sample and the resulting chemical analyses may be inappropriate for contaminant flux calculations. Thus conclusions may be biased and non-conservative as a result of incomplete or improper sampling. It may be easier to find evidence for attenuation than to establish sufficient attenuation.

## **DEVELOPMENT OF METHODS TO LOCATE AREAS OF SIGNIFICANT DISCHARGE**

There is a growing awareness that the application of existing technologies is key to valid monitoring of natural attenuation. One promising method is the sediment probe, a specifically designed for the detection of ground water upwelling (Lee, 1985; Lee and Beattie, 1991). Towed behind a moving boat, the sediment probe is in contact with sediments, and it measures sediment properties. Once areas of ground water discharge have been found and delineated, they may be assessed using traditional, quantitative methods (Lee and Dal Bianco, 1994; Harvey, et al., 1997; Lee, et al., 1999). Traditional methods such as piezometers (e.g., Lee and Harvey 1996; Geist, et al., 1998) may be used for pore water collection and measurement of hydraulic head and conductivity. Under some conditions, seepage meters (e.g., Lee and Cherry, 1978; Lee, 1977; Lee and Hynes 1978) may be appropriate for measuring the flux of ground water across the sediment/water interface.

The sediment probe has been used to find and confirm discharge areas on the cobble sediments and in the 2m/s currents of the Columbia River (Lee, et al. 1999). In that work, quantitative samplers showed that, without exception, probe "hot spots" were areas of ground water inflow and some of these inflows bore contaminants.

The sediment probe has also been used to locate ground water discharge into the shallow ocean (Vanek and Lee, 1991). Other methods have been developed to aid in demonstrating attenuation near the interface (e.g., Lee, 1988; Winters and Lee 1987).

Having been proven in a variety of settings, the sediment-probe method is now ready for use in identifying areas where it may be necessary to monitor attenuation, or the lack thereof. This is essentially a reconnaissance method, a targeting tool. It requires a slight contrast in dissolved solids concentrations between the ground water of interest and the overlying surface water. Where the plume itself is different in dissolved solids, it can tell us, "No, the contaminant is not here," or "Yes, it is, and, the signal keeps getting larger as we move in this direction." By applying such methods, it is possible to design a monitoring system for contaminant attenuation and to provide a basis for deciding whether to rely on the process of natural attenuation. Clearly, in order to show that attenuation is sufficient, it must be known where discharge occurs, particularly where it is most rapid, and evidence of acceptable flux of solutes must be obtained.

There is potential for incorporating additional sensors on the sediment probe to make it sensitive to conditions other than electrical conductance.

## **DEVELOPMENT OF METHODS FOR PLUME MITIGATION**

In settings where attenuation is found to be insufficient, subsurface treatment systems, like those first described by McMurty and Elton (1985), can be constructed to enhance natural attenuation mechanisms and therefore minimize impacts on surface waters. An example of such a treatment system is the wall and curtain at the Atomic Energy of Canada, Ltd.'s (AECL) Chalk River Laboratories.



The wall-and-curtain treatment system was installed in 1998 to mitigate the discharge of a strontium-90 plume. In this system, contaminated ground water is directed through a subsurface, permeable, granular curtain of a natural, ion exchange mineral, called clinoptilolite. Based on the results of *in situ* testing, clinoptilolite was highly absorbent for strontium. A bed of clinoptilolite 2 m thick was installed underground. It is predicted to retain the strontium-90 for at least 60 years, during which time its concentration will decay to one-fourth (or less) of the input concentrations. It is expected that this subsurface facility will operate passively at low cost with no maintenance except for the required effluent monitoring. Unlike other methods for subsurface treatment, the wall-and-curtain provides an adjustable capture zone and a single point of flow for checking regulatory compliance (Lee, et al., 1998).

## FINAL COMMENT

In the process of exercising these methods at major contaminant sites, I have concluded that two factors have combined to create a vicious circle. The factors are 1. general lack of understanding of ground water-contaminant seepage to surface water and 2. self interest among plume owners. The vicious circle is as follows: if there is little proof of a problem and little public understanding, there is little regulatory demand for better information and little funding for developing and applying methods.

Many contaminant plumes have been mapped to the margin of a river, lake, wetland or estuary. But, there is little advantage for a plume owner to map it further unless this is required. Piped effluents must meet or exceed drinking water standards, but there is little enforcement of the same water-quality standards where it is a ground water contaminant plume, not a pipe-flow, that is entering surface waters. Without measurements, there is little understanding and no violations. Or, if measurements at 2 or 3 points looked OK, then the discharge was deemed OK. We humans tend not to seek what we fear we might find. When things are out of sight, they are out of mind.

## CONCLUSION

Methods have been developed, applied successfully and have shown the movement of ground water contaminants to surface waters. It is hoped that this workshop will result in broader application of the methods highlighted here and other, equally appropriate, methods that have not been mentioned (my apologies). Hopefully with the issuance of these workshop proceedings, the EPA will begin the task of requiring site-specific evidence where natural attenuation is claimed to be a remedy, but is not monitored, and will require mitigation where attenuation is not sufficient.

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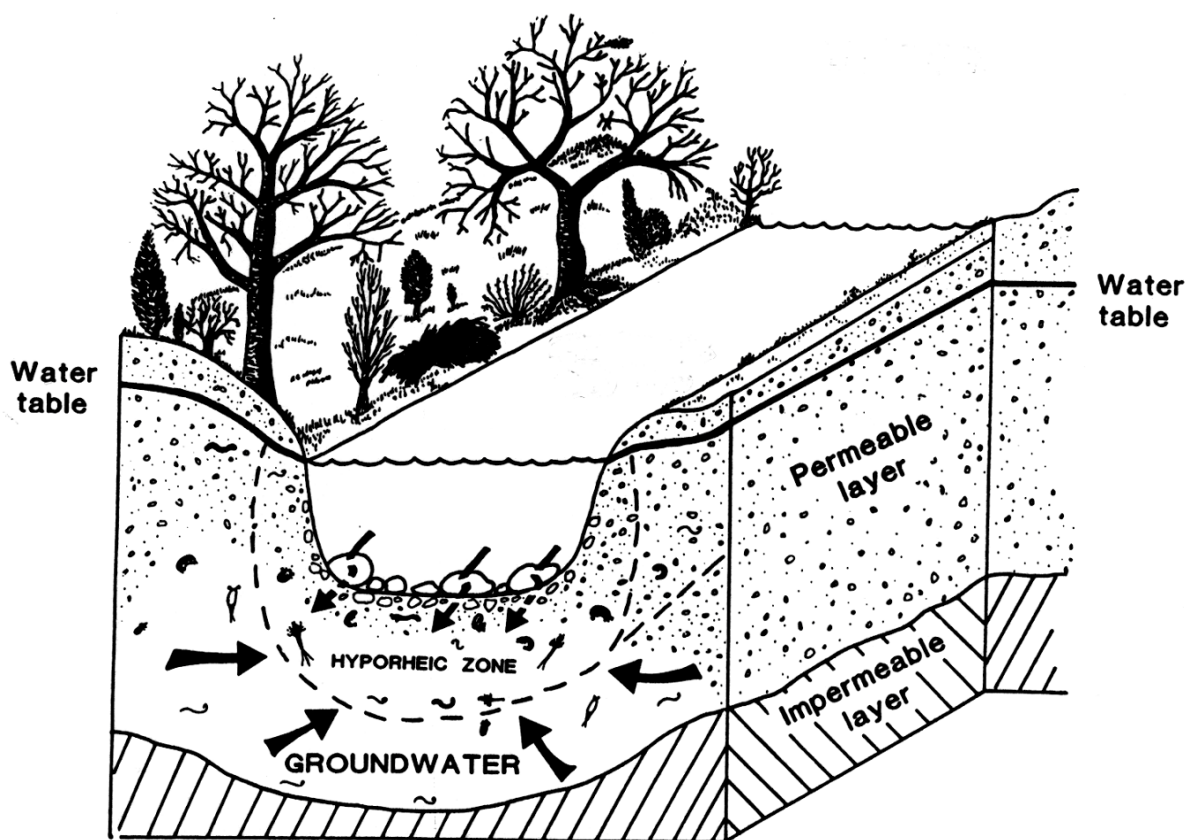
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# Field Technology and Ecological Characterization of the Hyporheic Zone

By D. Dudley Williams

The hyporheic zone is a 3-dimensional aquatic interstitial ecotone formed within the mixed substrate particles that comprise the bed of a natural, running water channel (Figure 1). It is a middle zone bordered by the surface water of the stream or river above, and by the true ground water below. Although it receives water from both of these sources, the relative strengths of input depend on the configuration of the bed materials and interstitial flow paths, and on the prevailing hydraulic heads. These heads vary spatially and seasonally to alter hyporheic habitat volume and to produce ragged-edged boundaries to the zone (Williams, 1993). Water that flows across these boundaries is subject to changes brought about by distinctive, local chemical and physical properties, microbial processes, and metazoan community dynamics.

Hyporheic research has been progressing at varying rates over the past 30 years, although, recently, progress has been more sustained and intense. Undoubtedly, one of the major factors that limited progress in the 1970s and 1980s was the perception that it is very difficult to sample the hyporheic



**Figure 1.** Diagrammatic section through a stream channel showing the approximate position of the hyporheic zone during winter, low flow conditions

zone in any meaningfully quantitative manner. True, extracting largely soft-bodied invertebrates from the interstices among highly heterogeneous and hard lotic bed materials is difficult. However, a sufficient number of techniques now exists (some of them old, but with recent modifications) that makes ecological characterization of this zone possible.

Many running water invertebrates can be collected from hyporheic sediments. Typically, maximum densities may occur around 10 to 40 cm below the streambed surface, but densities of 700 invertebrates per 1 liter of sediment at 100 cm depths are not uncommon (Williams and Hynes, 1974). The hyporheic fauna itself has two main components (Table 1). Differences in the spatial and temporal residence profiles of these two components suggest different functional roles for the two groups within the zone. Although not conclusively proven, there is evidence to suggest that the hyporheic zone may act as a refuge from extreme conditions on the streambed surface (Williams and Hynes, 1977). For example, spates are known to wash benthic organisms downstream as surface substrates are scoured, and droughts and toxic pollutant plumes kill surface-dwelling animals (Hynes, et al. 1974; Williams, 1987). The rapidity with which certain taxa recolonize these denuded substrates has been shown to be due, at least in part, to vertical migration from the hyporheic zone (Dole-Olivier, et al., 1997). Again, the discovery of diapausing nymphs of the cool water-adapted winter stonefly *Allocaenia vivipara* in the hyporheic zone during the summer warm-water phase of temperate streams is further evidence of a refugium (Harper and Hynes, 1970).

**Table 1.** The two primary components of the hyporheos (after Williams and Hynes 1974).

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(1) Species derived from hypogean environments such as ground water, subterranean water bodies, and waterlogged soil. These have been dubbed “permanent” members of the hyporheos as they complete their entire life cycles in the interstices. The permanent hyporheos includes rotifers, nematode worms, oligochaetes, mites, copepods, ostracods, cladocerans, tardigrades, and syncarid and peracarid crustaceans.

(2) Species derived from the streambed benthos—particularly the early-instar larvae of aquatic insects. These spend only part of their life cycles in the hyporheic zone, having to return to the stream surface in order to metamorphose into a terrestrial, adult stage. These have been dubbed “occasional” members of the hyporheos, although “transient” members may be a better term.

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While the hyporheic zone is a fascinating system for the furthering of purely academic enquiry, it also is emerging as an important site for the transformation and storage of nutrients (Triska, et al., 1994). For example, nitrification, a major chemolithotrophic process, occurs in the hyporheic zone, converting the predominant form of inorganic nitrogen in incoming waters from ammonium to nitrate. Although the amount and rate of production of biomass contributed to the lotic food web by nitrifying bacteria are typically lower than those generated by heterotrophs, in streams receiving high levels of nitrogen from riparian agriculture production through nitrification could be quite significant. Similarly, bacterial alkaline phosphatase activity is known to occur in the hyporheic zone, and release of phosphorus from organic P may supply this important nutrient to surface (benthic) and hyporheic biota.

In addition, there is some evidence that lithological and geochemical processes in the hyporheic zone may mediate the availability of N and P (Storey, et al., 1999). For example, substrate particles that have a high cation exchange capacity, as a consequence of their chemical composition and size, will tend to sorb inorganic P and ammonium. In the latter case, hyporheic sediments have the capacity to function as a transient storage pool for dissolved inorganic nitrogen. In these respects, the hyporheic

zone should be of interest to water managers and conservationists, as custodians of national water resources.

Hyporheic sampling techniques roughly fall into four categories (Table 2). Unfortunately, virtually all of these samplers have limitations. For example, well digging cannot be used in mid-stream and is not very quantitative; freeze cores may drive organisms away as they form; mechanical corers may have depth or substrate particle size limitations; and artificial substrates may fail to re-establish natural sediment profiles and/or detrital components. Further, many of these samplers have neither been evaluated in more than one location, nor evaluated against each other.

**Table 2.** The four main categories of hyporheic samplers.

(1) <b>digging of small wells</b> in the exposed (above water) areas of gravel bars and stream margins to reach the water table, and then straining the interstitial water so exposed through a fine-mesh net;	Karaman-Chappuis technique, see Schwocrbel (1970) Sassuchin (1930)
(2) <b>freeze cores</b> that use chemicals such as liquid nitrogen, liquid carbon dioxide, or a mixture of "dry ice" (crushed solid carbon dioxide) and acetone or alcohol to freeze the substrate around a standpipe driven into the bed;	Efford (1960) Stocker and Williams (1972) Danielopol, et al. (1980) Bretschko and Klemens (1986)
(3) <b>mechanical corers</b> that, when driven into the bed, either isolate a sample of the surrounding substratum and its fauna for subsequent removal, or suck up interstitial water and organisms from a desired depth;	Bou and Rouch (1967) Husmann (1971) Mundie (1971) Williams and Hynes (1974)
(4) <b>artificial substrate samplers</b> that involve placing a sterilized portion of natural stream bed into perforated containers that are sunk into the bed and then removed after a desired period of colonization.	Moon (1935) Coleman and Hynes (1970) Hynes (1974) Panek (1991) Fraser, et al. (1996)

Recently, we compared the field performance of four hyporheic samplers at a single riffle on the Speed River, Ontario (Fraser and Williams, 1997). These samplers were: the standpipe corer, the freeze corer, a pump sampler, and the colonization corer. Each sampler was assessed, at different sediment depths, for accuracy and precision in terms of total invertebrate density, taxon richness, and invertebrate size distribution.

Since previous studies have concluded that the standpipe corer and the freeze corer, following *in situ* electropositioning, provide good estimates of hyporheic density (Williams, 1981; Bretschko and Klemens, 1986), the *a priori* assumption was made to accept their data as the accuracy standard. Sampler precision was calculated as the coefficient of variation (CV), which is the standard deviation expressed as the percentage of the mean.

In terms of faunal density (Figure 2), the colonization corer estimates were significantly less than those obtained by the other three corers all of which produced very similar results.

In terms of overall taxon richness, there were no detectable differences among the samplers. Further, all of the samplers captured individuals representing greater than 90% of the available taxon

pool. For example, all of the samplers captured nematodes, molluscs, ostracods, copepods, mites, mayflies, stoneflies, caddisflies, beetles, and dipterans. However, tardigrades were captured only by the freeze and pump samplers; cladocerans were not captured by the freeze corer; and amphipods were not captured by the pump sampler. In terms of the percent insect larvae captured (another measure of taxon bias), the pump sampler collected the fewest, although this was significantly so only at a depth of 20 cm.

In terms of invertebrate size, as measured by chironomid larval length, there was a decrease with increasing depth for all of the samplers. The only difference detected among the samplers was that, at 20 cm, the pump sampler captured slightly smaller larvae than the other three.

For all four samplers tested and all of the measures compared (density, richness, and size), the level of precision was generally between 20 and 40%, but increased with depth. No sampler yielded a consistently higher level of precision than any other.

The conclusions that may be drawn from this comparative study are:

- (1) All four samplers would suffice for collecting purely qualitative data.
- (2) In terms of removing an exact, representative portion of habitat (to obtain absolute measures), only the freeze corer qualified. However, and in support of the *a priori* assumption, no statistical differences were detected between this sampler and the standpipe corer for any of the measured variables, at any depth.
- (3) The colonization corer consistently underestimated total invertebrate density.
- (4) The pump sampler was capture selective both in terms of invertebrate type and size - the bias towards non-insects and smaller insects probably reflecting a filtering effect of the interstices.

As to recommendations for possible standardization of hyporheic sampling are concerned, pragmatically the goals should determine the means. Some examples are given in Table 3. Regrettably, the holy grail of a perfect hyporheic sampler still seems to evade us and, indeed, may never be attainable. Nevertheless, samplers do exist that allow acceptable levels of sediment description, water sampling, and faunal characterization to be made—although perhaps not through one apparatus alone. Such techniques have the potential, either singly or in combination, to help researchers answer some of the sophisticated questions that 30 years of hyporheic study is now demanding.

**Table 3.** Examples of hyporheic samplers suited to specific information goals

- (1) If **survey information** is required, relatively quickly, on invertebrate densities and types at a variety of depths, then the standpipe corer would be suitable. This corer has been shown to produce a mean error density estimate of around 19%, and captures virtually all of the common taxa found in the hyporheic zone (Williams, 1981). Both Cummins (1975) and Elliott (1977) have suggested that this level of accuracy is acceptable in estimating benthic densities, and so perhaps the same should be applied to the hyporheos.
- (2) If a **larger sample volume, together** with a description of invertebrates and the undisturbed sediments in which they live, is required, then the freeze corer (preceded by electropositioning) would be the choice.
- (3) If **periodic assessment** (with moderate precision) of the hyporheos is required from a particular site, with minimal, long-term habitat disturbance, then the colonization corer would be appropriate - especially if routine hydrogeological and chemical data are needed also.

(4) The colonization corer also would be the most suited to **manipulative studies** of hyporheic dynamics—as it allows different combinations of hyporheic sediments (e.g., particle size and/or organic content) to be presented for colonization.

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## **DISCUSSION GROUP SUMMARIES**

# Hydrogeology Discussion Group Summary

By Thomas C. Winter and Joseph Dlugosz

## INTRODUCTION

The great variety of sediment types in the beds of most surface water bodies results in substantial variability in the location and rates of seepage across the bed. The exchange of water between ground water and surface water ranges from slow, diffuse seepage to rapid, concentrated flow at specific localities. Determining the location, rate, volume, and chemistry of water moving between these two components of the hydrologic system is difficult, expensive, and highly uncertain. Nevertheless, the need for understanding the hydrologic processes and measuring the interaction of water and dissolved chemicals between ground water and surface water is fundamental to environmental management. To address these challenges and needs, the hydrogeology discussion group focused on the hydrogeologic aspects of understanding and measuring the interaction of water and dissolved chemicals between ground water and surface water at sites where ground water has been contaminated.

To focus the discussion on the interface between ground water and surface water, the group made several presumptions: (1) the hydrogeologic framework of a site has been defined; (2) the source area of the contaminant is known; (3) the flow pathways and plume configuration are reasonably well defined; (4) the chemical characteristics and decomposition products of the contaminants are known; and (5) the contaminant is a potential threat to the environment. Given this information, it was suggested that the actual determination of the movement of ground water to the surface water body could be accomplished through a tiered approach: A sequence of actions could be followed that begins with a general reconnaissance of observable indicators of ground-water discharge and evolves to very detailed and focused sampling of hydraulic head, chemistry, and biology.

This summary of the discussion group presents:

- (1) Field methods that can be used for (a) reconnaissance of observable qualitative indicators of ground-water discharge to surface water, (b) direct measurement and calculated flow of water between ground water and surface water using physical data, and (c) indicators of flow between ground water and surface water using chemical data;
- (2) Considerations for temporal sampling of water flow and chemistry; and
- (3) Variations of field sampling strategies that may be needed in different hydrologic landscapes.

The material presented here is considered to be a supplement to another EPA report (U.S. EPA, 1991) that presented a review of methods for assessing non-point source contributions of contaminants to surface water. Some of the information presented briefly in this summary is discussed in much more detail in the EPA report.

## **FIELD METHODS FOR DETERMINING THE INTERACTION OF GROUND WATER AND SURFACE WATER**

### **Observable Qualitative Indicators of Ground-Water Discharge to Surface Water**

Many indicators of ground-water discharge to surface water can be used to determine specific localities where a contaminant plume may be entering a surface-water body. The most common indicators are seeps and springs; infrared mapping; aquatic plants; phreatophytes; unique sediment zones such as mineral precipitates; water color; odor from contaminants; and mapping of lineaments in fractured-rock settings. It was suggested that a field reconnaissance of these easily observable characteristics would identify specific localities where detailed measurements and sampling could be focused. If the skills of biologists are available, benthic organisms also can be useful indicators of ground-water discharge.

Observation of seeps and springs is relatively straightforward if the flow rates are high. In fractured-rock landscapes, mapping of lineaments can be useful if the fractures are open. Ground-water flow concentrated in the fractures enter surface-water bodies as springs. In settings where seepage rates are low, it is easier to observe seeps during colder times of year when ground water and air temperatures are considerably different, because the water vapor above seeps is visible. Furthermore, in climates where surface water freezes or snow is on the ground, areas of appreciable ground-water inflow remain open. The difference in temperature between ground water and surface water also makes infrared mapping a useful reconnaissance tool, especially in mid-summer when the difference in temperatures of ground water and surface water are at a maximum.

Some chemical constituents dissolved in anoxic ground water precipitate upon contacting oxygenated surface water. For example, iron and manganese oxides are common indicators of seep areas. Contaminated ground water commonly has color and odor. Water color and odor from contaminants can be used as an indicator of ground-water inflow, especially if the inflow consists of the contaminated water.

Aquatic plants can be indicators of ground-water discharge. The following are a few examples: (1) Swanson, et al. (1984) indicated that cattails are indicators of fresh ground-water input to saline prairie lakes in North Dakota, (2) Rosenberry, et al. (in review) indicated that Marsh Marigold was an indicator of springs in Minnesota, (3) Lodge, et al. (1989) indicated that submerged aquatic plant biomass was greater where ground-water inflow velocity was greater, and (4) Klijn and Witte (1999) discussed the relationship of plants to ground-water flow systems. In addition to aquatic plants, upland phreatophytic plants near a surface-water body are indicators of the presence of ground water at shallow depths.

Benthic organisms can be indicators of ground-water discharge to surface water. Numerous examples of the relationship of organisms to water flow and chemistry are provided by studies of the hyporheic zone beneath streams. With respect to lakes and wetlands as well as streams, ostracods are especially useful because they have specific tolerances to water temperature and chemistry. An additional benefit to using ostracods is that some of the chemical constituents and isotopes that are present in the water while the organisms are alive are incorporated into their shells. Therefore, study of ostracod shells in sediments can provide a valuable record of past ground water and surface water relationships.

## Direct Measurement and Calculated Flow of Water Between Ground Water and Surface Water Using Physical Data

The reconnaissance methods discussed above may be useful for identifying locations of ground-water inflow to surface water, but they do not indicate the quantities of water that move across the interface. Measurement of water quantity can be done by (1) using instruments that directly measure the water flux, or a physical or chemical property from which flux can be calculated, at the specific locality of the instrument (herein referred to as direct measurements); or (2) calculating the flux over a broader area of surface-water bed using streamflow data or ground-water flow nets. A drawback of direct measurements is that they sample a point in space, and, because of the great variation in sediment types in most surface water beds, measurements need to be taken at many places in the bed. Furthermore, most measurements are taken at a point in time because the devices generally are not equipped with recorders. For these reasons, it also is desirable to calculate the flux through broader areas of surface-water beds to obtain independent estimates of flux. This approach averages out the spatial variability of flux and it provides a check on values determined by direct measurements.

*Direct measurements:* Methods for directly measuring the flux of water between ground water and surface water include the use of seepage meters, mini-piezometers, temperature profiles in the sediments, heat-flow meters, hydraulic properties of sediments determined from cores, and direct-contact resistivity probes. Although these were considered by the discussion group to be methods for direct measurements, only seepage meters can be used for direct measurements of water flux. The other methods use devices that make direct measurements of hydraulic head, hydraulic conductivity, temperature, or electrical conductance, and the water flux then needs to be calculated from these data.

Seepage meters are chambers (commonly, cut-off 55-gallon drums) that are set on the bed of a surface water body (Lee, 1977). After the chamber is pushed into and allowed to settle into the sediment, a tube is inserted into an opening in the top or side of the chamber. The tube has a small bag attached at the end and a valve positioned between the chamber and the bag. The bag can be attached empty if ground water is known to be seeping in, or filled with a known volume of water if the direction of seepage is unknown or if it is known that surface water is seeping out. To measure the flux, the valve is opened and the change in water volume in the bag over a given period of time is a measure of flux per that period of time. Seepage meters are perhaps the most commonly used devices for measuring water flux between ground water and surface water, and different sizes and types of chambers other than 55-gallon drums have been used. A number of studies have evaluated the uncertainties in using the seepage-meter method for determining flux through surface-water beds (Shaw and Prepas, 1990; Belanger and Montgomery, 1992). Seepage meters have been used largely to make discrete measurements at a point in time, but a recording seepage meter was developed recently by Paulsen, et al. (unpublished manuscript) using ultrasonic flow technology.

Mini-piezometers are used to determine the hydraulic gradient between a surface-water body and the ground water beneath it. A small diameter well is inserted into the surface-water bed, and, in the most common design, a flexible tubing is attached from the well to a manometer board. Another piece of tubing is attached to the other side of the manometer and the other end is placed in the surface water. Both ground water and surface water are drawn into the manometer using a hand pump. After air is bled back into the manometer and the water levels in each tube stabilized, the difference in head can be measured directly (Lee and Cherry, 1978; Winter, et al., 1988). The difference in head between ground water and surface water can also be determined simply by measuring the level of ground water in the well and the level of surface water outside the well. Mini-piezometers provide data only on hydraulic gradient. To determine water flux, hydraulic conductivity of the sediments need to be determined as well as the cross-sectional area of the flux.

The transport of heat by flowing water has been used to determine the interaction of ground water and surface water. By measuring the temperature of surface water and the temperature at shallow depths in sediments, Silliman and Booth (1993) mapped gaining and losing reaches of a stream in Indiana. Sediment temperatures had little diurnal variability in areas of ground-water inflow because of the stability of ground-water temperatures. Sediment temperatures had much more variability in areas of surface water flow to ground water because they reflected the large diurnal variability of the surface water. This approach is useful for determining flow direction. Lapham (1989) used sediment-temperature data to determine flow rates and hydraulic conductivity of the sediments based on fundamental properties of heat transport. Heat-flow meters, consisting of a heating element and a ring of temperature sensors, placed at a distance from the heater, have been used to measure the rate and direction of water movement through sediments. A pulse of heat is applied to a heating device and the rate and direction of water movement is determined by measuring the time it takes for the heat pulse to be sensed by the thermistors in the direction of flow.

Hydraulic properties of sediments can be determined by laboratory studies of sediment cores. These data can then be used to calculate ground-water flux if the hydraulic gradient and area of surface-water bed through which the water flux is taking place is known. Probes that measure electrical resistivity have been used to locate contaminant plumes entering surface water. These probes are most effective if the conductance of the contaminant is substantially different than the conductance of the ambient ground water.

*Calculated from streamflow data and flow nets:* The quantity of water moving between ground water and surface water over scales larger than can be determined by direct measurement using individual sensors generally is determined by stream discharge data or by ground-water flow nets. The most direct method for determining ground-water inflow or stream losses to ground water is to make stream discharge measurements at different locations along a stream. The difference in discharge between two localities is the quantity of gain or loss of water for the reach of stream between the measurement sites. The accuracy of the values is related almost entirely to the accuracy of the discharge measurements.

The flow-net approach is probably the most common method used for determining the interaction of ground water and surface water. The term flow net is used broadly herein as any calculation of ground-water flux, including simulation models, that makes use of a network of wells for determining hydraulic gradients, estimates of hydraulic conductivity of the geologic units and sediments, and cross-sectional area of the interface of ground water and surface water. The accuracy of the values is related to the quantity and quality of the hydrogeologic data, and the grid spacing that is justified by these data.

## **Indicators of Flow Between Ground Water and Surface Water Using Chemical Data**

The chemistries of ground water and surface water commonly are different enough—especially at contaminated sites—that some chemical constituents or isotopic properties of water can be used to determine the interaction of ground water and surface water. Devices for collection of water samples for determination of the chemical characteristics of water passing through sediments consist of two basic types: (1) collection at the sediment-water interface; and (2) collection at various depths in the sediment by inserting a device into the sediments.

*Constituents:* Nearly all chemical constituents have the potential to be useful in determining the contribution of ground water to surface water. By calculating mass balances of the constituents, the flux of water can be quantified. Isotopes of some elements, such as nitrogen and radon, are particularly

useful because in some cases a specific contaminant source can be identified. Isotopes of water are among the most useful because they are part of the water molecule itself and are not subject to modification by chemical reactions. The age of ground water can be determined by analyzing for tritium and chlorofluorocarbons, which are useful for identifying ground-water flow paths.

*Sampling at the sediment-water interface:* Devices that have been developed for sampling water at the sediment-water interface include drag probes, seepage meters, diffusion bags, bubble collectors, and biosensors. Of these devices, seepage meters are the only ones that actually collect a water sample large enough to be analyzed in the laboratory for many constituents. Furthermore, by knowing the water flux, the flux of a constituent or isotope can be calculated. Drag probes, such as used for measurement of temperature, specific conductance, and radioactivity, are used primarily to locate areas of inflow. Vapor diffusion samplers are placed in the sediments and can collect certain contaminants that diffuse into the bag, and they also can measure microbiological activity through the production of hydrogen. Devices that collect gas bubbles are used to determine the chemical constituents in the bubbles, which are an indication of the gases being produced in the sediments.

*Sampling at depth in sediments:* Devices that have been developed for sampling or measuring water chemistry at depth in sediments consist of (1) multi-level samplers that are driven into the sediments; and (2) probes through which individual samples can be drawn from any depth—or a constituent measured—but can then be driven deeper to collect samples at other specific depths. Examples of the first are pore-water peepers, gel samplers, and multi-level samplers. Pore-water peepers are blocks of plastic that have chambers machined into them at specified intervals (Hesslein, 1976). A porous membrane is placed over the chambers and held in place by another cover of plastic that has holes machined at the same intervals. The chambers are filled with deionized water, and the device is driven into the sediments. The device is left in place for a period of time for the chemicals to diffuse across the membrane and equilibrate with the ambient pore water (usually weeks). The device is then removed and the water in the chamber is extracted and analyzed. Gel samplers are similar, but the collection device is a thin film of polyacrylamide gel that is placed on a flat Perspex probe, covered with a porous membrane, and held in place by a thin plate that has a window cut the full length of the probe (Krom, et al., 1994). The device also is driven into the sediments and left to equilibrate (usually only minutes to a day). After equilibration, the device is removed and the gel sectioned at any desired interval to obtain the samples.

Multi-level samplers are rigid tubes that have ports machined into them at specified intervals. Flexible tubing is attached to each port and brought to the surface. Water samples can then be drawn from individual ports using a pump at the surface. Squeezing or centrifuging pore water from segments of sediment cores can also be considered multi-level sampling. Of these methods, only rigid-tube multi-level samplers can be used for repeated sampling of precisely the same location and depth because the device can be left in place.

Examples of probes through which water samples can be withdrawn, or a measurement made, from a single depth and then pushed deeper to collect other individual samples include mini-piezometers and Geoprobos.

## CONSIDERATIONS FOR TEMPORAL SAMPLING OF WATER FLOW AND CHEMISTRY

The time interval for sampling water flow and chemistry depends on the phase of the program, physical characteristics or chemical constituents of interest, climatic setting, and hydrogeologic setting. In general, more sampling is needed in the initial phases of a program when the extent of a problem is being determined, and less sampling is needed for long-term monitoring. For example, it commonly is

desirable to continuously monitor water flow and hydraulic head in the initial phases of a study to characterize the variability on daily, seasonal, and annual scales. At the same time, sampling for chemical constituents also needs to be done more frequently at this time to relate the concentrations and mass transport of constituents to flow regime and to climate. Once the relationship of mass transport to flow and climate is reasonably well understood, the frequency of sampling can be reduced.

Hydrogeologic setting comes into play in sampling frequency because some settings are inherently more simple, thus easier to characterize and monitor flow and chemistry, than others. Similarly, the climate that drives the hydrologic system is much less variable, thus easier to characterize and monitor, in some regions than in others. If a sampling program includes biological factors, sampling frequency may need to include considerations related to the life cycles of the organisms.

An important climate consideration in both initial site characterization and long-term monitoring is the effect of extreme climatic events. Extreme climatic events, such as droughts and deluges of precipitation, can have a greater effect on a site than many years of more normal conditions. These effects include rearrangement of bed sediments, changes in water flow paths, mass-transport of chemicals, and biological conditions of a surface water bed. One catastrophic event can greatly alter the perception of how well a hydrologic system is understood, and how it should be managed or mitigated. Although difficult to anticipate, a plan for sampling during catastrophic events should be in place.

## **VARIATIONS IN FIELD MONITORING AND SAMPLING STRATEGIES FOR DIFFERENT HYDROLOGIC LANDSCAPES**

A generic field design for determining the interaction of surface water with ground water includes the use of piezometer nests, water-table wells, and devices to measure or calculate the flow of water and chemicals across the surface-water bed. The conceptual model in Figure 1 of the Executive Summary shows ground-water seepage inflow on one side of the surface-water body and surface-water seepage out on the other. Actual conditions could be as indicated, have ground-water inflow on both sides, or have surface-water seepage out on both sides. The important point of the diagram is to stress that the interaction of ground water and surface water can be reasonably well understood only by addressing the larger-scale processes related to the position of the surface-water body within ground-water flow systems as well as the smaller-scale processes related to geology of the surface-water bed and climate.

The advantage of having permanent installations, such as wells and piezometers, in the upland is that they can be easily equipped to obtain continuous records. The disadvantage of having these installations is that they do not indicate the precise location or chemistry of seepage across the sediment-water interface. The advantage of the devices used within the surface-water body is that they can be used to pinpoint the location, rates, and chemistry of seepage water. The disadvantage of using these devices is that few can be used to obtain continuous records. Furthermore, few devices used within the surface-water body can be left in place for long periods of time because of floods, currents, ice, and water safety.

Although the generic field design may be applicable to many actual field settings, it is conceivable that the design would need to be altered somewhat for different hydrologic landscapes. For example, some landscapes, such as riverine and coastal, have wetlands at the base of terraces in the uplands. If a source of ground-water contamination was located on the terrace, the contaminant plume could conceivably discharge to the wetlands at the base of the terrace. In this case it would be desirable to place an additional piezometer nest in the wetland. Other modifications to the field design might be

related to the geologic complexity of the site. For example, if the geologic framework has a series of aquifers and aquitards or lateral geologic discontinuities, it might be necessary to place piezometers in the different geologic units in order to better understand the ground-water flow paths.

Frequency of sampling for chemical constituents also would depend on hydrologic setting. For example, in coastal areas affected by tides, the water flow and chemical transport paths could be greatly affected by the tidal exchange and storm surges. In northern and mountainous areas, runoff and ground-water recharge from snow melt can have a substantial effect on ground-water flow paths and chemical transport.

Because of the variety of hydrologic landscapes and the variability of climate, a need exists for development of type localities that would become benchmarks for the various landscape types. At these type localities, design of field installations, effectiveness of various sensors and devices, sampling frequency, and study and site characterization approaches could be tested and evaluated. Such knowledge could lead to efficient and cost effective approaches to dealing with contaminated sites in the hydrologic landscapes represented by a given type locality.

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# Chemistry Discussion Group Summary

By Allen Burton and Ned Black

## INTRODUCTION

The chemistry discussion group agreed to adopt the broad term ground-water/surface-water transition zone," unless it was specifically addressing the classical stream hyporheic zone. In this summary, individual topics that were discussed frequently over the course of the day are summarized under single headings. The group's discussions sometimes veered into issues belonging to the biology discussion group, such as the importance of establishing clear reasons for adding the transition zone habitat to the risk assessments performed at contaminated sites. Some group members expressed concern that project managers should establish the justification for sampling a transition zone site (e.g., complete pathways to receptors) prior to extensive use of the sampling and analytic techniques we discussed.

An obvious—but important—point to remember is that the contaminants in question are the same ones (e.g., dissolved or NAPL chlorinated solvents and petroleum hydrocarbons, pesticides, dissolved or particle-bound metals) that we encounter in contaminated ground waters and surface waters. Thus, we need to collect information on the same parameters we use to predict the geochemical fate of these contaminants in both ground water and surface-water bodies. We also need to collect the chemical and physical information commonly used in ecological risk assessments and natural attenuation assessments to determine the dominant biological processes and the potential confounding factors in bioassays. Finally, we need to collect chemical information which helps locate zones where a ground-water plume or hyporheic flow is entering a surface-water body. There is overlap among these parameters, but we should remember the three different uses of chemical information:

1. Contaminant chemistry and fate
2. Biological processes
3. Identification of flow paths

The transport of dissolved contaminants from surface water into the subsurface through hyporheic flow or ground-water recharge from a losing stream was included in our discussion of the transition zone. With regard to flow paths and sources of contamination, the deposition of contaminated sediments was excluded from our discussion. Other groups within EPA are addressing the issue of contaminated sediments.

It is possible to list many chemical and physical parameters (see below) to measure in order to satisfy the three information needs listed above. As for any ecological risk assessment, a screening process will determine what level of site chemistry characterization should be performed. In other words, it is not necessary to collect the same information at all sites. In order to justify extensive work on a site, a screen must demonstrate the presence of contaminants at levels sufficient to present risk to actual or potential receptors. For the chemistry discussion group, screening information also included parameters for determining site geochemistry and contaminant flow paths, although collection of this information might be deferred until after a screen.

One or more standard conceptual model should be developed to identify the important questions to ask and data to collect at different types and scales of sites. Sampling efforts in the transition zone may

be more costly than standard sampling of surface water or shallow ground water. At the very least, project managers and responsible parties familiar with only surface waters or only ground water will have to be taught to use different tools.

## **LIST OF PARAMETERS AND TOOLS**

### **Screening Tools**

- Semi-permeable membrane devices (SPMDs)—  
Widely accepted as a presence/absence screening tool. Requires extensive calibration (e.g., of equilibration times) and sensitivity analysis to determine exact concentrations. EPA researchers, in cooperation with other government or academic scientists, should perform sensitivity experiments to determine if there are situations where SPMDs can be easily used to measure concentrations.
- Drag probes for temperature, conductivity, and gamma anomalies—  
Useful in lakes, estuaries, and large rivers to determine zones of ground-water discharge.
- Piezometers and mini piezometers—  
Multiple piezometers with low-flow sampling can provide adequate samples of transition zone interstitial water and, of course, ground water. In order to sample just the transition zone, extreme care is required in depth placement of the screens. Piezometers can be placed both on land and in stream or lake beds.
- Freeze sampling techniques—  
Typically used to obtain biological samples, but could also be used to sample water and substratum for chemical analysis.
- Colonization corers—  
Also a biological sampler, but can incorporate nested piezometers.
- Bead pipes (ceramic beads).
- Dye tracers of ground-water and stream flow.
- Walk river bed with a hand auger.
- During low flow, note odor and visual observations.
- Photoionization detector (PID).
- Passive diffusion samplers.
- Analyze bubbles of gas (marsh or lake setting).
- Multi-level samplers.
- Seepage meters.
- Cores (solids analysis and visual).

- Laser-induced fluorescence (LIF), qualitatively determine VOC presence, BTEX, SVOCs, dense non-aqueous phase liquids (DNAPLs).
- Cores of trees (For instance, in a mangrove swamp. However, the contaminant may actually be metabolized in roots so false negatives are possible.).
- Field chemistry with a HACH spectrometer (nitrate, ammonia).
- Chemetrics for sulfides.
- Differential global positioning system (GPS).
- Velocity meter.
- Tidal stage.

### **Post-Screening Tools**

- Multi-level wells.
- Everything on screening tools list.

### **TIME SCALES**

Hyporheic and transition zone chemical and biological processes follow several different time scales. At a minimum, these can be described as daily cycles (e.g., temperature and river stage), normal weather changes, invertebrate and fish life cycles, seasonal changes and long-term climatic changes and events (such as extreme weather events). The difficulties of meshing the natural time scales of the environment with our schedules for sampling contaminated sites are shared with risk assessments and cleanups at all outdoor sites. Clearly, an environment such as the transition zone with strong diurnal and seasonal controls on biology and chemistry requires multiple sampling events if we desire great confidence that all pertinent processes are understood. And just as clearly, constraints on sampling budgets and the desire of regulators to respond to contaminated sites with an appropriate level of effort make limited sampling schedules the overwhelming norm. The most protective option may be to plan our sampling to coincide with the expected worst-case time of day and season. For the transition zone in a variety of habitats, the worst case sampling time may not be known. Thus, one of the mandates of the Regional study areas recommended below will be to determine the worst (i.e., the best) times to sample. For some transition zone habitats, recognized international experts will be able to offer suggestions for sampling schedules.

### **SPATIAL CONSIDERATIONS**

As with a ground-water plume, the spatial extent of contaminants is important information. For sites with a contaminant plume flowing from the subsurface into a water body, the effect in the transition zone may be limited to a discrete discharge zone. Also, the discharge zone for a contaminant plume may occur some distance from shore. An effective way to locate a discharge zone is to sample along a series of transects in the ground water. For a stream, it is also important to sample the bank opposing the discharge area. It must be remembered that a ground-water plume can flow entirely under a stream without any discharge. For classic hyporheic transport parallel to the flow of a stream, discharge can occur anywhere in the bed. For a site with a hard substratum, the impact of the

contaminants will be in the open water column. Although contaminants so discharged are an environmental problem, the impact on the transition zone, or the exact nature of the transition zone itself, may be hard to define. In lakes, zones of discharge from and recharge to ground water can occur in complex patterns.

### **CONCENTRATION AND FLUX**

In a screening or predictive risk assessment, contaminant concentrations are used for comparisons to toxicity benchmarks. However, the flux, or loading, of contaminants is also important information that bears on both the impact of the contaminants on the habitat and on the physical, chemical, and biological transformations of the contaminants at the transition zone. The flux of contaminants can change in magnitude and direction with changes in surface water temperature and flow stage.

### **DETECTION LIMITS**

The issue of detection limits for transition zone sampling is the same as for all other sites subject to risk assessments. Before a sampling and analysis plan is developed, the exact values of the toxicity benchmarks to be used for screening purposes must be determined. Otherwise, the sampling budget may be used to collect information of no use to the risk assessors.

### **RECOMMENDATIONS**

EPA should create a series of Regional study areas of contaminated transition zone sites, with appropriate uncontaminated reference sites. These would be studied by EPA Regional and ORD laboratories and academic grantees. The sites should be scaled appropriately to the typical sites for the Region. For instance, the hyporheic chemistry, biology, and hydrology of small mountain streams impacted by mines could be very different than a zone of chlorinated solvent-contaminated ground-water discharge in one of the Great Lakes. Ground-water discharge and hyporheic flow in estuaries will have the further complicating factor of tides. Sites of all sizes will be encountered by the Agency. Members of the chemistry discussion group felt strongly that extrapolating from small streams to large rivers and lakes is unacceptable. Also, some methods work in small streams, but not in areas of high flow. As with any landscape approach, the species and the dominant chemical and physical processes of the environment change with different landscapes.

# Biological Discussion Group Summary

By Cliff Dahm and Bruce Duncan

This session opened with the following question: “Is the hyporheic zone considered an ecological habitat to be protected or a ‘treatment opportunity’ zone for restoration of contaminated ground-water discharges to surface water?”

The group agreed early in the discussion to define the zone of interest (the ground-water/surface-water transition zone) as the “transition zone” rather than use the term “hyporheic zone,” which has a more restricted meaning where surface waters and ground waters are actively mixing. Mixing in this zone is very important, and in a stream, surface water moving into this zone can return back to surface water within a short distance and be “processed” through the transition zone multiple times.

An early question raised by the participants was how the zone can be defined biologically in order to focus on and demonstrate exposure of organisms. This requires more than a hydrological definition. There also is a need to link the transition zone to valued resources, such as fish. If there is an impact on the meiofaunal community, does that affect trout? This characterization of food web links, which is needed to demonstrate risk and answer the question “who cares?,” led to two important points: (1) What are the important services that this zone performs? and (2) if these services are impaired, how can we make that determination? Superfund managers now accept the importance of benthic macroinvertebrates to stream ecosystems; there is not the same recognition for organisms such as meiofauna or microbes in the transition zone.

Scale was another concern. There is a need to look at the spatial extent of impact to assess whether the contaminant discharge results in a risk to critical habitat such that action is warranted. Some hydrogeologists expressed frustration that they already know there is contamination in upwelling areas, but biologists countered that: (1) we do not know what the “pristine” state should be; and (2) even if the contamination is not cleaned up, there are other communities in other parts of the stream. So would analysis of the transition zone really matter? One attitude was: If someone is discharging without a permit, then they are in violation. “Who cares” is not an issue. Often, “no action” is what happens because an adverse impact cannot be demonstrated over a realistic scale.

A concern was raised about the reluctance of managers to invest in studies of transition zones. Given that we are not successful in getting biological measurements in ground water or surface water, how can we convince managers to do biological measurements at the interface? How do you convince someone that the transition zone is important when there are competing resources requiring protection? The solution is to demonstrate the functions that occur in the transition zone and what happens when those functions are lost.

The *Guidelines for Ecological Risk Assessment*<sup>1</sup> should be used to evaluate the transition zone:

- Who is present or affected? What do stakeholders care about in the system? What are the management goals (some are predefined such as no net loss of wetlands, or meeting Ambient Water Quality Criteria)?

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<sup>1</sup> Risk Assessment Forum. EPA/630-R-95/002F, April 1998. 171 p. <http://www.epa.gov/ncea/ecorisk.html>.

- Identify the assessment endpoints (i.e., some biological entity or function that you care about), the exposures, the measurements to be made, and then the effects. The ecological risk paradigm should cover everything and help maintain a big picture perspective.

The link between contaminated sediments and contaminated ground water in the transition zone was another issue. How is the issue of contaminated ground water different from the issue of contaminated sediment? The biological definition of the transition zone does not cover this; change in chemical conditions and rates are needed as well.

There are examples where removal of contaminants occurs within the transition zone with no removal in ground water. Ground-water wells cannot reveal the full story. More thought should be put into field sampling of mobile contaminants. You cannot just sample sediment. For example, you might have sand that appears very clean, but has contaminated ground water moving through it. Sediment and water are part of a system and need to be dealt with together, not separately nor sequentially. Also, there is a need to consider the contribution from contaminated sediments (top down) into the ground water. Sources need to be distinguished because of the polluter's perspective.

During the presentation session on the first day of the workshop, the following questions predominated:

- Why should we be interested in biology?
- Why should the public care or be interested?
- What are the services and processes that the transition zone provides?
- Why is the transition zone important ecologically?
- What biogeochemical measures would be ideal?

Participants were interested in contaminant migration and fate; others were interested in the effects on biological resources (macrobiota, communities, microbial processes) in the transition zone. When considering applicable biological measures, the biological discussion group had difficulty identifying microbial measurements with broad applicability. There is good success with macroinvertebrate indicators, less so with microbiota and meiofauna. A multidisciplinary approach is needed to provide synergy.

The discussion followed three aspects of the transition zone: (1) Why is the zone important ecologically? (2) What are the methods that can be used to assess ecological structure and function? and (3) What research is needed to better determine the ecological importance of this transition zone and to develop needed tools for sampling this zone?

#### **WHY IS THE TRANSITION ZONE IMPORTANT ECOLOGICALLY? WHAT ECOLOGICAL SERVICES ARE PROVIDED?**

These issues led to additional questions: Do all transition zones need to be protected, especially if you see no impact to the surface water? Is there intrinsic value to the transition zone itself, apart from the surface water? Historically, people study "ecological entities." The recent trend is to look at transition zones or ecotones. We do not know much about ecotones as an ecosystem entities. The hyporheic zone is one important ecotone. Some surface organisms have a phase in the hyporheic zone, which implies that productivity could be affected. The hyporheic zone also serves as a "nursery" for secondary producers. Less is known of the permanent hyporheic zone species—they often can be distinct, undescribed species.

The group discussed the importance of transition-zone function and compared it to wetlands. Regulations require restoration of wetlands if they are destroyed. This concept could be applied to the transition zone; the goal could be to restore function rather than restore appearance (no net loss). It was pointed out that we need both function and structure (species).

Another question was “why should the public care about the important function of microbiology?” or “what would the environmental effect be from the loss of that function?” Several structural and functional elements are extremely important in this system. Transition zones often provide high quality habitat and are sites of contaminant reduction and nutrient and carbon cycling. A good example was made for fish. Three major biological services are tied to fish: refugia, food sources, and reproductive zones. The links from microbes to macrobiota to fish are essential to the aquatic food web. Trout are known to seek out transition zones. When a river is contaminated, refugia can sustain the fish. The table below summarizes functional values identified for microbiota and macrobiota/fish.

Transition Zone Functional Values	Microbiota	Macrobiota/Fish
1. Food source	√	
2. Preferred habitat for some species (upwelling area)		√
3. Refugia for macro (predator avoidance)(biodiversity)		√
4. Microbially active zone	√	
5. Habitat for food base	√	√
6. Cleaning zone (filters), vegetation, aquatic and riparian	√	
7. Energy transfer	√	√
8. Discharge areas may have high biodiversity		√

#### (1) High quality habitats/refugia

Discharge zones can provide thermal refugia for anadromous fish both for resting and for spawning. Upwelling areas may be important by providing chemical/olfactory signals to anadromous and migratory fish. The zone provides a microbial food supply to the fish and the upwelling areas can act as incubators. Salmon need high quality water including cool water refugia in otherwise warm stream reaches. Conversely, ground-water discharge environments may be the only areas where it is warm enough to survive in very cold areas. Snow dimples have been used for years as surface manifestations of ground-water discharges. Also, small areas in a lake could provide a large percentage of the trout population with support. These can be unique habitats and important energy sources. Certain fish seek out upwelling areas and shellfish may also live in these zones. Macrophytes (e.g., shallow eelgrass beds) may also benefit. Macrophytes may establish preferentially in beds related to discharging ground water. Sometimes ground-water discharges into marine areas are the only areas where emergent vegetation can grow. Another question is whether some macroinvertebrates and fish avoid contaminated ground-water upwelling areas. Trout have good olfactory sense and will avoid metals at concentrations well below toxic levels.

These zones also may limit benthic invertebrate exposure to low oxygen and contaminants by creating oxygenated, clean zones. These zones may also be areas of plant and animal biodiversity. They can be areas of high water quality in alluvial aquifers. Some European countries are interested in identifying high quality ground-water discharge zones (good quality refugia) in the midst of contaminated rivers to preserve as critical habitat.



## (2) Contaminant attenuation/removal.

The transition zone is important for chemical and biochemical reactions that influence the quality of the ground water discharged into the surface water. Metals, halogenated organic solvents, polycyclic aromatic hydrocarbons, volatile organic compounds (VOCs), and nutrients can be degraded or removed from ground water within the transition zone.

Volatile organic compounds (VOCs) were discussed in particular. The issue was whether there are concentration thresholds of VOCs above which they poison biological communities. Where there is a large VOC plume, there could also be bioaccumulating contaminants. If the VOCs were then degraded, but the bioaccumulative contaminants (e.g., PCBs, creosote) were not, then bioaccumulation of toxicants still would occur. This has implications for remedial decisions, especially if contaminants are brought in through ground water. Some participants expressed the opinion that VOCs are ignored generally because their toxicity thresholds are much greater than those for heavier contaminants, and therefore they seem to show no risk in the water column. However, risk thresholds based on continuous exposure to a hazard such as VOCs are different than those used in water quality criteria.

## (3) Cycling of nutrients and carbon

Nutrients and carbon cycle very actively in this zone. Strong redox gradients enhance biogeochemical activity and microbial processes. Both aerobic and anaerobic processes often occur within close proximity of each other. Microbial biomass can serve as the base of a detrital food chain that can be important to overall ecosystem productivity.

## (4) Food base for benthic organisms

Microbes and fungi can provide food for other transition zone organisms that are more intimately involved in the benthic food web of the surface water body. Many macroinvertebrates use the transition zone extensively, and they are food for other organisms. If the zone is contaminated, the result for invertebrates could be mortality, biomagnification and/or bioaccumulation.

## **WHAT METHODS CAN BE USED TO ASSESS THIS TRANSITION ZONE ECOSYSTEM?**

Current methods for studying transition zones generally are not standardized and sometimes not well developed. For example, scales may be mismatched (wells are too big to sample over decimeter or centimeter gradients). Regardless of these difficulties, it is very important that ecologically related sampling in the transition zone be coordinated with hydrogeological and chemical surveys at ground water discharge sites. It was useful in the discussion to distinguish two groups of organisms, microbiota and meiofauna/macrobiota. It was noted that it is difficult (but important) to show contaminant effects on these groups.

### (1) Microbiota

- a. *Community structure.* There is no standard method to determine microbial community structure. Some methods in use include culturing, metabolic profiling, fatty acid fingerprinting, molecular probes, or nucleic acid characterization. These methods are either limited or time-consuming. Other methods involve 1) collection using ceramic beads or other artificial substrates that collect a sample population in the transition zone; 2) artificial cores with natural materials; and 3) artificial habitats/substrates. Procedures, methods, and equipment are usually designed to answer the specific questions at hand. A method to evaluate drinking water called UDI (Under Direct

Influence) was mentioned. The suggestion was made to focus on the algal community as a surrogate. The algal community and the benthic interface has diagnostic value because there is a rich literature of algae as bioindicators. The comment was made that including diatoms would be time consuming and not too practical. A suggestion was made to develop tools to measure activity first, then measure structure.

- b. *Microbial activity/function.* Again, there is no single ideal method. Methods in use or proposed include bioassays (such as the Microtox bioassay), determination of metabolic rates and pathways, describing the dominant terminal electron accepting process (methanogenesis, sulfate reduction, iron reduction, manganese reduction, denitrification, or aerobic respiration), measuring molecular hydrogen and testing for metal tolerance.

It may be difficult to generate interest in microbial function—microbes in septic tanks that provide organic degradation are a familiar example. The transition zone is important for carbon cycling, nutrient cycling, and a detrital-based food chain. Contamination should not interfere with these processes and the decomposer community. So, what would be the appropriate method to evaluate decomposition? Is the desired method to identify the amount of carbon no longer available (tied up in ligands or refractory) or metabolized?

Another suggestion was to evaluate biological oxygen demand (BOD) and/or chemical oxygen demand (COD). For example, the presence of soluble reduced metals will result in high COD and affect interface chemistry. If ground water has high BOD/COD and dissolved oxygen (DO) is present, that observation is important. However, all agreed that BOD and COD are presently impossible to resolve across small scales, although fine-scale characterization of DO is possible.

## 2. Macrobiota/Meiofauna

- a. *Community structure.* Several methods exist for sampling organisms in the transition zone (see D. Williams' abstract on page 39 of this report) and various standard metrics can be computed (community composition, density, species richness). Benthic and ground-water taxa can be distinguished.
- b. *Function.* The following were suggested: bioaccumulation studies and stable isotope analyses (e.g.  $^{15}\text{N}/^{14}\text{N}$ ,  $^{13}\text{C}/^{12}\text{C}$ , and  $^{34}\text{S}/^{32}\text{S}$ ) for food chain relationships. Functional feeding groups can be evaluated.

It was suggested that these basics (community structure and function at all levels) be understood first before developing more methods to conduct toxicity testing.

## **WHAT RESEARCH IS NEEDED TO BETTER UNDERSTAND THE ECOLOGICAL IMPORTANCE OF AND ASSESS EFFECTS ON THE TRANSITION ZONE?**

### (1) Basic biological research

Most recommendations centered around basic science needs regarding the transition zone (e.g., life histories, faunal surveys, activity measurements) and sampling/evaluation tools. Life history characteristics of transition zone organisms are generally lacking. Food chain relationships that describe the linkages among microbial, meiofaunal and macrofaunal organisms also are lacking. A suggestion was made to develop methods to conduct a subsurface biomass study. Because no large reference databases exist (compared with surface water data), faunal surveys should be done for major

riverine ecosystems using a hydroclimatic landscape approach (see T. Winter's abstract on page 46 of this report). These surveys would be used to develop reference conditions in a national database. If there are differences between geographic areas, it may be best to look at functional differences rather than community differences so data can be compared across broad regions. The Chemistry Group also suggested establishing regional hyporheic study sites.

## (2) Macrobiota

Species richness and growth could be evaluated. The physiology of transition zone invertebrates is poorly known (e.g., O<sub>2</sub> uptake rates and mechanisms are often unknown). Respiration studies are needed as well as information on trophic structure. Stable isotopes of nitrogen might be an effective way to determine food chain relationships. Dissolved oxygen availability should be accurately measured. Good biological indicators are as yet uncertain and likely vary for differing flow paths or discharge zones. One should look at biological impacts but use chemical and hydrologic conditions to help define sampling zones.

## (3) Indicators of ground-water discharge zones

The Chemistry Group discussed the scenario of a plume entering a stream and how to detect effects in the subsurface. They suggested looking in four dimensions: vertically, horizontally, temporally, and downstream. In general, a point source will be easier to detect than a diffuse plume. You will need several transects across the river. What biological components should be measured? Potential electron acceptors and dissolved hydrogen are good biogeochemically informative constituents to measure. You can characterize the microbial community in many ways. Culturing methods normally select for small subsets of the total microbial community. Molecular techniques also can be used, but presently none of these methods are easily and routinely applied.

Indicator choices depend on the question to be answered. Which attributes are you protecting? Microbial assays need to be used, even if these assays are not yet perfected. Promising techniques are currently under development. Morphological measurements in the system are easier to make than biological measurements. Intensive sampling near the point of discharge plus additional transects would be useful. Sampling should include "vertical distributions" through the food chain.

## (4) Biological indicators of GW discharge zones

Are there any biological attributes that help define ground-water discharge zones? For example, can you look for benthic algal blooms? Are fish numbers and distributions in context with other indicators a useful means to locate discharge zones where high quality aerobic ground water is present. Some species may tend to remain in an area even if contaminated. The mechanisms by which fish and other species avoid contaminants is very complicated. Distribution of fish does not necessarily follow water quality parameters. Are ostracods good indicators? The consensus was no. It was suggested that midge larvae might be better indicators for ground-water discharge zones. One documented indicator is the presence of high biomass benthic algal mats, but this is limited to zones with enhanced nutrient discharge. Some discharge zones are dead zones, especially where anaerobic, metal-rich ground waters are discharging. There is an important research need to try and correlate between bottom type and patchiness with ground-water discharge. In lake ecosystems, these zones may be linked to aggregations of zooplankton. Acoustic techniques that detect these aggregations may be able to locate ground-water discharge points in lakes

### (5) Chemical/physical indicators of ground-water discharge zones

Temperature and conductivity probes are simple, easily-used, and rugged tools for determining ground water discharge locations. These methods could be routinely used to guide sampling in many aquatic ecosystems. Bottom drags with temperature and conductivity probes also can be considered if site conditions warrant. Protocols are needed to allow better comparisons among sediment samples and data from temperature and conductivity probes. Although DO probes are somewhat unstable in the field, investigators could use combined temperature, conductivity, Eh, and DO measuring instrumentation to look for discharge zones. Oregon State University has a suite of fiber optic sensors/probes that are commercially available and potentially useful in these transition zones. Redox measurements in the field are a problem because of a lack of equilibrium in many samples, and redox potential is often dominated by iron biogeochemistry. Tools needed for improved sampling of ground water discharge zones include:

- Sampling devices to collect organisms effectively and quantitatively along transition zones;
- Dependable and cost-effective geophysical and tracer tools to delineate transition zones and guide biological sampling; and
- Routine survey tools to better characterize microbial community structure and activity and assess water quality and condition.

### (6) Scale

Strong gradients in physical and chemical parameters commonly exist in the transition zone. For example, the distribution of redox sensitive solutes can be very steep. Sampling often must be at the centimeter scale or finer resolution. All participants agreed that we need better methods to sample gradients and narrow transition zones. Microcosms or fine-scale bioassays may be approaches to consider.

### (7) Hydrology

Knowledge of hydrologic characteristics of the transition zone is crucial. For example, transpiration rates may be very important to the hydrology of these interface zones, but there are large regional differences. Chemical and isotopic tracers may be the best methods to determine the effect of the transition zone on overall stream quality. Some tracers also are sensitive to in-stream processes. Other participants pointed out the need for subsurface measures in addition to surface water sampling. Unresolved questions include:

- What techniques are available for measuring the volume of water entrained into the hyporheic zone?
- What are biological consequences of remediation (pump and treat) that reverse flows in the transition zone?

Injecting oxygenated water could change the redox chemistry within the hyporheic zone. Highly regulated rivers (dammed) affect the hydrology of this interface as well.

### (8) Signal-to-noise and partitioning sources

Some practical sampling questions were raised about characterizing the transition zone. How is it different from a place without ground-water recharge or discharge? The responsible party will need to prove that the background contamination “noise” is greater than their contribution. How can you

compensate for variability (from the regulator's perspective)? We need screening tools (inexpensive) to identify the problem and focus the sampling. What methods can distinguish ground water from sediment sources? Ground-water discharge may become contaminated as it flows through the hyporheic zone, becoming a "fingerprinting" challenge.

#### (9) Temporal variability

Temporal variability is important: hourly variability in the hydrology, chemistry, and biology of the transition zone has been noted. When are the best-case and worst-case times for sampling; which season or seasons should be sampled? Different life stages have different susceptibilities and exposures. Ecologists and hydrogeologists need to collaborate. Ecologists can specify time of year and depths of concern; hydrogeologists can determine the hydrologic regime and geochemistry.

#### (10) Remote sensing

Field studies combined with remote sensing now can be used to better understand the heterogeneity and landscape characteristics of transition zones. Hydrology and food resources for important species are not homogeneously distributed but often highly localized. Remote sensing provides a tool for assessing landscape-scale patterns of hydrology and biotic distributions. Certain patterns on the landscape (e.g., localized plankton blooms) may be surficial indicators of processes occurring in the transition zone. Researchers and managers need to combine extensive and intensive analyses.

#### (11) Toxicity testing

Are there any non-lethal endpoints or tools that could be used to determine or screen for toxicity on transition zone organisms? Growth studies are generally more sensitive than mortality or fecundity studies. Are there any ground-water toxicity tests or ground-water bioassays? One suggestion was that Elmid beetle larvae in the hyporheic zone may be suitable test species.

#### (12) Nutrients

The role of transition zones in overall nutrient cycling is still poorly known. Nutrient effects need to be related to species effects, such as effects on sea grasses or corals. The management goal would be to protect "normal" nutrient cycling. Most people live near coasts, and impacts on transition zones that affect riverine delivery of nutrients or ground-water discharge of nutrients in estuarine or coastal waters are critical processes that need to be better understood and monitored. In general, we do not know the trends in nutrient delivery from these transition zones for rivers, estuaries, or coastal waters. In addition, the rates and locations for nutrient transformations by microbial organisms in transition zones in coastal regions deserves further study. There have been relatively few attempts at quantifying these processes.

Similarly, nutrient cycling processes in the hyporheic zone should be better studied. Hyporheic zones receive dissolved oxygen when surface water recharges ground waters. Oxygen participates in important biogeochemical processes such as aerobic respiration, nitrification, metal oxidation, sulfur oxidation, and methane oxidation. For example, if ammonium levels are high in ground waters, nitrification rates can increase and lead to higher concentrations of dissolved nitrate. Where these processes occur and the seasonality of such processes can affect both surface water and ground water quality. Can the portion of nutrient loading in a surface water body that is derived from ground water be distinguished from that derived from surface sources? The U.S. Geological Survey (USGS) has

done some related work on this topic in Massachusetts. The contribution from ground water in polluted areas is at least as great as the contribution from rivers in many coastal areas. Tools exist for toxicity testing, but comparable tools do not exist for assessing impacts on nutrient cycling. What methods exist to test whether nitrate is being removed or if that function is impaired? Researchers are working on these methods, but they are not yet regularly employed in monitoring programs.

#### (13) Dissolved oxygen

The availability of dissolved oxygen plays a major role in the characteristics of ground waters in transition zones. Not all oxygen depauperate discharge zones are caused by pollution; some are naturally low in DO due to hydrologic flow paths (residence time) and rates of microbial metabolism on sediment organic matter. Anaerobic ground waters may contain increased concentrations of dissolved metals, sulfur, and methane. Dissolved oxygen is a master variable in processes and chemical characteristics of transition zones.

#### (14) Reference comparisons

A disturbed zone needs to be compared to a “normal” reference. How do you identify conditions for comparison? How can you identify effects of the contaminants? How can biological conditions be used as a reference? “Acceptable” conditions need to be defined. Some biotic species (e.g., caddisflies and mayflies) can be used to define reference conditions. Paleontology tools can be used to determine prior conditions. Either reference or gradient comparisons can be used to evaluate changes. The group recommended assessments that allow cross-comparison after remediation (monitoring). The group considered how to define reference conditions in ground water for a superfund site. One approach would be to evaluate current approaches for macroinvertebrates. It would be crucial to locate samples in ground water outside the area of influence. Defining what is meant by reference or reference condition always is challenging. The area should have the same ground-water characteristics in terms of hydrology and chemistry, but without the contamination. This is difficult, because the plume may be a small part of the total ground-water discharge and dispersed contamination may be widespread at a site. It may be easy to find nearby discharge locations that apparently are not contaminated, but it will be critical to carefully assess if these aquifer sediments and ground waters are actually not contaminated.

#### (15) Correlations between hydrology, sediment, and biology

There have been some correlations described between hydraulic conductivity and ground-water discharge, but not further linked with the biology. Differences in biota occur between upwelling and downwelling areas. Silty or clayey soils (sediments) can inhibit the ground-water flux. Most freshwater macroorganisms do not like turbid water. There may be a juxtaposition of preferred soil type and discharge zones. Adequate characterization of soil structure, porosity and organic matter content are necessary. Clogging, percent organics, amount of DO, and other variables need to be measured. Organisms often preferentially select substrate, so standard artificial substrates sometimes can be used as a surrogate for enhanced comparability between sites.

#### (16) Bioaccumulation

Diffuse flows and low concentrations of contaminants are hard to measure. Measuring biota that receive contaminants from multiple sources will increase the problem of documenting that a problem exists only from a single ground water source. Bioaccumulation is not always a problem. Lipid bags may not be a very good method for assessing bioaccumulation, because one of the main biological

components is accumulation through the food chain. Semi-permeable membrane devices (SPMD) “fat bags” might be a better method. Another possible method would be to look at higher trophic levels such as fish. Nitrogen isotope signatures change over time and are dependent on the trophic level of the animal. Therefore, fish  $^{15}\text{N}/^{14}\text{N}$  ratios and bioaccumulation analyses can be used in combination to deduce an impact from contaminant delivery through ground waters to surface waters.

### **WHAT BIOLOGICAL MEASUREMENTS DO YOU WISH YOU HAD AT YOUR SITES?**

During this discussion, participants identified key measurements that biologists, chemists, and hydrologists would have liked to have had in studies of transition zones:

- Botanical analysis indicative of natural acidic stream condition for studies considering anthropogenic acidification. Sediment probes and piezometers have been used, but no biological data have been collected.
- Sediment and interstitial water toxicity data on *Daphnia*. Toxicity testing in general would be valuable as we usually get only chemical information. Would the results from those methods be any different than from existing bioassays?
- A test where you can measure impacts on nutrient cycling.
- How many replicates can be processed to account for patchiness? How patchy can it get?
- Toxicity tests for biota in the hyporheic zone following their reaction to exposure or accumulation over time. The tests should be analogous to fish indicators (e.g., hiccuping) or integrative tests such as bee pollen sampling of contamination over a certain radius.

There was general agreement that it would be useful to develop a suite of toxicity tests for microbes and invertebrates. Microtox is the only commonly used test (luminescence is the endpoint), usually for screening. Certain contaminants lower luminescence and many microbes thrive on contaminants. Microbial toxicity tests therefore may not show anything. There is a lot of natural variability spatially and temporally in electron accepting process. Results depend on the location and timing of sampling. Microtox is usually used for sediment toxicity. One needs to design and interpret the test based on the endpoint of concern.

### **OTHER QUESTIONS/SUGGESTIONS**

- Is organic carbon available to the food-base (labile organic carbon content) a sensitive indicator of microbial activity?
- Can microbiota in the transition zone be thought of as sources of primary productivity like microbial communities in estuarine sediments?
- In Europe, invertebrate organisms are sometimes used as indicators of ground-water quality. Transition zone organisms in the U.S. also could be evaluated for their potential as indicators.
- How can adverse ecological impacts in the transition zone be recognized? Would an indication be when you do not have the anticipated biodiversity?
- What scale should be used to define adverse impacts? The scale depends on the site’s risk management goal.
- Encourage thinking about the need to better integrate biology, hydrology, and biogeochemistry.
- The workshop report should include references to available methods for microbial, epifauna and meiofauna sampling. There are methods available for many species.

## **POSTER SESSION ABSTRACTS**



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

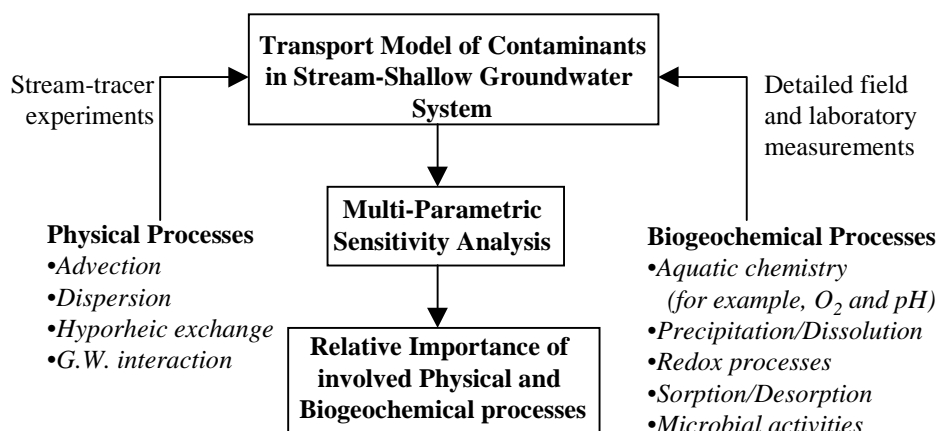
By Jungyill Choi, Judson W. Harvey, and Martha H. Conklin

## 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:

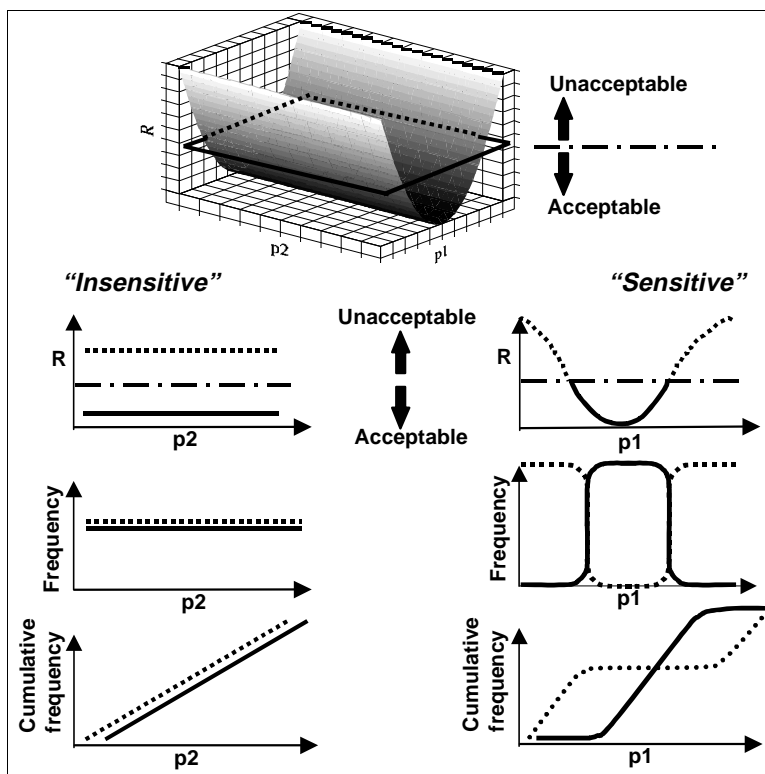
- Select the parameters to be tested.
- Set the range of each parameter to include the variations experienced in the field and laboratory measurement.
- For each selected parameter, generate a series of, for example, 500 independent random numbers with a uniform distribution within the design range.
- 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:

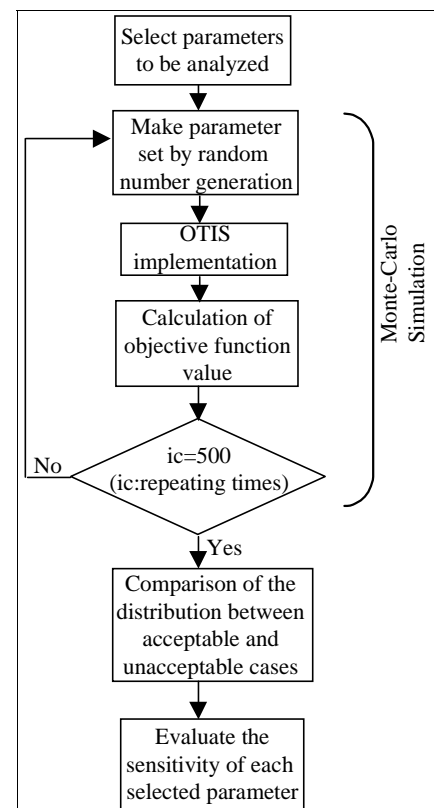
$$f = \sum_{i=1}^n [x_o(i) - x_c(i)]^2$$

where  $f$  is the objective function value and  $x_c(I)$  and  $x_o(I)$  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

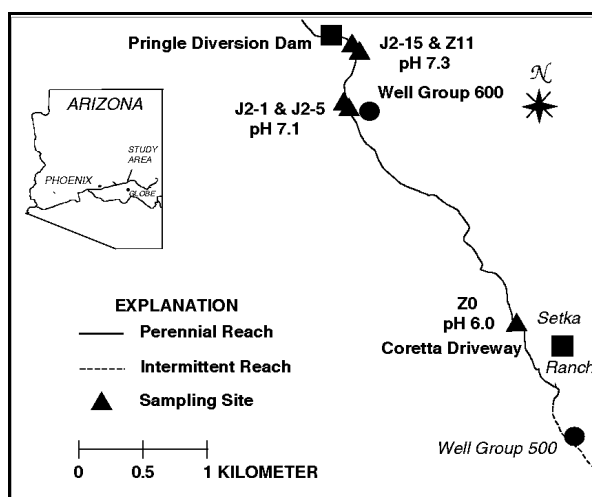
By Justin C. Marble, Timothy L. Corley, and Martha H. Conklin

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 ( $\text{mg Mn(II) g}^{-1}$ ) 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<sup>2</sup>-1, J<sup>2</sup>-5, J<sup>2</sup>-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 <sup>1</sup>	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

<sup>1</sup> As CaCO<sub>3</sub>.

**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<sup>-1</sup> 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<sup>-1</sup>). The values reported represent the average of 2 subsamples with the maximum and minimum values measured being within  $\pm 2$  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<sup>2</sup>-1) and algae (e.g., *Microcystis*, *Vaucheria*, and *Oocystis*) dominated in the downstream section (J<sup>2</sup>-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<sup>2</sup>-1, and J<sup>2</sup>-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<sup>2</sup>-1 and J<sup>2</sup>-15. A subset of the water speedwell samples from sites J<sup>2</sup>-1 and J<sup>2</sup>-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<sup>2</sup>-15 than at J<sup>2</sup>-1 and Cu was higher at J<sup>2</sup>-1 than at J<sup>2</sup>-15. Bioaccumulation of Mn and Co exhibited consistently higher bioaccumulation at J<sup>2</sup>-15 compared to J<sup>2</sup>-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<sup>-1</sup>).

Rabbitfoot grass samples from J<sup>2</sup>-1 and J<sup>2</sup>-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<sup>2</sup>-1 than J<sup>2</sup>-15. A factor of about 2 between values at J<sup>2</sup>-1 and J<sup>2</sup>-15 was 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<sup>2</sup>-5 on June 25, 1997 (pH 7.1, Mn(II) concentration 47.0 mg L<sup>-1</sup>) had an Mn concentration of 10760 mg L<sup>-1</sup>.

Metal	J <sup>2</sup> -1	J <sup>2</sup> -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<sup>-1</sup>).

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 <sup>2</sup> -15	12/12/96	5550
Pinal, J <sup>2</sup> -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<sup>-1</sup>).

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 <sup>2</sup> -1	6/25/97	3870
Pinto, Haunted Canyon	6/18/97	505
	6/18/97	97
Pinto, Miami	6/18/97	47

**Table 5.** Water speedwell bioaccumulation (mg kg<sup>-1</sup>) 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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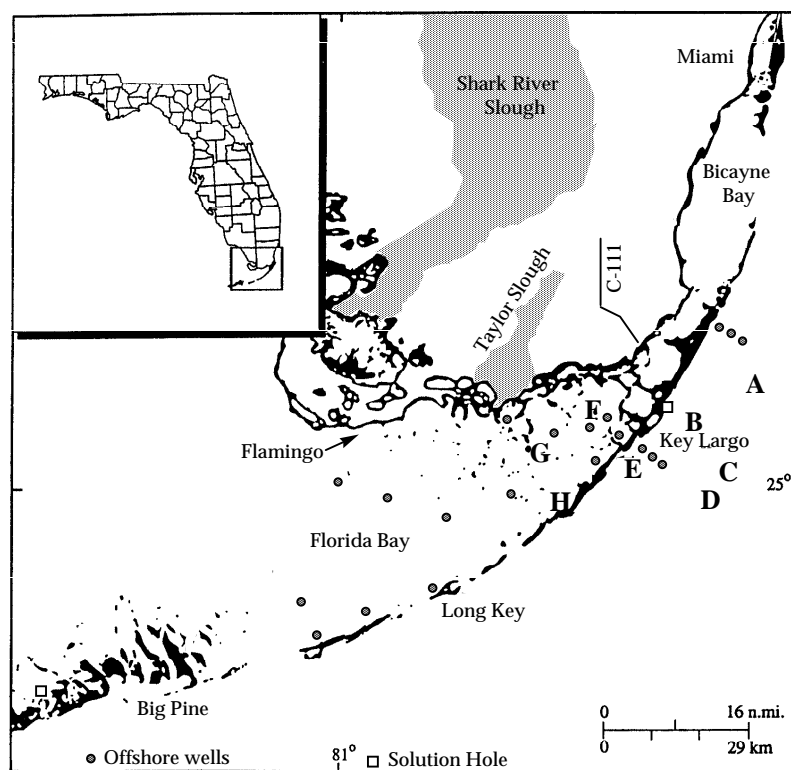
# Tracing Groundwater Flow into Surface Waters by Application of Natural and Artificial Tracers

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.,  $\text{NO}_x$ , turbidity). In this research, subsurface water movement was evaluated with natural and artificial tracers in the karst limestone of the Florida Keys (Figure 1).

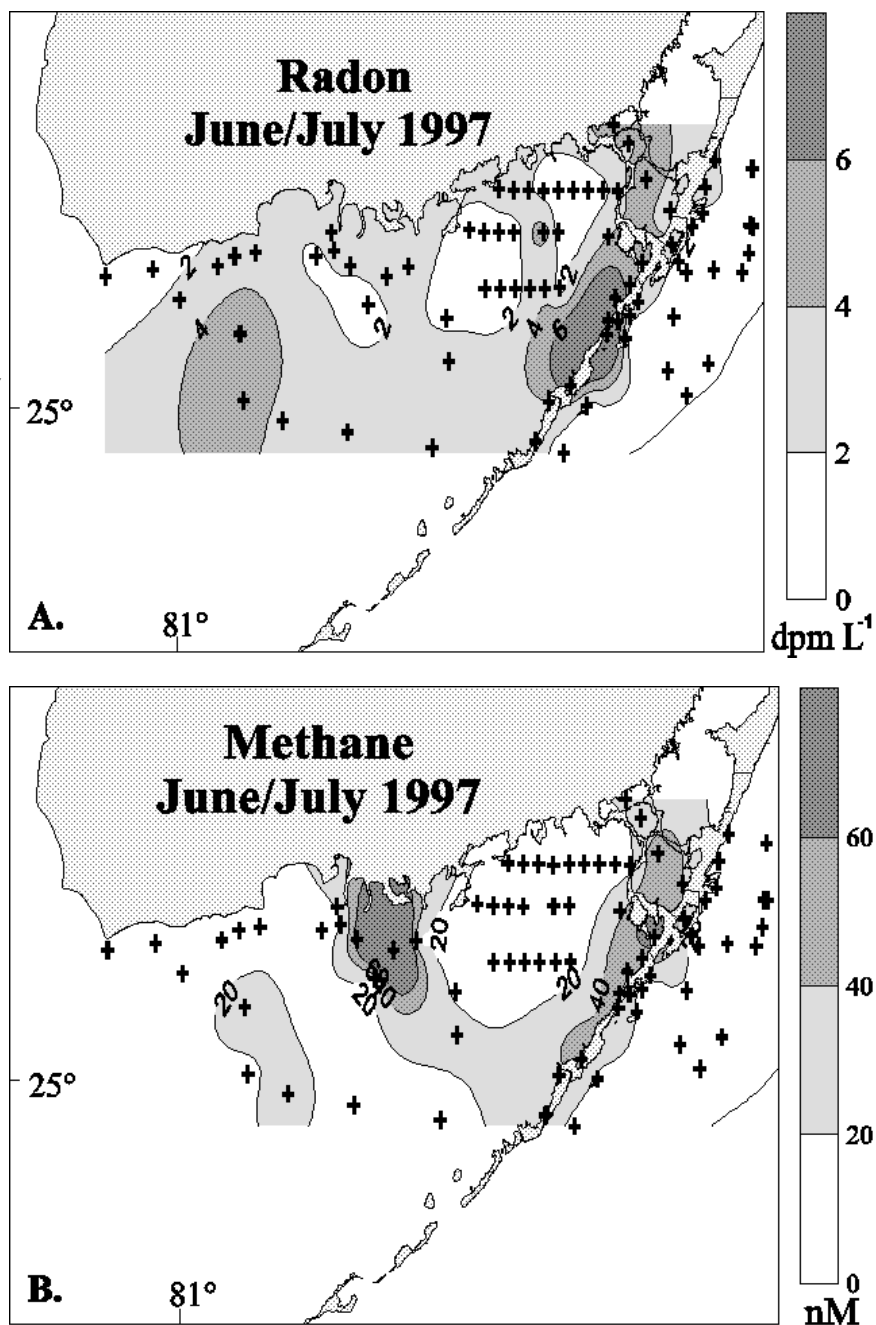
In the Florida Keys, natural tracers ( $^{222}\text{Rn}$  and  $\text{CH}_4$ ) were used to locate areas of increased groundwater/surface water interactions by reconnaissance surveys of the concentrations of radon and methane in the bay waters (Corbett, et al., 1999). These trace gases function as natural 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

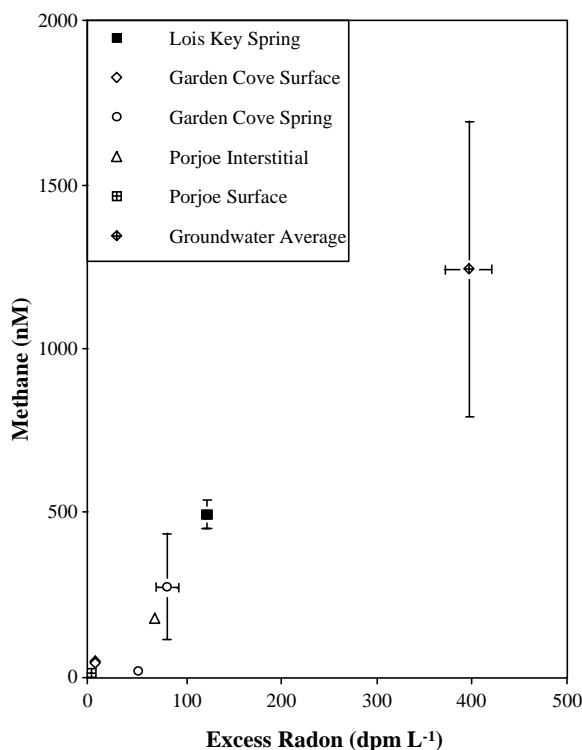


**Figure 1.** Florida Bay separates the Florida Keys, located off the southern tip of Florida, from the mainland. Water samples were collected primarily from north of Long Key and East of Flamingo. Groundwater samples from offshore wells were collected where indicated by the circles. Letters refer to 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  $^{222}\text{Rn}$  and  $\text{CH}_4$  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  $^{15}\text{N}$  enrichment in areas near the keys. We observe a strong spatial gradient in  $^{15}\text{N}$  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  $^{15}\text{N}$ -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 ( $110 \pm 60 \text{ mmol N m}^{-2} \text{ y}^{-1}$ ) and phosphate ( $0.21 \pm 0.11 \text{ mmol PO}_4^{3-} \text{ m}^{-2} \text{ y}^{-1}$ ) 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 than these estimates (Corbett, et al., 1999).



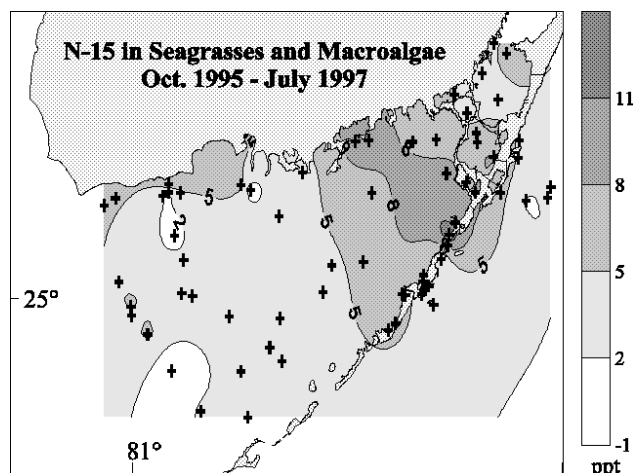
**Figure 2.** Contours of radon (A) in dpm L<sup>-1</sup> and methane (B) in nM for samples collected in June/July 1997. Solid crosses indicate sampling locations. Note the darker contours, indicating higher concentrations of both parameters, near the upper Keys. (Figure from Corbett et al., 1999)



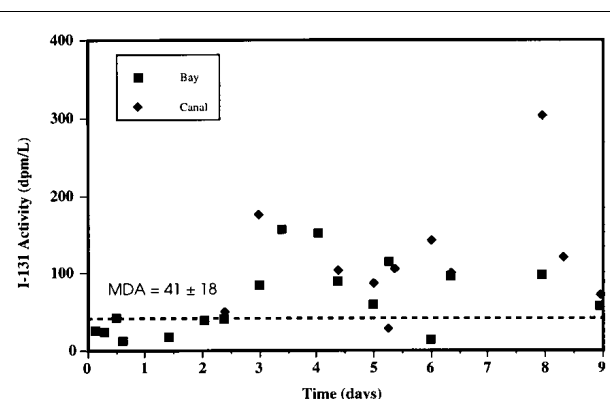
**Figure 3.** Radon and methane concentrations in waters sampled throughout the Keys. The groundwater tracer concentrations are based on the overall average of all samples collected. (Figure from Corbett et al., 1999).

Artificial tracers ( $\text{SF}_6$ ,  $^{131}\text{I}$ ,  $^{32}\text{P}$ ) 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 ( $\text{SF}_6$ ,  $^{131}\text{I}$ ) 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



**Figure 4.** Contours of  $^{15}\text{N}$  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.

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 (ft<sup>3</sup>/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 <sup>1</sup>**

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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<sup>1</sup> 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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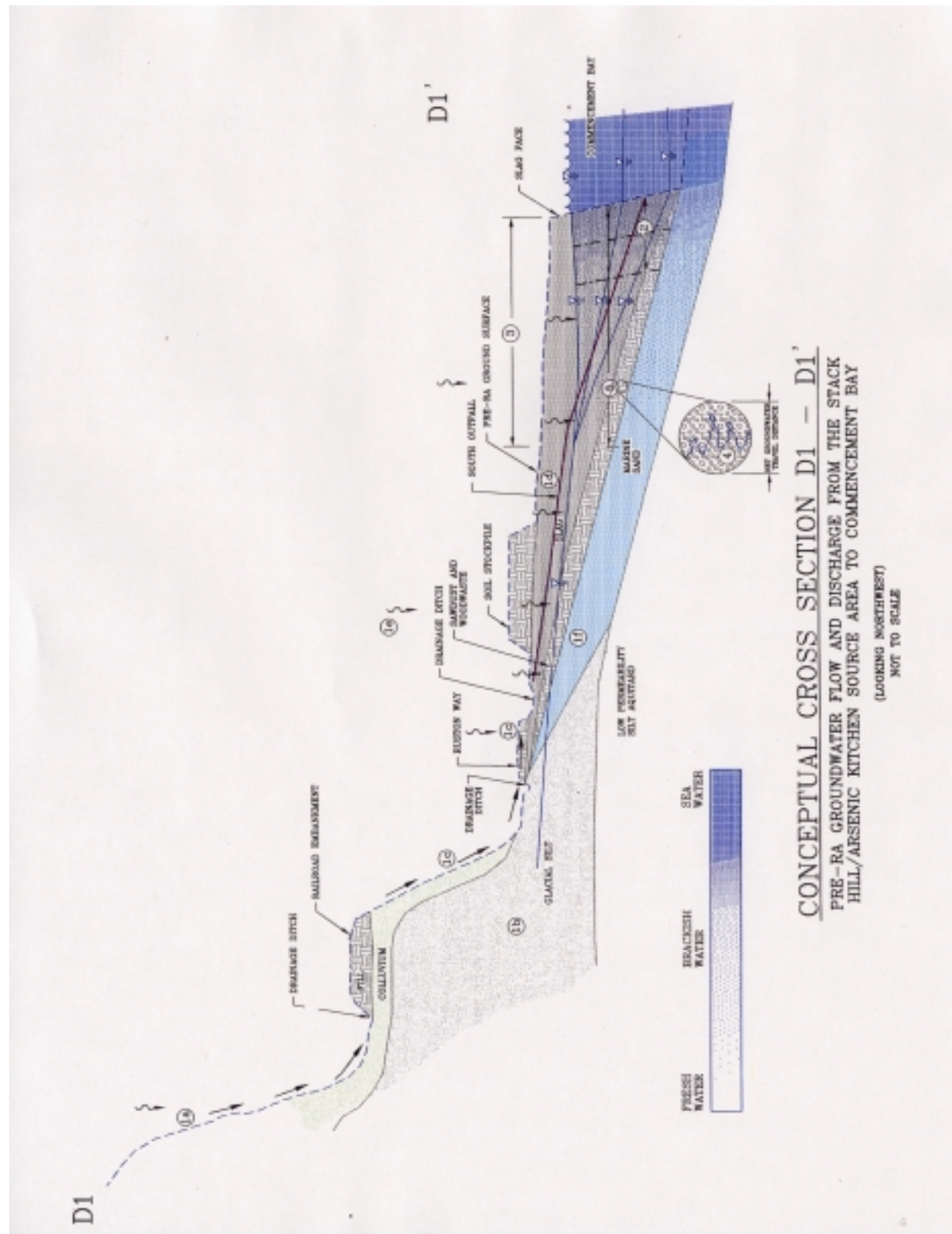


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Conceptual Cross-Section D1 - D1'

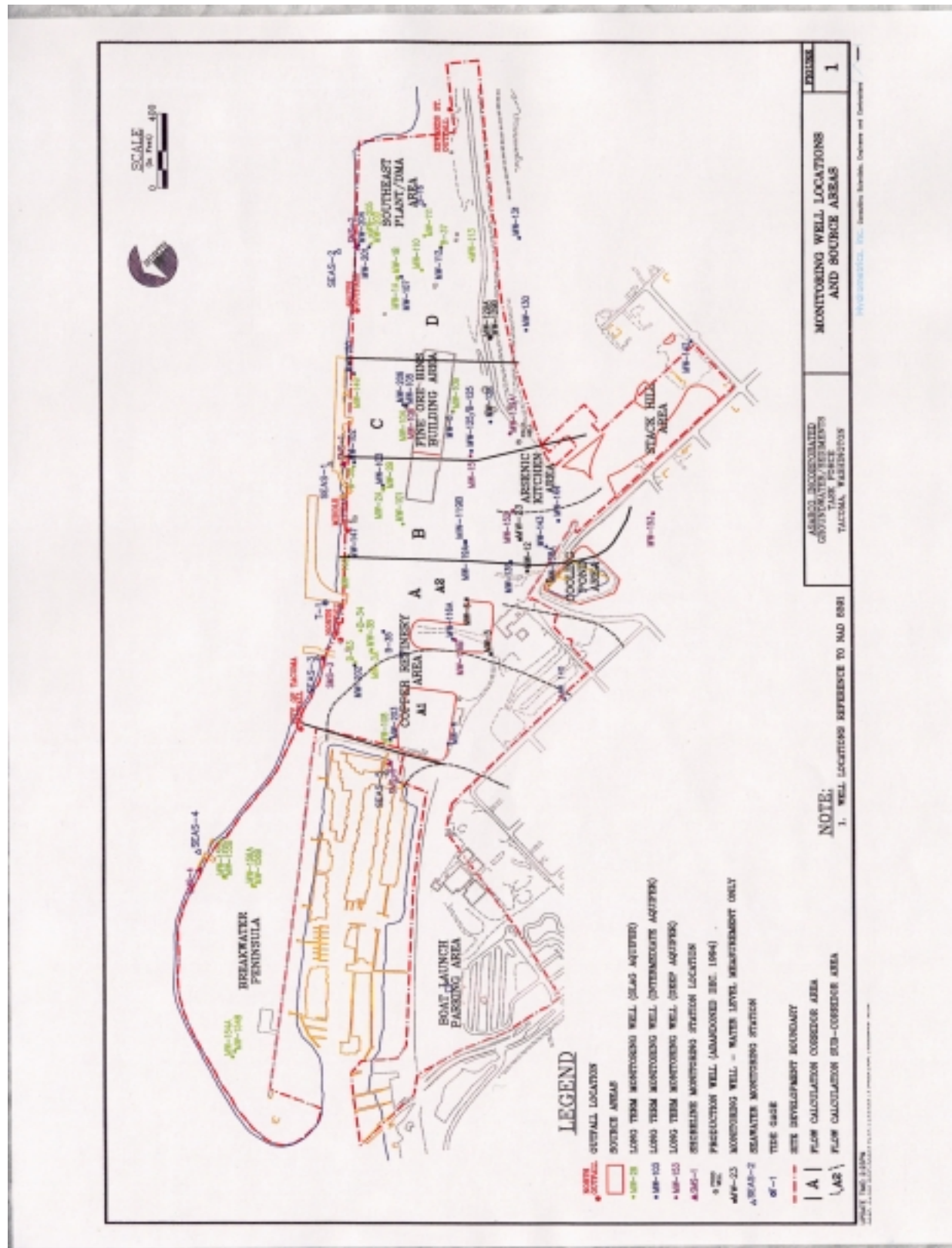
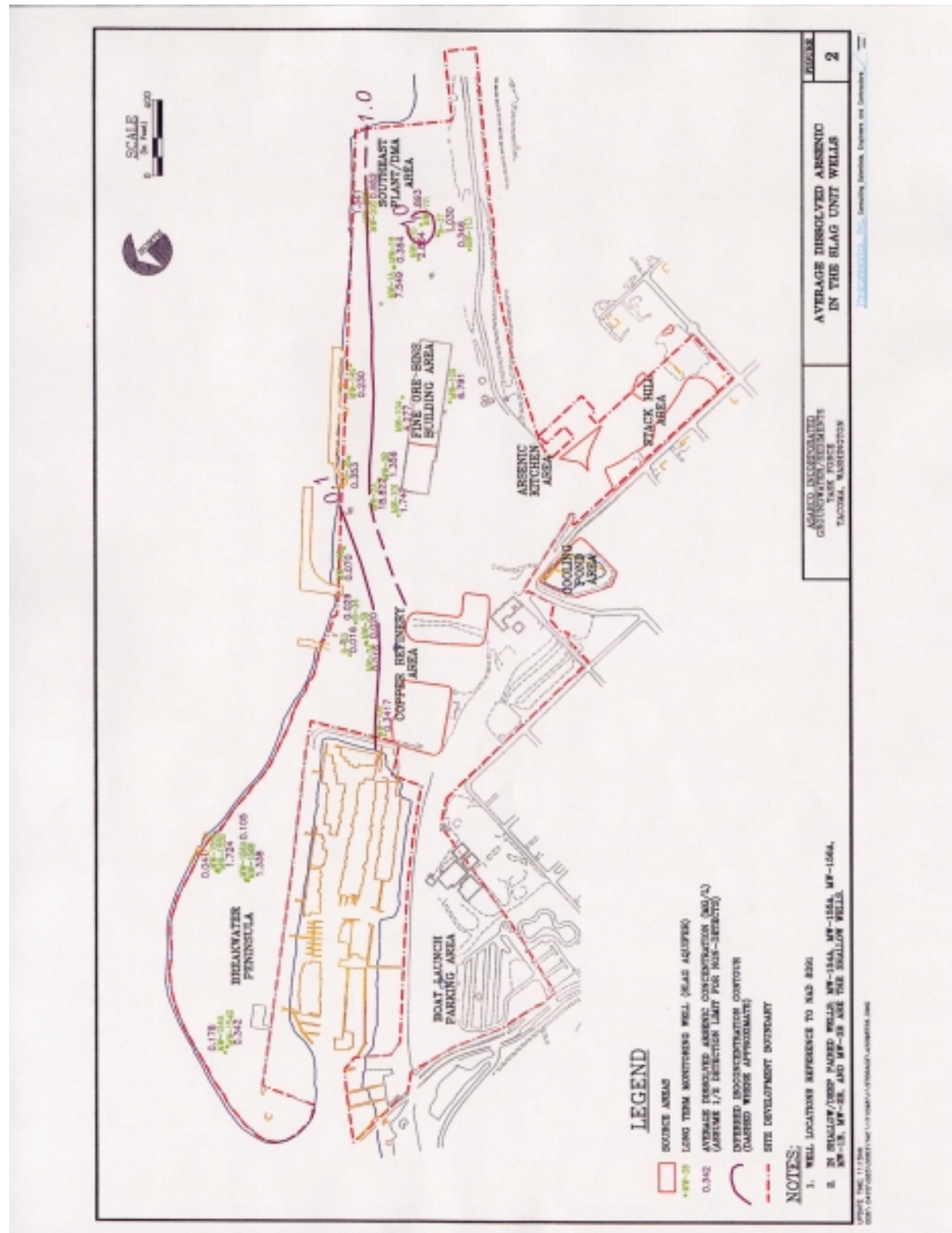


Figure 1



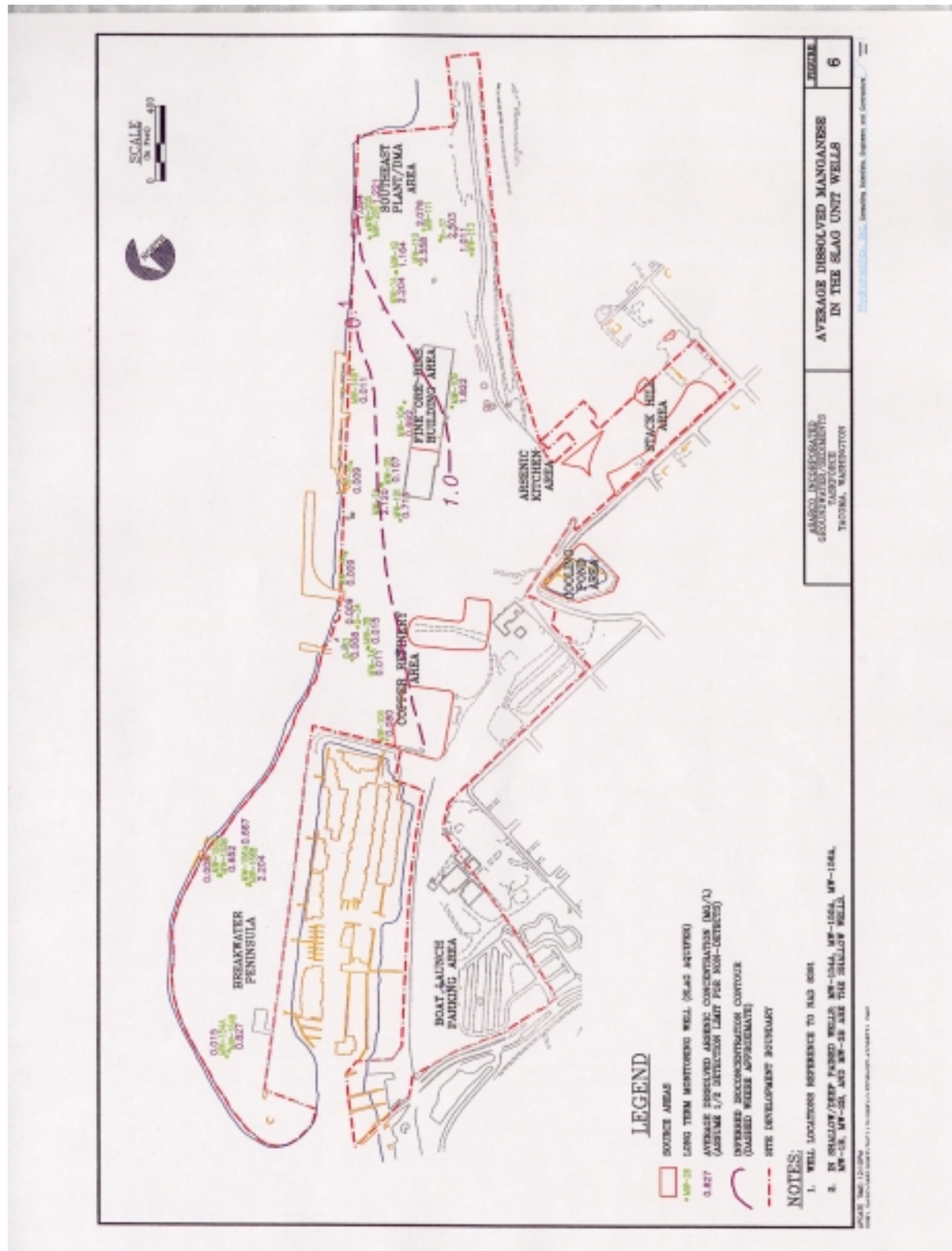


## Figure 2



Figure 3





### Figure 6

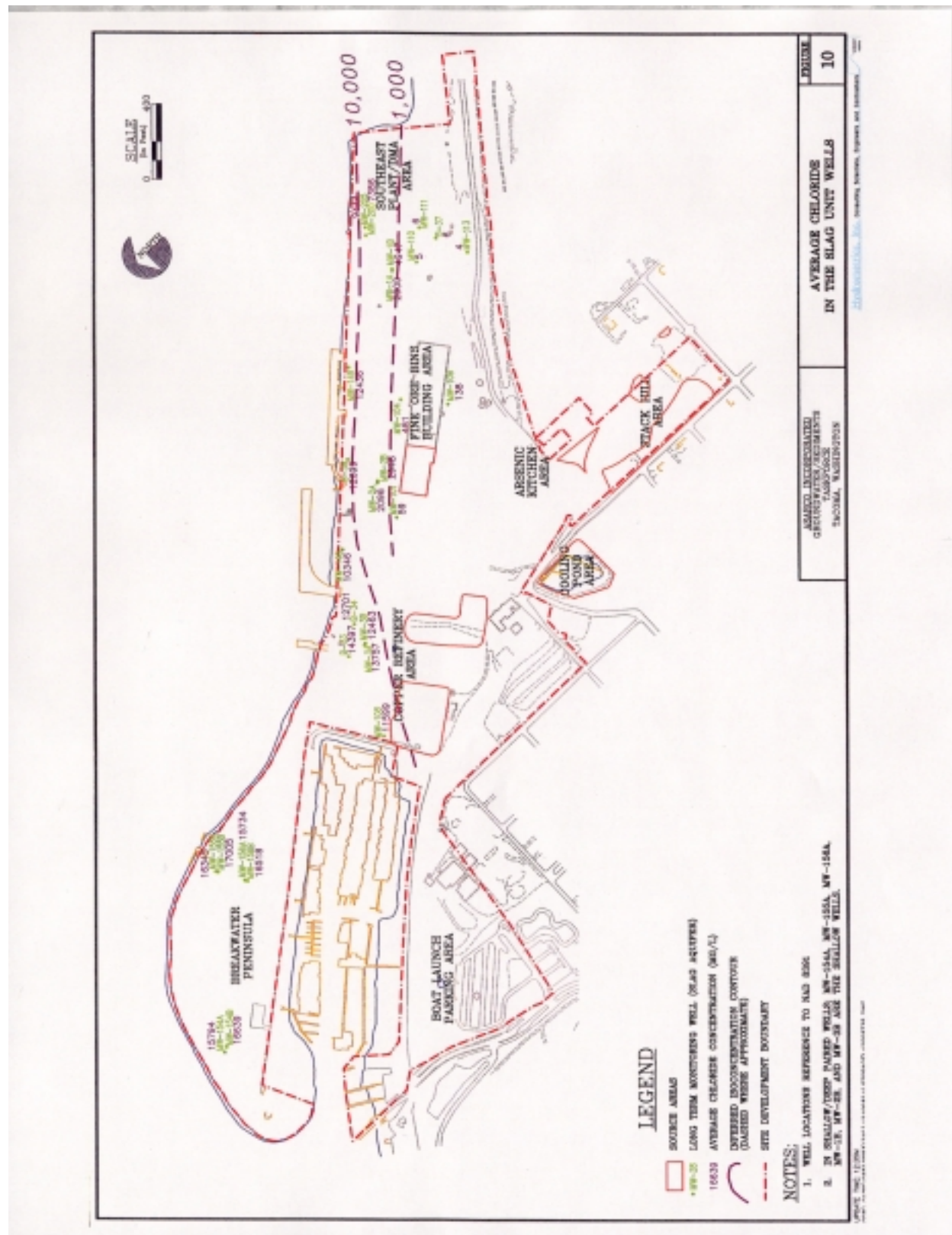


Figure 10





Figure 11





### Figure 13

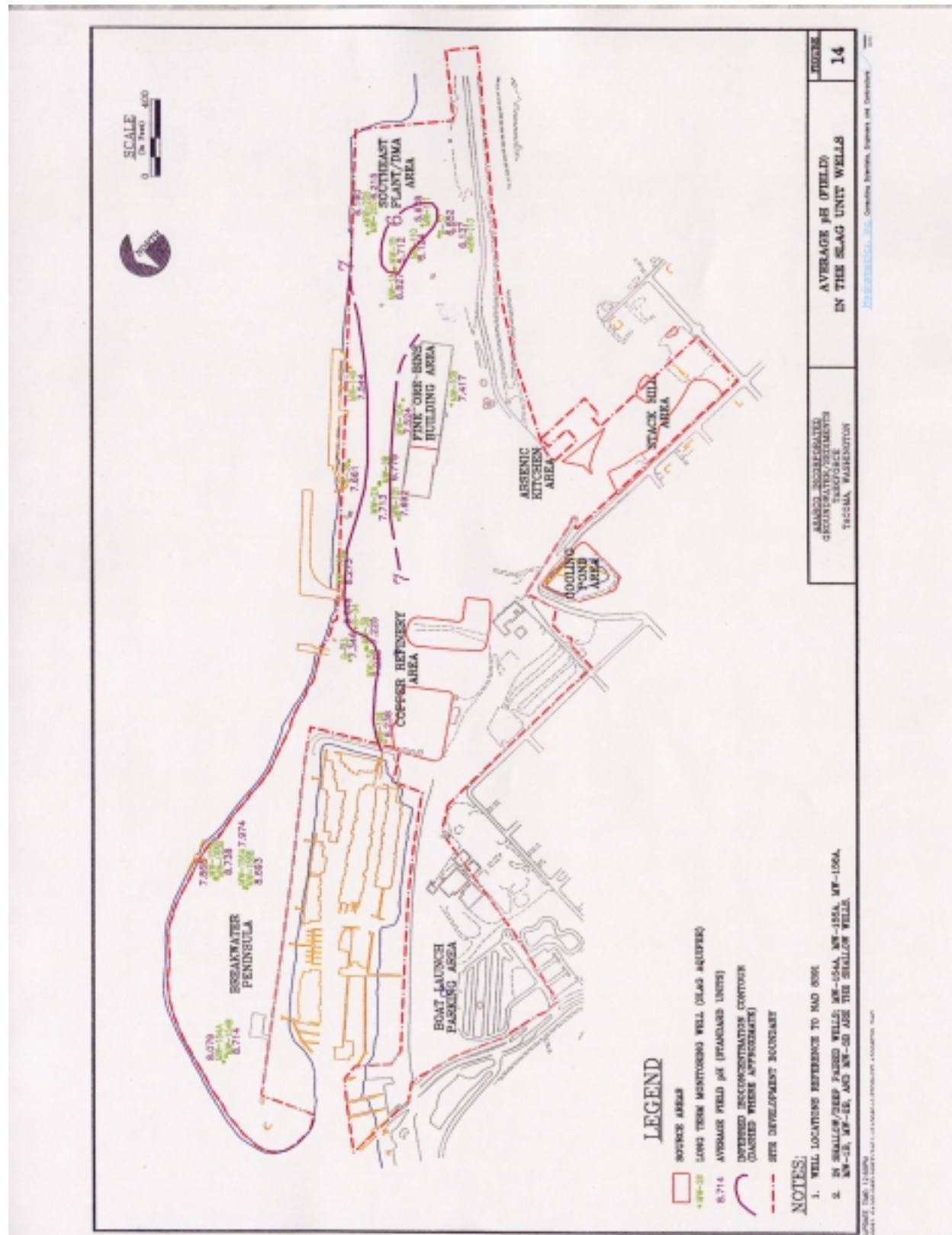


Figure 14

# 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 ( $\mu\text{S}/\text{cm}$  at  $25^\circ\text{C}$ ), water temperature ( $T$ ,  $^\circ\text{C}$ ), dissolved oxygen ( $\text{DO}$ ,  $\text{mg}/\ell$ ), and hydraulic head ( $h$ ,  $\text{cm}$ ). 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  $\mu\text{S}/\text{cm}$  while the river water averages  $\sim 150 \mu\text{S}/\text{cm}$ . 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

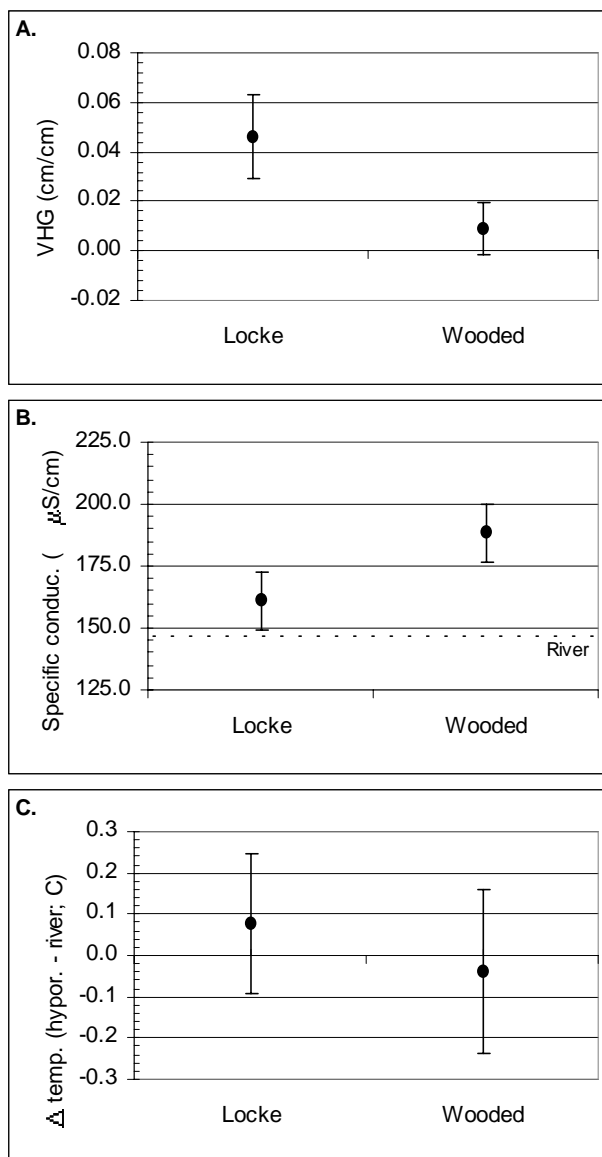
(VHG = h/depth of piezometer). Slug tests were used to estimate the volume of hyporheic discharge from the sediments into the river channel.

## RESULTS AND DISCUSSION

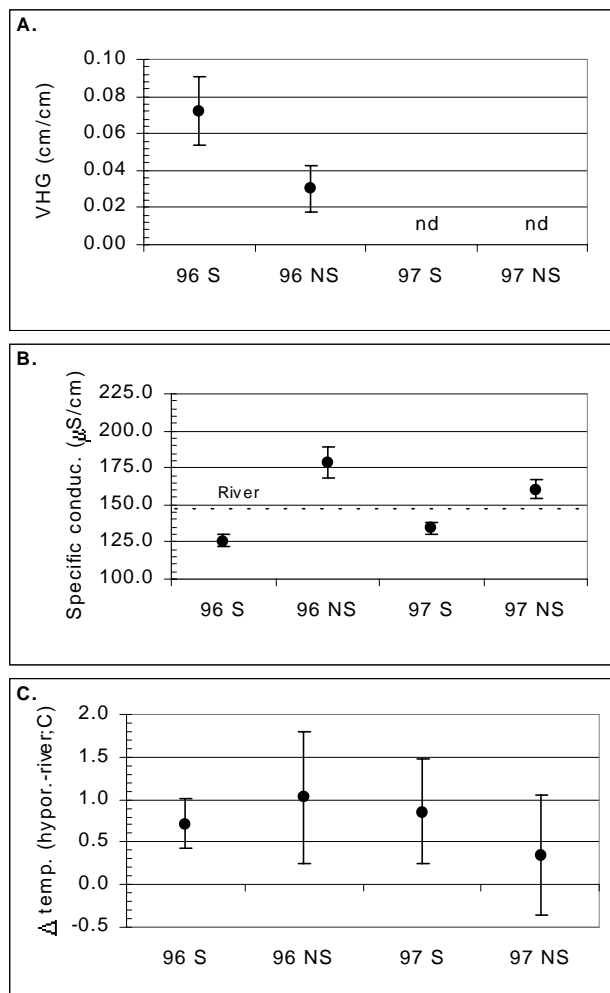
The results showed that fall chinook salmon spawning locations were highly correlated with hyporheic discharge that was composed of mostly river water and not undiluted ground water. Hyporheic water that discharged into fall chinook salmon spawning locations was consistently greater in magnitude, and 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  $9.0 \times 10^{-4}$  cm/s at Locke Island and  $3.0 \times 10^{-4}$  cm/s at Wooded Island. Thus, specific discharge of hyporheic waters was approximately 3 times larger at Locke Island than Wooded Island.

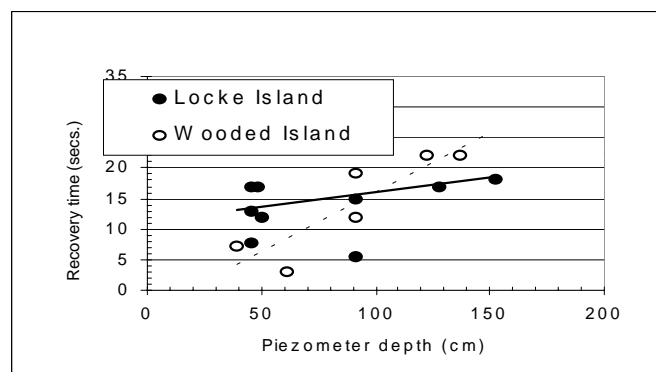
River water was presumed to have entered highly permeable riverbed substrate at locations upstream of spawning areas. Geomorphic bed features (i.e., islands, gravel bars, riffles) of alluvial rivers are able to create hydraulic gradients sufficient to direct surface water into the bed (Stanford, et al. 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 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.



**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 discrete 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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# 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<sub>4</sub>). Water samples were collected at a depth of approximately two to five feet below the river bed using a GeoProbe<sup>®</sup> 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.

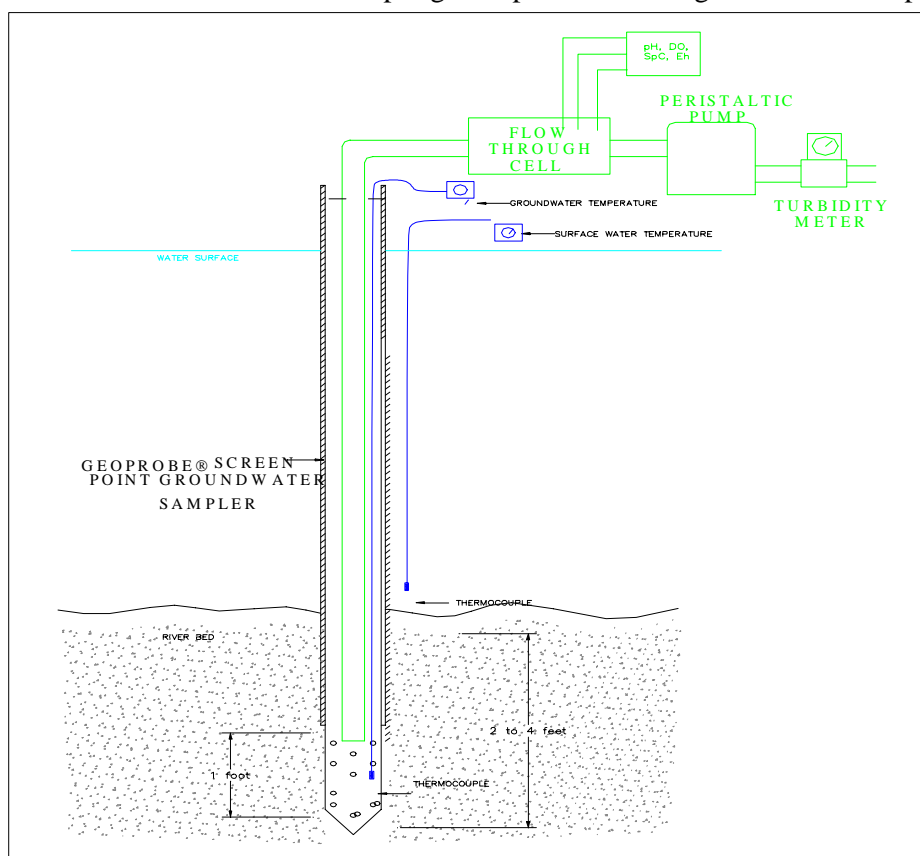
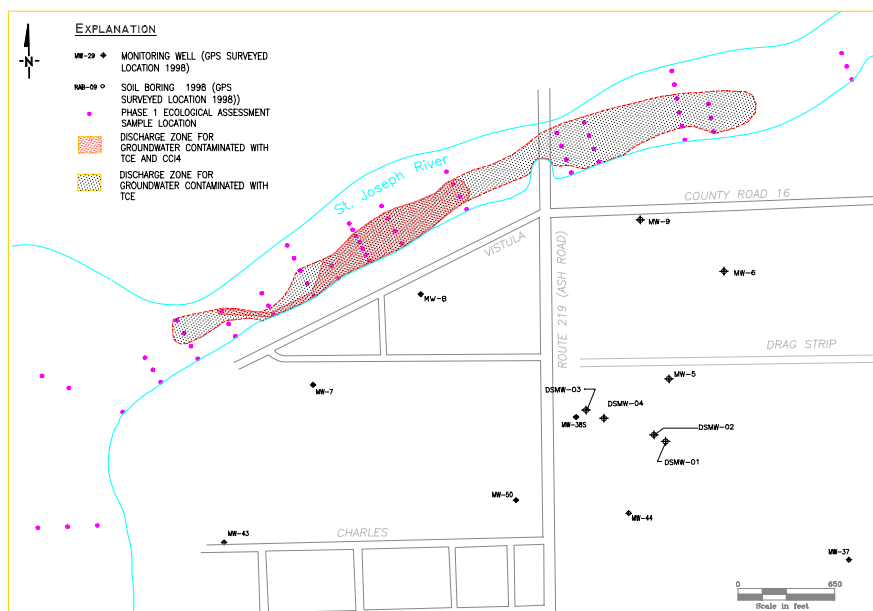


Figure 1. Schematic of sub-riverbed sampling equipment

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.

<b>Table 2. VOC Analytes</b>
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 ( $\mu\text{g}/\ell$ ). Groundwater containing  $\text{CCl}_4$  is discharging to the river along a 2'500 foot length of the river, and the  $\text{CCl}_4$  discharge zone is contained within the TCE discharge zone. The maximum  $\text{CCl}_4$  concentration was 940  $\mu\text{g}/\ell$ . The sampling locations, and the TCE and  $\text{CCl}_4$  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  $2.3 \times 10^{-4}$  per second. The mean rate constant determined in the laboratory was approximately 30% lower. An average rate constant of  $2.3 \times 10^{-4}$  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 through 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) subsample 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

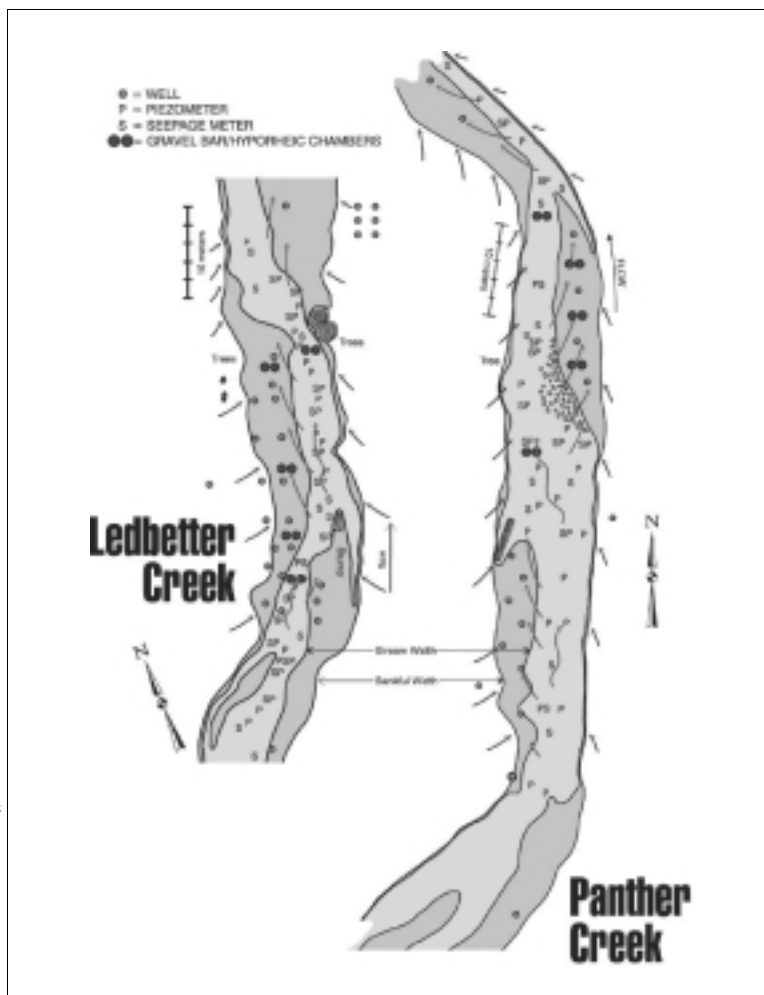
been comparisons between an agriculturally impacted third-order stream (Ledbetter Creek) and a pristine third-order stream (Panther Creek) with similar sediment heterogeneities and watershed characteristics.

## METHODS

Sediments collected from each stream were sieved ( $\leq 3$  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.

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  $h^{-1}$ .



**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.



## 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.

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<sub>2</sub> 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  $\mu\text{g NO}_3 + \text{NO}_2 \text{ L}^{-1}$  sediment  $\text{h}^{-1}$ , was higher in Ledbetter Creek than in Panther Creek (Table 3). The Ledbetter Creek sediment bacterial community is composed of taxa, which appear adapted to high levels of  $\text{NH}_4\text{NO}_3$  fertilizer applications.

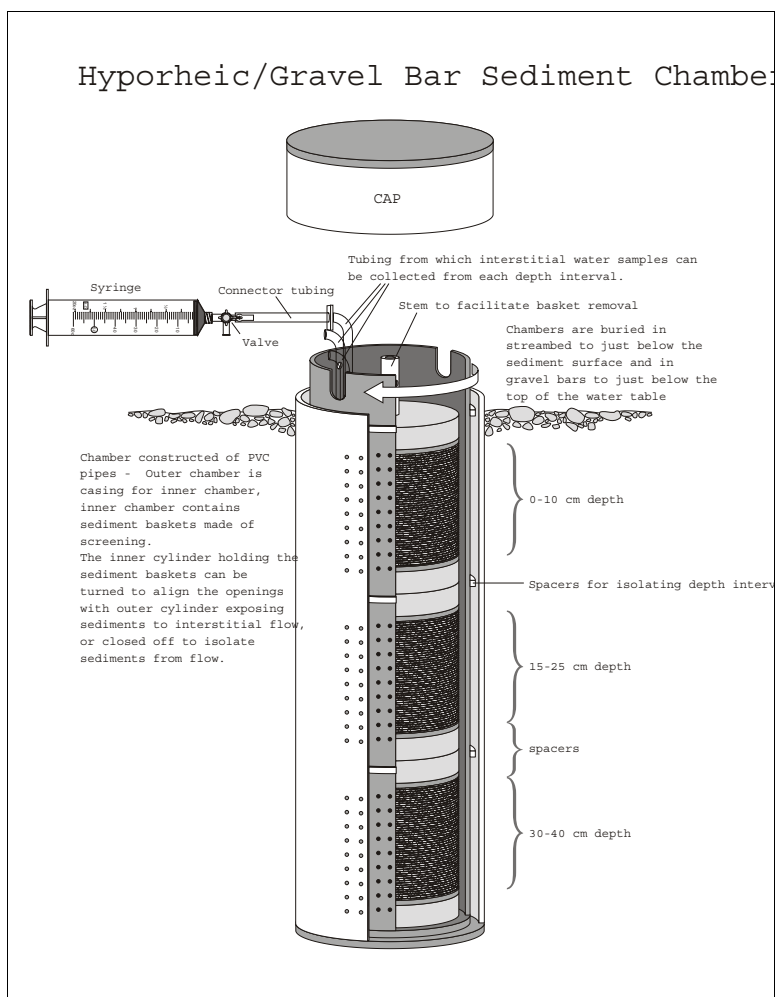


Figure 2. Schematic of gravel bar/hyporheic chamber design.

Table 1. Alkaline phosphatase activity (APA = $\mu\text{m}$ nitro-phenylphosphate reduced $\text{g}^{-1}$ 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 ( $\mu\text{g C m}^{-2} \text{ h}^{-1}$ ) at Ledbetter and Panther Creek as estimated from incorporation of  $^3\text{H}$ -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  $\text{NO}_3+\text{NO}_2$  in sediments ( $\mu\text{g NO}_3+\text{NO}_2$  produced  $\text{L}^{-1}$  sediment  $\text{h}^{-1}$ ) in Ledbetter and Panther Creek chambers. AG = agriculturally impacted, P = pristine.

Stream	Site	$\Delta\text{NO}_3$ ( $\mu\text{g L}^{-1}$ )	% Increase	Rate ( $\mu\text{g NO}_3 \text{ L}^{-1}$ sediment $\text{h}^{-1}$ )
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

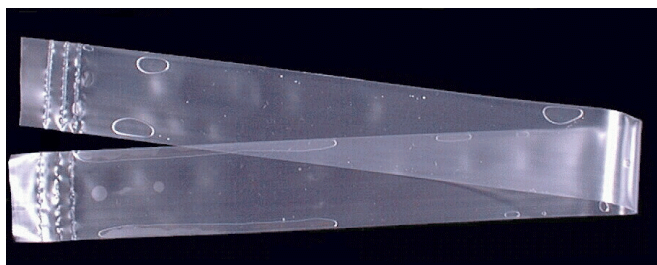
By J.N. Huckins, J.D. Petty, H.F. Prest, J.A. Lebo, C.E. Orazio, J. Eidelberg, W.L. Cranor, R.W. Gale, and R.C. Clark

## 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  $\mu$ 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  $\text{cm}^2/\text{ml}$  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  $\mu$ m 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 presence of a lipid film on the membrane interior surface) between the triolein and the membrane even where air bubbles exist.

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

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

where  $C_w$  is the TWA analyte concentration in water (ng/l),  $C_{\text{SPMD}}$  is the concentration in the whole device (membrane + lipid) in ng/l,  $V_{\text{SPMD}}$  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  $V_{\text{SPMD}} = 5\text{mL}$ . Thus, in the linear region of analyte uptake, an SPMD with  $V_{\text{SPMD}} = 1\text{ mL}$  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:

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

where  $K_{\text{SPMD}}$  is the equilibrium SPMD-water partition coefficient. For compounds with  $\log K_{ow}$  of 4.0 and > 4.0,  $K_{\text{SPMD}}$  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  $0.75 K_{ow} V_{\text{SPMD}}$  ( $\log K_{ow} \leq 4.0$ ) and  $0.3 K_{ow} V_{\text{SPMD}}$  ( $\log K_{ow} > 4.0$ ). 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 ( $V_{\text{SPMD}} = 5\text{ mL}$ ) is only a little more (i.e., 1.1L) than a 1L grab sample. Thus, standard SPMDs are useful only for sampling compounds with  $K_{ow} > 300$ , 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 ( $t_{1/2}$ ):

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

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 ( $R_s/K_{\text{SPMD}} V_{\text{SPMD}}$  or  $k_2$ ) from SPMDs during an environmental exposure and comparing them to PRC  $k_2$ s measured during the experimental determination of sampling rates ( $R_s$ s), the laboratory derived  $R_s$ s of analytes can be adjusted to account for the effects of field exposure conditions.

## **COMPARABILITY TO BIOMONITORING ORGANISMS**

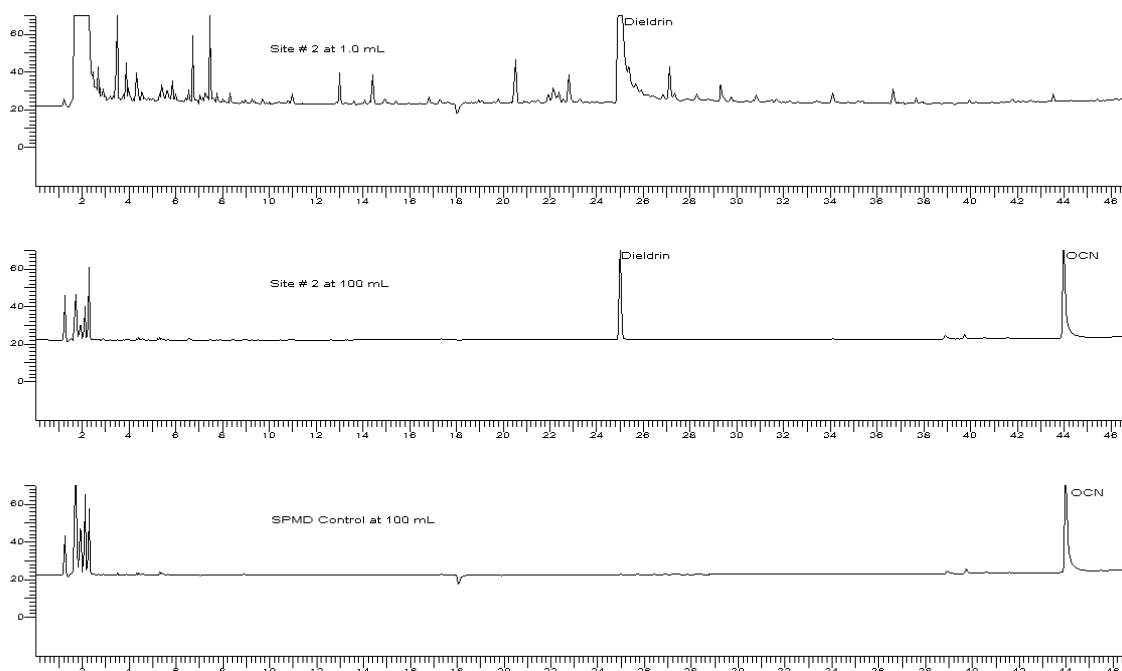
The accumulations of organic contaminants by SPMDs and aquatic organisms have been compared in a number of studies (2,4-6). Some studies have shown that the concentration patterns and uptake rates of several classes of chemicals by SPMDs and fishes are similar (6,7). However, it is unrealistic to expect 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  $k_2 \gg$  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 organo-chlorine 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 commensal 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

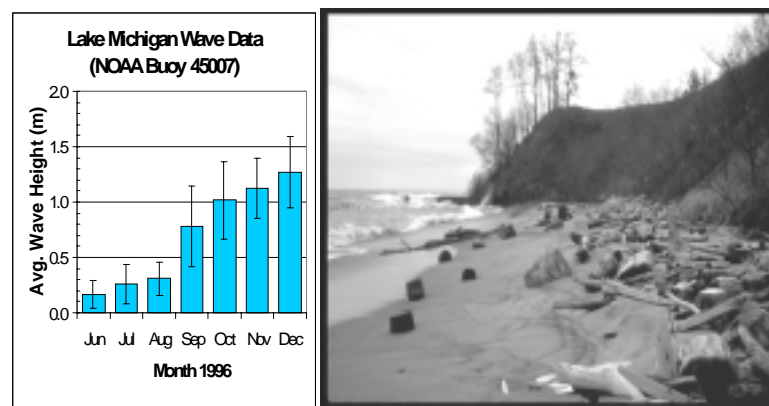
Multi-level arrays were placed to capture spatial variations in contaminant distribution and predominant TEAPs, seasonal changes and effect of wave activity, and spatial infiltration of lake water into the GSI [Lendvay, et al., 1998b; Lendvay, et al., 1999b]. The arrays were semi-permanent to evaluate 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].

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 ( $22^{\circ} \pm 1^{\circ}\text{C}$ ). 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].



**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 scattering of large debris, not present prior to the storm.

$$\frac{dC}{dt} \approx \frac{\Delta[VC]_{\text{Field}}}{\text{day}} = \lambda C_0 \quad (1)$$

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 ( $\lambda$ ) 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 ( $z_{\text{shallow}}$ ) is ratioed to the total depth ( $z_{\text{total}}$ ) 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.

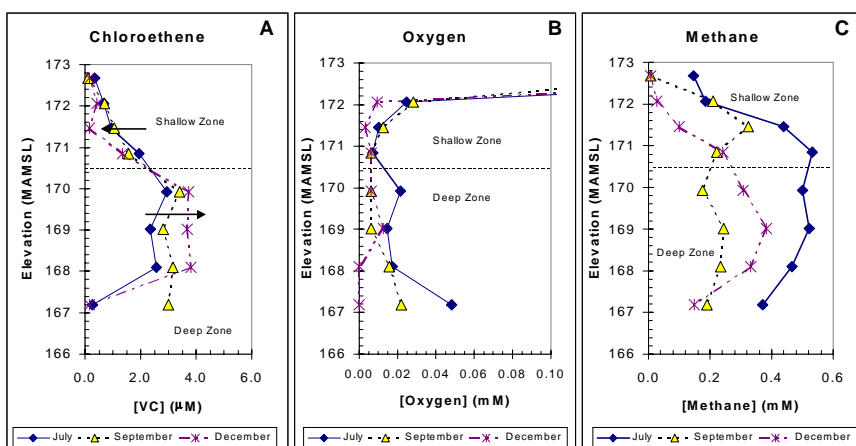
$$\frac{dC}{dt} \approx \frac{\Delta[VC]_{\text{Field}}}{\text{day}} = \lambda C_0 \quad (2)$$

## 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

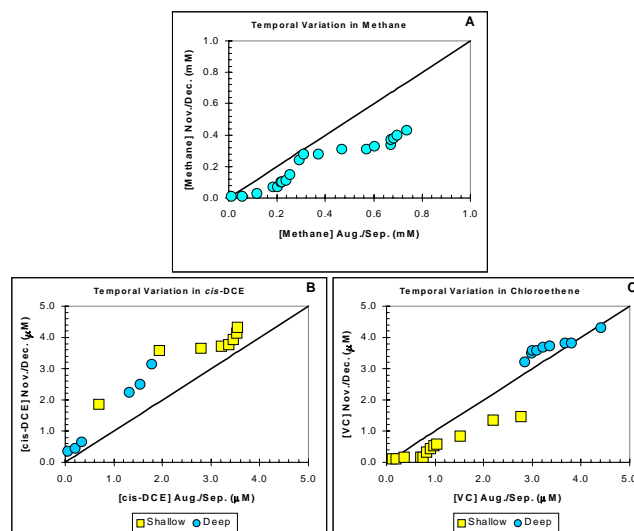


**Figure 2:** Vertical concentration profiles for chloroethene (A), oxygen (B), and methane (C) at ML-3 for three different time periods.

(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.

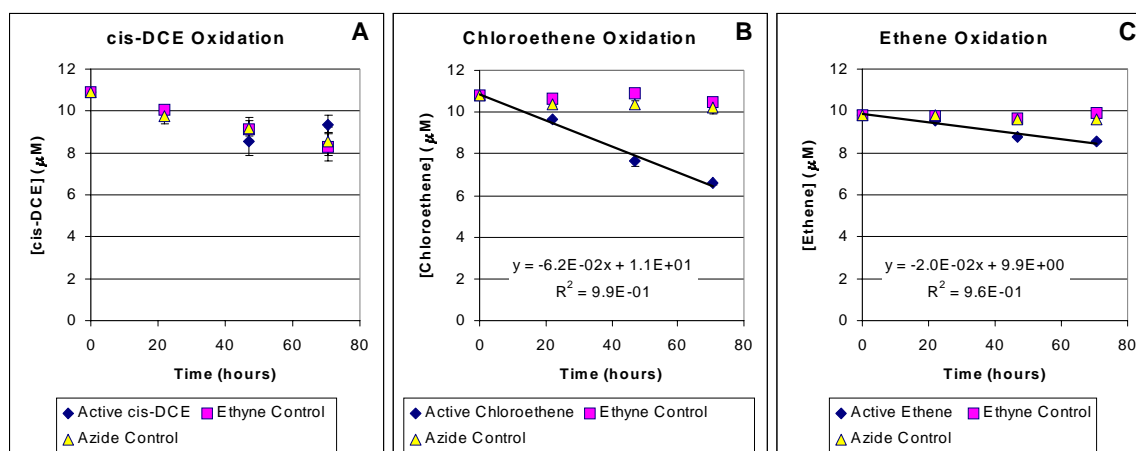
To elucidate specific field microbial processes responsible for chloroethene transformation, scattergrams comparing chloroethene or methane with oxygen in the shallow zone were evaluated for statistical correlations [Lendvay, et al., 1998a]. In the case of both chloroethene and methane, peak concentrations 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.

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.



**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 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 <sup>2</sup> ))
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

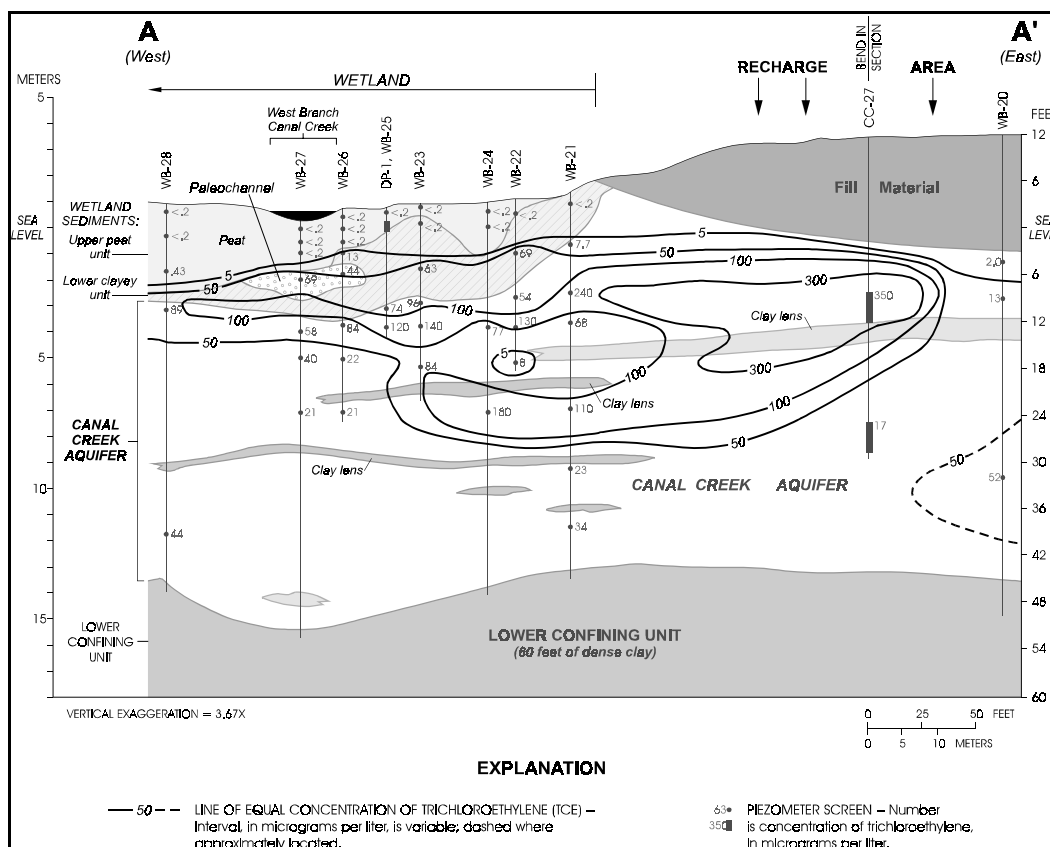


Figure 1. Concentrations of TCE in ground water along section A-A', June-October 1995.

degradation through hydrogenolysis and dichloroelimination pathways. Total concentrations of TCE, PCA, and their degradation products, however, decrease to below detection levels (generally less than  $0.5 \mu\text{g}/\ell$ ) 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,

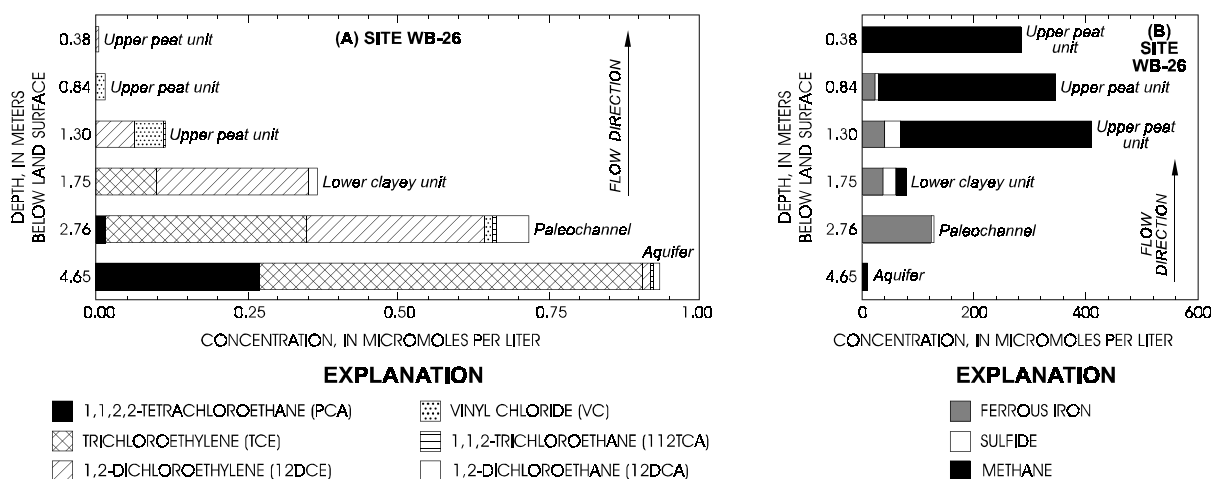
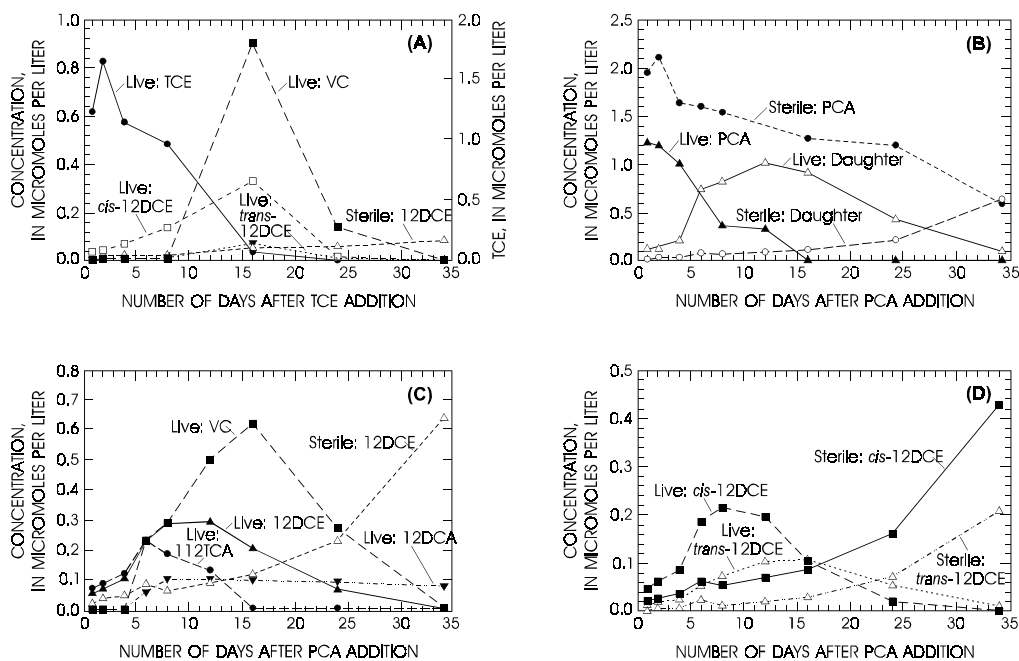


Figure 2. Vertical distribution of (A) the parent contaminants TCE and PCA and possible anaerobic daughter products and (B) selected redox-sensitive constituents at site WB-26, June-October 1995.

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  $\mu\text{mol/L}$  of TCE or 2.9  $\mu\text{mol/L}$  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<sup>-1</sup> (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<sup>-1</sup>) 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<sup>-1</sup> (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)

Assessment Endpoints of General Concern to NOAA (with some specific examples)

- 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**

Steps

- 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**

### Steps:

- 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

### Considerations specific to sites with groundwater contamination:

- 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  $1.27 \times 10^{-3}$  cm/s to  $3.94 \times 10^{-5}$  cm/s, equivalent to a mean value of 16  $\ell/m^2/d$ . Integrating over the horizontal extent of the seepage zone, the total daily discharge was estimated to be  $1.72 \times 10^6$   $\ell/day$  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  $1.50 \times 10^6$   $\ell/day$  for this section of the bay.

## DIRECT CONTACT RESISTIVITY MEASUREMENTS

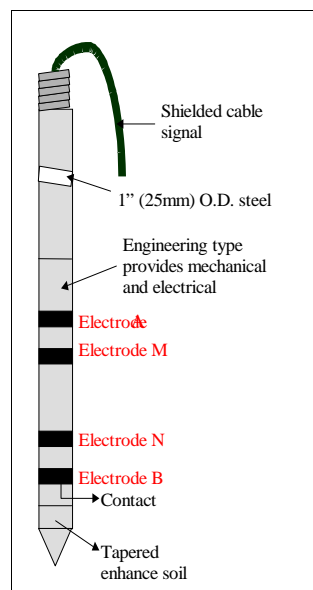
To characterize near-shore sediments in a simple and rapid manner, we used geophysical logging to determine the electrical resistivity of surface sediments off-shore. Electrical measurements have been used for some time to characterize the lithology and hydraulic characteristics of geological structures. 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  $\sigma_s$  is the electrical conductivity of the saturated bulk sediment,  $\sigma_w$  is that of the interstitial solution, and the Archie exponent  $n \sim 1-2$ . 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.

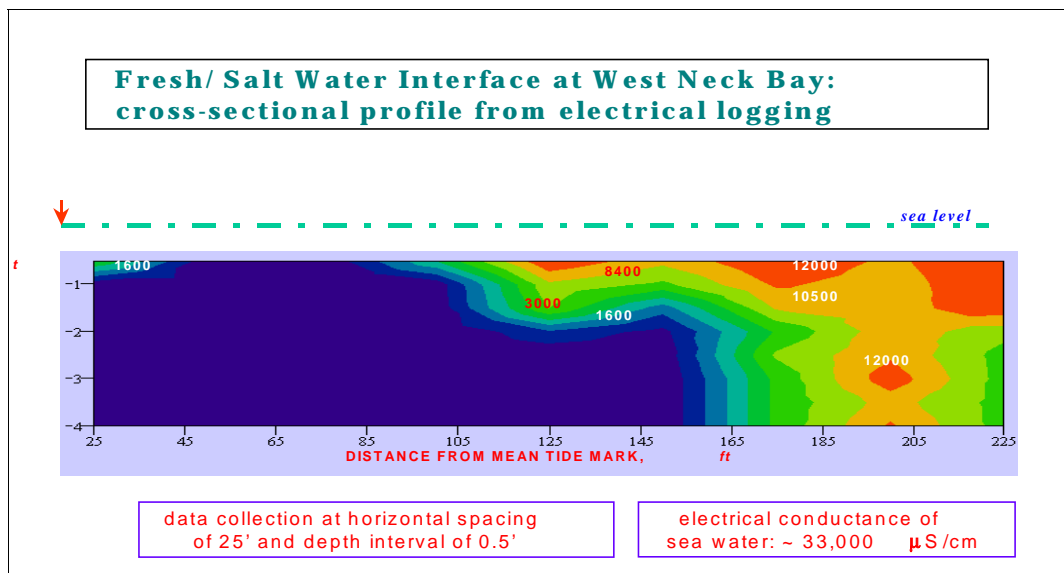


Figure 3.

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.

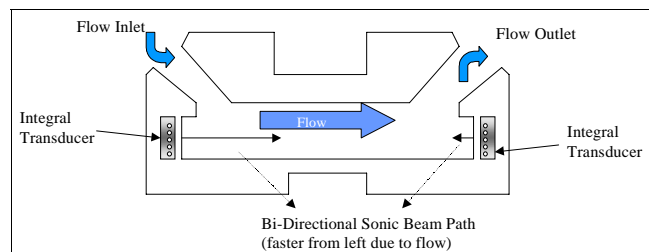


Figure 4.

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  $\mu$ S/cm in freshwater zones to 12,800  $\mu$ 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. Electrical



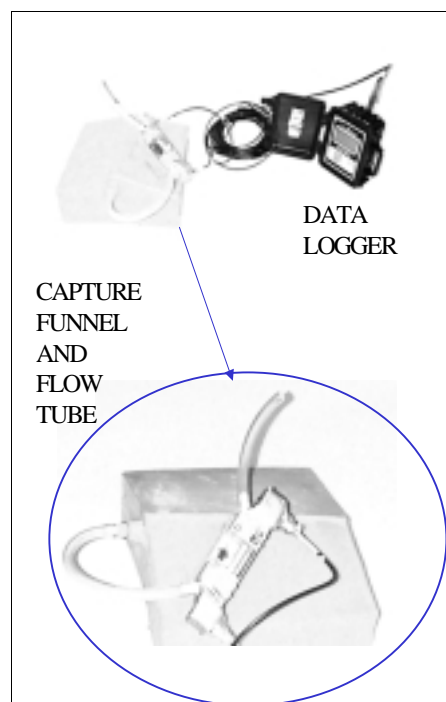


Figure 5.

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 address the spatial variability of the bay bottom and changes in near shore hydraulic gradients associated with tidal flux and precipitation.

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.

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  $1.27 \times 10^{-3}$  cm/s to  $3.94 \times 10^{-5}$  cm/s (with a mean value equivalent to  $16 \text{ l/m}^2/\text{d}$ ) 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  $1.72 \times 10^6 \text{ l/day}$  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  $1.50 \times 10^6 \text{ l/day}$  for this section of the bay (Schubert, 1998).

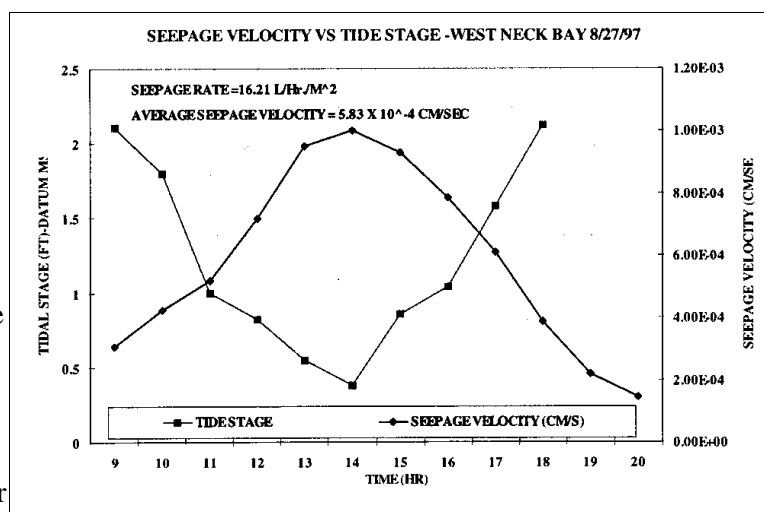


Figure 6.

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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-m<sup>l</sup> (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<sup>1</sup> septum of the cap). The samples were analyzed for volatile organic compound (VOC) content within 48 hours of sample collection. A 50- $\mu$ L vapor sample was slowly withdrawn and immediately analyzed on a Photovac<sup>1</sup> 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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<sup>1</sup>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

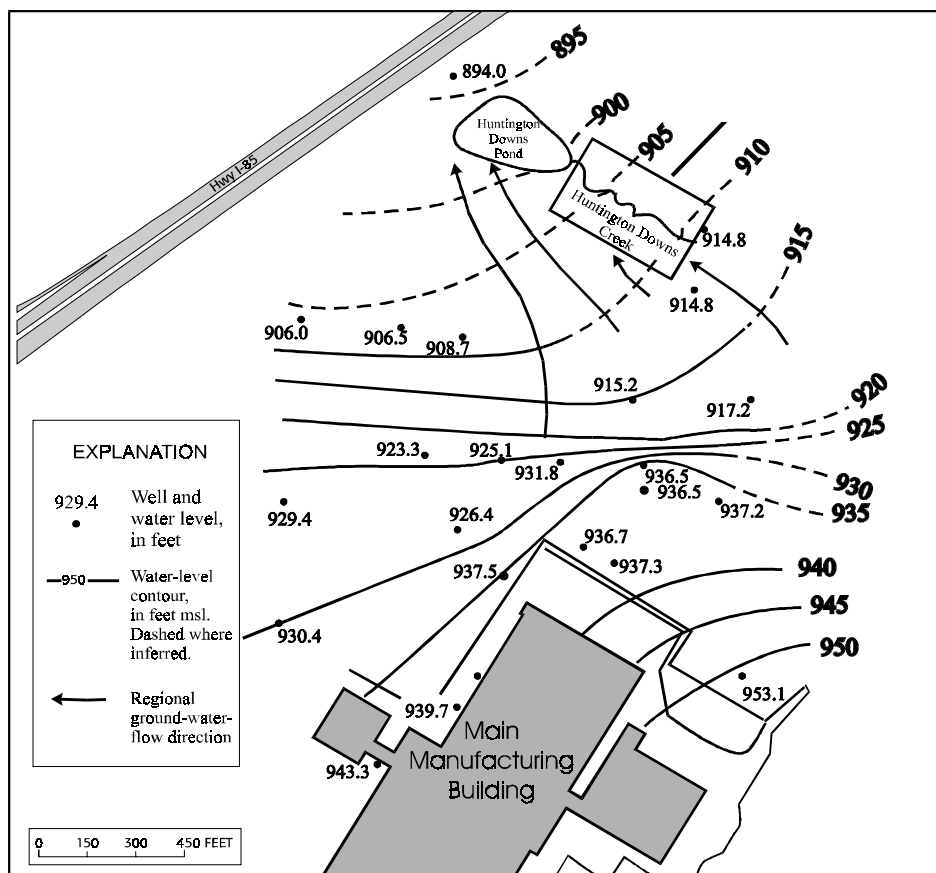


Figure 1. Ground-water flow directions near Huntington Downs Creek (Modified from Rust Environment and Infrastructure, 1995).

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.

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

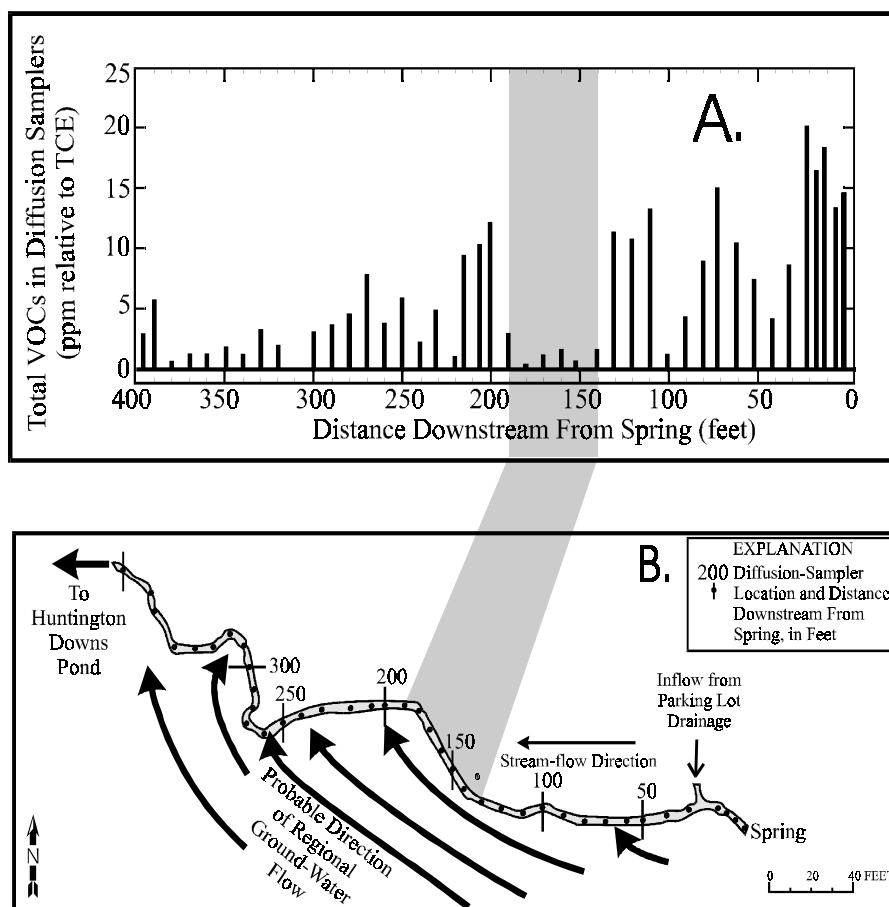


Figure 2. Concentrations of volatile organic compounds (VOCs) detected in vapor diffusion samplers beneath Huntington Downs Creek (A), and locations of samplers in creek (B), June 1994.

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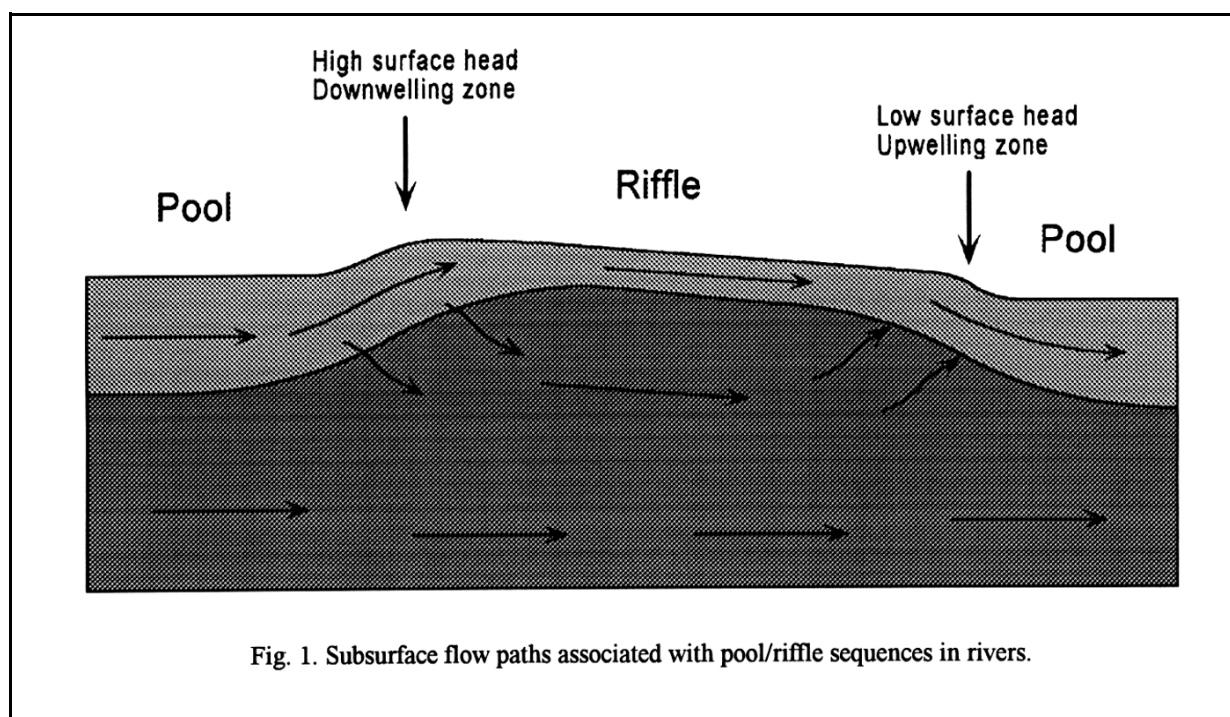
# Factors Controlling Hyporheic Exchange in a Southern Ontario Stream: Modeling Riffle-Scale Patterns in Three Dimensions Using MODFLOW

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?

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.

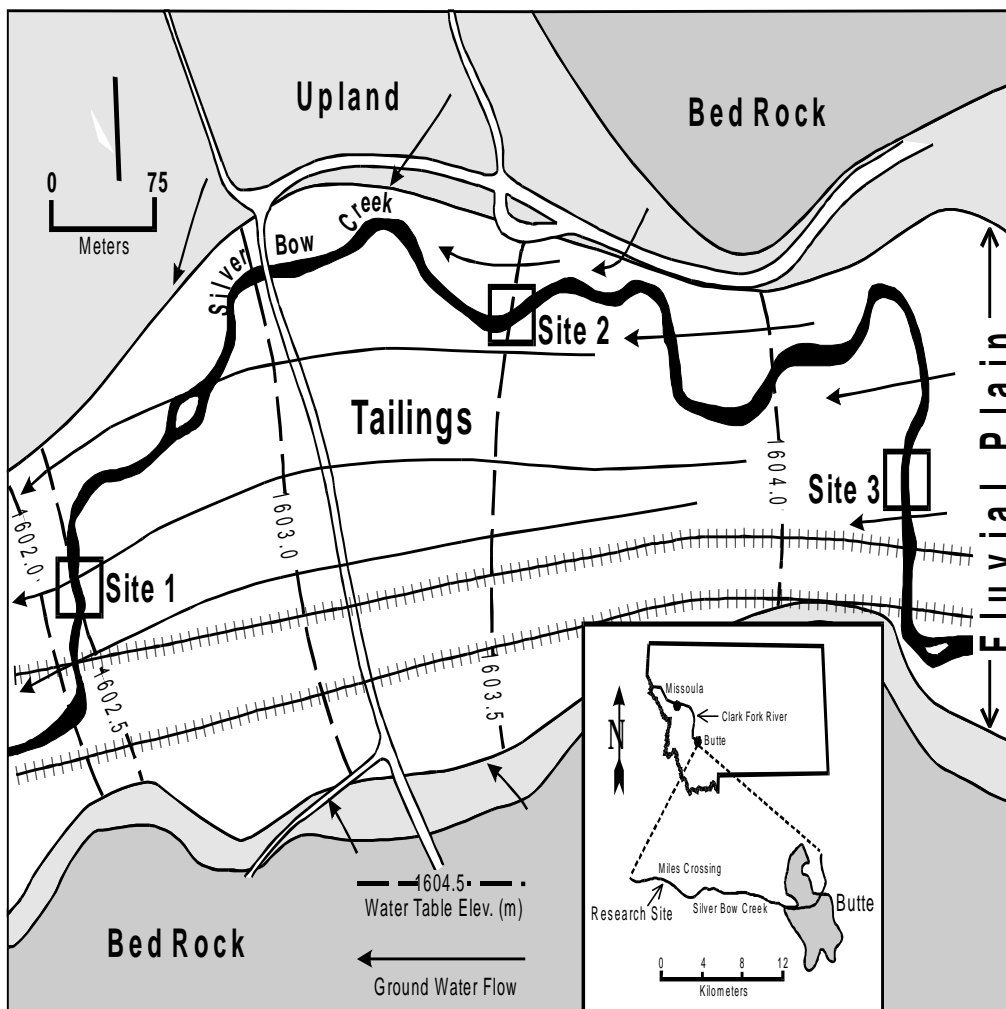
The complexities of the substrate in most streams/rivers make determining the relationships between solute and solid phases difficult. To address this issue we have used ceramic beads as an artificial substrate to examine what solid phases are in equilibrium within the shallow hyporheic zone. Combined 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 plain 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 plain 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.**

<b>Water Quality</b>	<b>Silver Bow Creek (Nagorski, 1997)</b>	<b>Fluvial Plain Groundwater (Benner, 1995; Shay, 1997)</b>
<i>Constituent</i>	<i>Std. Units and mg/l</i>	<i>Std. Units and mg/l</i>
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 <sub>3</sub> -N	1.3	1-2
SO <sub>4</sub>	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 least 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  $\mu$ m acid-washed filter and into two acid washed sample bottles. Bed water samples for cation analyses were preserved with trace metal grade  $\text{HNO}_3$  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 or 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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## **Appendix B: Discussion Group Focus Issues**

### **A. Hydrogeologic Data Collection**

1. What data are needed to estimate or document temporal changes in ground-water discharges to various surface water bodies? When and at what frequency should the data be collected?
2. How do the methods of measuring ground-water discharge to surface water depend on hydrogeologic setting and surface water regime?
3. What are the best methods of measuring ground-water discharges to various surface water bodies?
  - a. How should measurements be made?
  - b. Where should measurement be made?
  - c. Over what area should measurements be made?
  - d. When should measurements be made?
4. How do we determine the relative proportion of contaminated ground-water flux as a proportion of the total ground-water flux and/or mass balance for a given area?

### **B. Chemical Data Collection**

1. What are the relevant chemical processes?
2. How should chemical concentrations be measured when determining the flux of contaminated ground water to a surface water body?
  - a. Where should the measurements be taken?
  - b. How should samples be obtained?
  - c. Over what area should measurements be taken?
  - d. Over what time period and at what frequency should samples be taken?
3. What are the data quality objectives needed to support an ecological impacts assessment? What are the proper methods of collecting water and sediment samples to determine ecological impacts? What is the role of moisture and organic carbon data?
4. How should samples be collected to determine contaminant retention in the biologically active zone?
5. How should contaminant retention be evaluated in the hyporheic zone and bottom sediments?

### C. Biological Data Collection

1. Is the hyporheic zone considered an ecological habitat to be protected or a “treatment opportunity” zone for restoration of contaminated ground water discharging into surface water?
  - a. How can the hyporheic zone be defined biologically? \*
  - b. What are the ecological endpoints in the discharge or hyporheic zones? What ecosystem functions occur in these zones? \*
  - c. What are the appropriate scales to measure adverse effects to ecological endpoints in riverine, estuarine, and lacustrine hyporheic systems? \*
  - d. What modifications to existing Guidance or creation of new Guidance are needed to account for the unique ecological and hydrological aspects (receptors, functions, and routes of exposure) of the hyporheic zone? \*
2. What is the appropriate biological information (data) needed to assess ecological impacts?
  - a. What should be the structure for evaluating adverse impacts to key ecological endpoints?
    - (1) What biological monitoring should be performed? Which ecological structures and functions should be evaluated and why? \*
    - (2) Should it be phased and if so how should priorities be set for the data gathering?
  - b. How can screening numbers be developed for the hyporheic zone that are protective of ecological endpoints of concern? Are AWQC and NOAA Sediment Effects Criteria (ER-L and ER-M data) sufficient as screening numbers for protection of ecological endpoints; or, should other levels be used or developed for hyporheic zone screening for protection of ecological endpoints?
3. How should physical biological data be collected?
  - a. What are the best sampling methods to characterize the biological endpoints and then measure these for unacceptable impacts? Under what circumstances should filtered or unfiltered water samples (groundwater and surface water) be taken for environmental purposes? \*
  - b. What sampling locations are appropriate for biological data collection?
  - c. When should interstitial water samples from sediment (using semi-permeable membrane devices or other techniques) or whole sediment samples be collected for environmental purposes? Is there a role for sediment elutriate to be sampled?

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\* Asterisks represent priority issues for the biology discussion group.

4. Which ecological endpoints are at risk within the ground water/surface water mixing zone for different surface water regimes?

D. Monitoring Goals and Objectives

1. Identify and characterize zones of interest associated with surface water bodies susceptible to impact by contaminated groundwater.
2. Determine if discharge of contaminated groundwater is impacting surface water quality or biota in the zones of interest.
  - a. Characterize existing impacts.
  - b. Evaluate the effect of contaminant loading (including seasonal and temporal variations) on water quality and ecology.
  - c. Absent current impact on water quality, determine if long-term contaminant loading within a discharge zone poses a threat to future surface water quality and/or biota.
3. Determine the impact that different hydrogeologic settings and surface water regimes have on the selection of monitoring methods.
4. Identify prescriptive standards that must be attained.
  - a. Evaluate the applicability of applicability of a 'mixing zone' to the surface water body
  - b. Establish regulatory-based (chemical) and/or biota-based compliance standards.
5. Determine the sources of impacts.



## **Appendix C: Case Study Summaries**

Workshop participants submitted 14 case study summaries of ground water/surface water investigations for inclusion in this report. The purpose of providing these summaries is two-fold. First, to provide a resource for further information on the various monitoring methods. The case study summaries represent a range of contaminated media and contaminants within different hydrogeologic landscapes. Contact names are provided for further information on the use of such monitoring methods and their utility in obtaining the desired site data. The case studies are also provided as part of an informal assessment of what techniques are and are not commonly used. The following four tables provide this assessment.

Table 1 lists the case study sites and the main contaminant types present as well as the type of monitoring done at each site (physical, geochemical, or biological). Tables 2, 3, and 4 expand on the type of physical, geochemical, and biological monitoring being done, to summarize in some detail the type and number of sites using a given monitoring procedure. The tables include a total for the types of methods used and the number of total different places all the methods have been used at. They show that physical and geochemical methods are about equally distributed in use, but bioassays (and related biological monitoring) are much less widely used at the sites.

This appendix is not meant to be a comprehensive list of sites having ground water/surface water interaction and contamination problems, but simply a tabulation of the types of sites which were represented through those attending the Workshop, and also a listing of the types of methods which have been used in the field when dealing with this type of complex ground water/surface water interaction and contamination sites. It is interesting to note that while the most used monitoring methods are wells and piezometers, that there are many other monitoring options that have been used at sites where there is a ground water to surface water transition zone.

**Table 1**  
**GW/SW Case Studies Summary:**  
**Contaminants Studied and Monitoring Methods Used**

Site Name	Contaminants Monitored							Monitoring Methods		
	EcoRisk	VOCs	NO <sub>3</sub>	Metals	PAHs	PCBs	Pesticides or Herbicides	Physical	Geochemical	Bioassay
Alcoa/Lavaca Bay	✓			✓	✓			✓	✓	
Angus, Ontario	✓	✓						✓	✓	
Everglades National Park	✓		✓	✓				✓	✓	✓
Hertel Landfill	✓	✓		✓			✓	✓	✓	
I-85 Manufacturing	✓	✓						✓		
BMI Complex		?						✓	✓	
Ledbetter Cr.	✓		✓				✓	✓	✓	✓
Peconic Estuary	✓	✓	✓				✓	✓	✓	✓
Pinal Creek	✓			✓				✓	✓	
St. Joseph	✓	✓						✓	✓	✓
Union Pacific	✓	✓			✓			✓	✓	✓
Wyckoff Eagle Harbor	✓	✓			✓		✓	✓	✓	✓

**Table 2**  
**Case Studies Summary of Data Collection Techniques Used**

<b>Data Collection Techniques</b>	<b>Total</b>	<b>Site Names</b>
Current meters	2	Everglades National Park Pinal Creek
Diffusion sampler	1	I-85 Manufacturing
Direct Push Samples	2	I-85 Manufacturing Wyckoff Eagle Harbor
Geophysical Measurements	2	Peconic Estuary Wyckoff Eagle Harbor
Geoprobe	1	Wyckoff Eagle Harbor
GW Water level surveys	2	Angus, Ontario Wyckoff Eagle Harbor
GW Mini-piezometer	5	Angus, Ontario Ledbetter Cr. Peconic Estuary Pinal Creek Wyckoff Eagle Harbor
<b>(Continued)...</b>		
Ground water monitoring wells	8	Alcoa/Lavaca Bay Hertel Landfill BMI Complex Ledbetter Cr. Peconic Estuary Pinal Creek Union Pacific Wyckoff Eagle Harbor
Ground water multilevel sampling device	2	Angus, Ontario St. Joseph
Ground water Waterloo Profiler	1	Angus, Ontario
Ground water piezometers	3	Alcoa/Lavaca Bay Everglades National Park Hertel Landfill
In-stream solute tracer	1	Pinal Creek
In-stream auto sampler	1	Pinal Creek
NAPL studies	3	Alcoa/Lavaca Bay Union Pacific Wyckoff Eagle Harbor
Potentiomanometer	1	Angus, Ontario
SCAPS survey	1	Wyckoff Eagle Harbor

**Table 2**  
**Case Studies Summary of Data Collection Techniques Used**

<b>Data Collection Techniques</b>	<b>Total</b>	<b>Site Names</b>
Sediment sampling	4	Angus, Ontario I-85 Manufacturing, Union Pacific Wyckoff Eagle Harbor
Sediment probe	2	Angus, Ontario Ledbetter Cr.
Seepage meters	5	Everglades National Park Ledbetter Cr. Peconic Estuary Pinal Creek Wyckoff Eagle Harbor
Slug testing	1	Angus, Ontario
Soil cores onshore	2	Angus, Ontario Wyckoff Eagle Harbor
<b>(Continued)...</b>		
Soil cores offshore	3	Angus, Ontario St. Joseph Wyckoff Eagle Harbor
Streambed temperature survey	2	Angus, Ontario Wyckoff Eagle Harbor
Surface water monitoring	2	BMI Complex Wyckoff Eagle Harbor
Time Domain Reflectometry	1	Angus, Ontario
Tracer	1	Pinal Creek
Velocity and tracer-dilution gaging	1	Pinal Creek
<b>27</b>	<b>62</b>	

**Table 3**  
**Case Studies Summary of Geochemical Techniques Used**

<b>Geochemistry</b>	<b>Total</b>	<b>Site Names</b>
Age-dating of GW	1	Pinal Creek
Alkalinity	2	Hertel Landfill Pinal Creek
Ammonia	1	Hertel Landfill
Biochemical Oxygen Demand (BOD-5)	1	Hertel Landfill
Cation/Anion	1	Angus, Ontario
Chemical Oxygen Demand (COD)	2	Hertel Landfill Wyckoff Eagle Harbor
Chloride	2	Hertel Landfill Wyckoff Eagle Harbor
Chlorophyll	1	Peconic Estuary
CO <sub>2</sub>	1	Ledbetter Cr.
Ethene, ethane, methane	3	Everglades National Park Ledbetter Cr. Angus, Ontario
Field chemistry tests	1	St. Joseph
<b>(Continued)...</b>		
Field Parameters (pH, Temp., EH, DO, Elec. Cond.)	9	Alcoa/Lavaca Bay Angus, Ontario BMI Complex Ledbetter Cr. Peconic Estuary Pinal Creek St. Joseph Union Pacific Wyckoff Eagle Harbor
Hydrogen Gas—Dissolved	1	St. Joseph
Isotopes	1	Pinal Creek
Major ions	2	Pinal Creek St. Joseph
NAPL studies	2	Wyckoff Eagle Harbor Union Pacific
Nitrogen—Dissolved	3	Hertel Landfill Ledbetter Cr. St. Joseph
Nitrogen—Total	1	Ledbetter Cr.

**Table 3**  
**Case Studies Summary of Geochemical Techniques Used**

<b>Geochemistry</b>	<b>Total</b>	<b>Site Names</b>
Nutrients	4	Everglades National Park Ledbetter Cr. Peconic Estuary Pinal Creek
Organic Carbon--Dissolved	2	Angus, Ontario Hertel Landfill
Phosphate	2	Hertel Landfill Ledbetter Cr.
Radium isotopes	1	Everglades National Park
Radon-222	1	Everglades National Park
Redox-sensitive metals	1	Everglades National Park
Salinity	1	Wyckoff Eagle Harbor
Sediment chemistry	2	Hertel Landfill Wyckoff Eagle Harbor
Sulfate	2	Hertel Landfill Ledbetter Cr.
<i>(Continued)...</i>		
Sulfide	3	Angus, Ontario Hertel Landfill St. Joseph
Total Dissolved Solids	2	Hertel Landfill Wyckoff Eagle Harbor
Total Suspended Solids	1	Hertel Landfill Wyckoff Eagle Harbor
31	57	

**Table 4**  
**Case Studies Summary of Biological Techniques Used**

<b>Biological Data</b>	<b>Total</b>	<b>Site Names</b>
Bacteriophages	1	Everglades National Park
Benthic macroinvertebrate	1	Ledbetter Creek
Benthic community analysis	2	Wyckoff Eagle Harbor Ledbetter Creek
Biofilm colonization chambers	1	Ledbetter Creek
Biomonitoring of plant effluent	1	Wyckoff Eagle Harbor

**Table 4**  
**Case Studies Summary of Biological Techniques Used**

<b>Biological Data</b>	<b>Total</b>	<b>Site Names</b>
Brown tide cell counts	1	Peconic Estuary
Diver surveys	1	Wyckoff Eagle Harbor
Fish pathology	1	Wyckoff Eagle Harbor
Laboratory cultures	1	Wyckoff Eagle Harbor St. Joseph
Laboratory bioassays	1	Wyckoff Eagle Harbor
Sediment chemistry	1	Wyckoff Eagle Harbor
Sediment vertical profiler	1	Wyckoff Eagle Harbor
Trawls	1	Wyckoff Eagle Harbor
WET testing of plant effluent	1	Union Pacific
14	15	

## Case Studies

1) SITE NAME: Alcoa (Point Comfort)/ Lavaca Bay		
2) City/State: Point Comfort, Texas	5) Surface Water Body: Lavaca and Matagorda Bays	8)Contaminants:  <b>Ground Water</b>  Hg, PAHs, DNAPL (Hg and tar)  <b>Soil</b>  Creosote compounds, PAHs, Hg  <b>Surface Water</b>  Rarely detected  <b>Pore Water</b>  Hg, MeHg, PAHs  <b>Sediment</b>  PAHs, Hg
3) Regulatory Authority:  CERCLA	6) Range of Tidal Variation:  0.5-1.5 ft	
4) Contact:  Ron Gouguet Coastal Resource Coordinator U.S. EPA, Region 6 1445 Ross Avenue Suite # 1200 Dallas, TX 75202-2733 Phone: 214-665-2232 Gouguet.Ron@noaa.gov  Gary Baumgarten Remedial Project Manager U.S. EPA, Region 6 1445 Ross Avenue Suite # 1200 Dallas, TX 75202-2733 Phone: 214-665-6749 Baumgarten.Gary@epa.gov	7) Risk: <b>Human Health</b> Fish consumption     <b>Ecological</b> Fish Benthos Shell fish	
9) Monitoring Methods:		
<b>Physical Measurements</b>	<b>Geochemical Parameters</b>	<b>Bioassays</b>
Monitoring wells, piezometers, water level surveys, DNAPL studies	Field parameters, DNAPL studies, salinity	Unknown at this time

### 10) COMMENTS:

Contributions of contaminated groundwater appear to be responsible for maintaining Hg and PAH concentrations in surficial bay sediment above risk based levels of concern. Also, this appears to be the case for maintaining tissue concentration at levels of concern. The remedy (CERCLA) is expected to curtail the GW release, remove some sediment and stabilize sources.



<b>1) SITE NAME: Angus Ontario</b>		
<b>2) City/State:</b> Angus, Ontario, Canada	<b>5) Surface Water Body:</b> Pine River	<b>8)Contaminants:</b>  <b>Ground Water</b>  Chlorinated VOC-tetrachloroethylene  <b>Soil</b>  tetrachloroethylene  <b>Surface Water</b>  Rare detections of very low tetrachloroethylene concentrations  <b>Pore Water</b>  tetrachloroethylene, trichloroethylene, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, vinyl chloride  <b>Sediment</b>  tetrachloroethylene, trichloroethylene, cis-1,2-dichloroethylene
<b>3) Regulatory Authority:</b>  Ontario Ministry of Environment and Energy	<b>6) Range of Tidal Variation:</b>  Not applicable	
<b>4) Contact:</b>  Brewster Conant Jr. Hydrogeologist Department of Earth Sciences University of Waterloo Waterloo, Ontario N2L 3G1 Phone: 519-885-1211 x 2973 bconantj@sciborg.uwaterloo.ca  Dr. John A. Cherry Professor of Earth Sciences University of Waterloo Waterloo, Ontario N2L 3G1 Phone: 519-885-1211 x4516 cherryja@sciborg.uwaterloo.ca	<b>7) Risk:</b> <b>Human Health</b> Drinking water (groundwater) Sediment contact  <b>Ecological</b> Benthic and hyporheic aquatic life	
<b>9) Monitoring Methods:</b>		
<b>Physical Measurements</b>	<b>Geochemical Parameters</b>	<b>Bioassays</b>
Drivepoint wells, mini-piezometers, Waterloo Profiler and mini-profiler, multilevel GW sampling devices, soil cores (on and off shore), ground penetrating radar (GPR), time domain reflectometry (TDR), sediment probe (conductance), streambed temperature surveys, water level surveys, potentiomanometer	Field parameters, dissolved oxygen, sulfide, cations/anions, ammonia, dissolved organic carbon, chlorinated VOCs (PCE, TCE, DCEs, and VC), ethene, ethane, methane	None

**10) COMMENTS:**

Data collected primarily as part of Mr. Conant's PhD research. Pine River typically flows at 1.5 to 2.9 cubic meters per second.

<b>1) SITE NAME: Everglades National Park/ Florida Bay</b>		
<b>2) City/State:</b> South Florida	<b>5) Surface Water Body:</b> Wetland, estuary, bay	<b>8)Contaminants:</b>  <b>Ground Water</b>  Nutrients Metals?  <b>Soil</b>   <b>Surface Water</b>  Nutrients  <b>Pore Water</b>  Nutrients Metals?  <b>Sediment</b>  Nutrients Metals?
<b>3) Regulatory Authority:</b>	<b>6) Range of Tidal Variation:</b>  <10 cm	
<b>4) Contact:</b>  Dr. Peter W. Swarzenski USGS-GD 600 4 <sup>th</sup> Street South Petersburg, FL 33701 Phone: 727-803-8747 x3072  Dr. Judson W. Harvey USGS-WRD (NRP) 12201 Sunrise Valley Drive MS 430 Reston, VA 20192 Phone: 703-648-5876	<b>7) Risk:</b> <b>Human Health</b> Injection wells?    <b>Ecological</b> Eutrophication-related issues	
<b>9) Monitoring Methods:</b>		
<b>Physical Measurements</b>	<b>Geochemical Parameter</b>	<b>Bioassays</b>
Current meters, piezometers, seepage meters	Radium isotopes, radon-222, CH <sub>4</sub> , nutrients, redox-sensitive metals	Bacteriophages

**10) COMMENTS:**

A great overview of USGS projects related to South Florida can be found at <http://sflwww.er.usgs.gov/>

<b>1) SITE NAME: Exxon Refinery</b>								
<b>2) City/State:</b> Billings, Montana	<b>5) Surface Water Body:</b> Yellowstone River	<b>8)Contaminants:</b>  <b>Ground Water</b>  Hydrocarbons BTEX, SVOC, VOC  <b>Soil</b>  Hydrocarbons BTEX, SVOC, VOC  <b>Surface Water</b>  Benzene  <b>Pore Water</b>  Benzene  <b>Sediment</b>  Benzene						
<b>3) Regulatory Authority:</b> RCRA	<b>6) Range of Tidal Variation:</b>  Not applicable							
<b>4) Contact:</b>  Tina Diebold Region 8-Montana Office Phone: 406-441-1130 x227	<b>7) Risk:</b> <b>Human Health</b>        <b>Ecological</b> Do not know yet							
<b>Monitoring Methods:</b> <table border="0"> <tr> <td><b>Physical Measurements</b></td> <td><b>Geochemical Parameters</b></td> <td><b>Bioassays</b></td> </tr> <tr> <td>Wells, laser induced fluorescence, grab samples</td> <td>None</td> <td>None</td> </tr> </table>			<b>Physical Measurements</b>	<b>Geochemical Parameters</b>	<b>Bioassays</b>	Wells, laser induced fluorescence, grab samples	None	None
<b>Physical Measurements</b>	<b>Geochemical Parameters</b>	<b>Bioassays</b>						
Wells, laser induced fluorescence, grab samples	None	None						

**10) COMMENTS:**

<b>1) SITE NAME: Hertel Landfill Superfund Site</b>		
<b>2) City/State:</b> Plattekill, New York	<b>5) Surface Water Body:</b> Wetlands	<b>8)Contaminants:</b>  <b>Ground Water</b>  Primarily arsenic, chromium, iron, manganese VOCs and CVOCs Pesticides  <b>Soil</b>  Arsenic, chromium, VOCs  <b>Surface Water</b>  Iron, manganese, pesticides  <b>Pore Water</b>    <b>Sediment</b>  Pesticides, metals
<b>3) Regulatory Authority:</b>  CERCLA	<b>6) Range of Tidal Variation:</b>  Not applicable	
<b>4) Contact:</b>  Dean Maraldo Hydrogeologist U.S. EPA, Region 2 ERRD/PSB/TST 290 Broadway New York, NY 10007-1866 Phone: 212-637-3260 maraldo.dean@epa.gov  Sharon Trocher RPM U.S. EPA, Region 2 EPA/ERRD/NYRB 290 Broadway New York, NY 10007-1866 Phone: 212-637-3965 trocher.sharon@epa.gov	<b>7) Risk:</b>  <b>Human Health</b> Touching or drinking contaminated well water or accidentally ingesting contaminated soil    <b>Ecological</b> Pollutants have seeped into on-site wetlands, posing a threat to ecologically sensitive resources, wildlife, or aquatic biota.	
<b>9) Monitoring Methods:</b>		
<b>Physical Measurements</b>	<b>Geochemical Parameter</b>	<b>Bioassays</b>
Monitoring wells, piezometers	Surface and ground water: phosphate, COD, nitrate-nitrite, TOC, ammonia, alkalinity, BOD-5, TKN, sulfide, sulfate, chloride, TDS, TSS	None

**10) COMMENTS:**

Capping of this 13-acre municipal landfill was completed in the fall of 1998. At this time the primary COCs are metals in the groundwater and surface. The 1991 ROD remedy included a pump-and-treat component for groundwater which has been put on hold pending post-cap data evaluation.

<b>1) SITE NAME: I-85 Manufacturing and Distribution Center</b>		
<b>2) City/State:</b> Spartanburg, South Carolina	<b>5) Surface Water Body:</b> Tributary to Fairforest Creek	<b>8)Contaminants:</b>  <b>Ground Water</b>  Tetrachloroethylene  <b>Soil</b>  Tetrachloroethylene  <b>Surface Water</b>  Tetrachloroethylene  <b>Pore Water</b>  Unknown  <b>Sediment</b>  Pending
<b>3) Regulatory Authority:</b> State Superfund	<b>6) Range of Tidal Variation:</b>  Not applicable	
<b>4) Contact:</b>  Judy Canova Project Manager SCDHEC 2600 Bull St. Columbia, SC 29201 Phone: 803- 896-4046 canovajl@columb34.dhec.state.sc.us	<b>7) Risk:</b> <b>Human Health</b> Contact Inhalation Ingestion  <b>Ecological</b> Fish Invertebrates	
<b>9) Monitoring Methods:</b>		
<b>Physical Measurements</b>	<b>Geochemical Parameters</b>	<b>Bioassays</b>
Diffusion samplers, direct push samplers, grab samples	None	None

**10) COMMENTS:**

The unusual characteristic of this site is the high concentration of tetrachloroethylene observed in surficial samples from the tributary - up to 10 ppm. It is suspected that NAPL is discharging to the base of the stream based on groundwater quality data. At the location of highest contamination within the stream, there is no visible aquatic life, vertebrate or invertebrate. Contamination persists above ambient water quality criteria for over half a mile. The length of the discharge coupled with extreme topographic variation reduces possible remedial options for the stream.

<b>1) SITE NAME: Kerr-McGee Chemical/ BMI Complex</b>		
<b>2) City/State:</b> Henderson, Nevada	<b>5) Surface Water Body:</b> Lake Mead, Colorado River	<b>8)Contaminants:</b>  <b>Ground Water</b>  Ammonium perchlorate  <b>Soil</b>  Not analyzed  <b>Surface Water</b>  Ammonium perchlorate  <b>Pore Water</b>  Not analyzed  <b>Sediment</b>  Not analyzed
<b>3) Regulatory Authority:</b> State	<b>6) Range of Tidal Variation:</b>  Not applicable	
<b>4) Contact:</b>  Mitch Kaplan Environmental Scientist U.S. EPA, Region 9 75 Hawthorne Street San Francisco, CA 94105 Phone: 415- 744-2063 Kaplan.Mitch@epa.gov  Doug Zimmerman Chief, Bureau of Corrective Action Nevada Dept. of Environmental Protection Phone: 775- 687-4670 x3127	<b>7) Risk:</b> <b>Human Health</b> Ingestion    <b>Ecological</b> Unknown (under investigation)	
<b>9) Monitoring Methods:</b>		
<b>Physical Measurements</b>	<b>Geochemical Parameters</b>	<b>Bioassays</b>
Monitoring wells, surface water monitoring	Field parameters	None

**10) COMMENTS:**

<b>1) SITE NAME: Ledbetter Creek</b>		
<b>2) City/State:</b> Murray, Kentucky	<b>5) Surface Water Body:</b> Kentucky Lake Reservoir	<b>8)Contaminants:</b>  <b>Ground Water</b>  Nitrates, herbicides, pesticides, fecal coliforms  <b>Soil</b>  Nitrates, herbicides, pesticides  <b>Surface Water</b>  Nitrates, herbicides, pesticides, fecal coliforms  <b>Pore Water</b>  Nitrates, herbicides, pesticides, fecal coliforms  <b>Sediment</b>  Nitrates, herbicides, pesticides, fecal coliforms
<b>3) Regulatory Authority:</b> State of Kentucky	<b>6) Range of Tidal Variation:</b>  Hydroelectric/Flood Control Dam operations result in 2-6 ft change in water depth at stream site.	
<b>4) Contact:</b>  Susan P. Hendricks Hancock Biological Station 561 Emma Drive Murray, KY 42071 Phone: 502-474-2272 susan.hendricks@murraystate.edu  David S. White Hancock Biological Station 561 Emma Drive Murray, KY 42071 Phone: 502-474-2272 david.white@murraystate.edu	<b>7) Risk:</b> <b>Human Health</b> Contact   <b>Ecological</b> Surface-subsurface microbial communities Surface-subsurface macroinvertebrate communities Fish community Habitat degradation from high sedimentation/siltation, reduced surface-subsurface exchange	
<b>9) Monitoring Methods:</b>		
<b>Physical Measurements</b>  Monitoring wells, water table heights, mini-piezometers, sediment temperature probes, seepage meters	<b>Geochemical Parameters</b>  Dissolved oxygen, turbidity, pH, ORP, specific conductance, NO <sub>3</sub> +NO <sub>2</sub> ,NH <sub>4</sub> ,SRP, Total N, Total P,SO <sub>4</sub> ,CO <sub>2</sub> , CH <sub>4</sub>	<b>Bioassays</b>  Biofilm colonization chambers for bacterial productivity, activity, and diversity; benthic and hyporheic macroinvertebrate community structure.
<b>10) COMMENTS:</b>		



<b>1) SITE NAME: Peconic Estuary System</b>		
<b>2) City/State:</b> Suffolk County, New York	<b>5) Surface Water Body:</b> EPA National Estuary Program- Peconic Estuary System	<b>8)Contaminants:</b>  <b>Ground Water</b>  VOCs, nitrates, pesticides  <b>Soil</b>  <b>Surface Water</b>  VOCs, nitrates, pesticides  <b>.Pore Water</b>  Nitrates, VOCs  <b>Sediment</b>
<b>3) Regulatory Authority:</b>  National Estuary Program- Peconic Bay Estuary, Suffolk County, New York	<b>6) Range of Tidal Variation:</b>  Approximately 2.5-3.5 ft	
<b>4) Contact:</b>  Ron Paulsen Hydrogeologist Suffolk County Health Services-Bureau of Water Resources Phone: 516-853-2220 Ronald.paulsen@ co.suffolk.ny.us  Christopher Smith Cornell University Cooperative Extension Marine Program Leader Phone: 516-727-3910 Csmith@cce.cornell.edu	<b>7) Risk:</b> <b>Human Health</b> Estuary is receiving water body for groundwater discharges that contains pesticides, VOCs and elevated nitrates  <b>Ecological</b> The Peconic Estuary System has been subjected to the harmful alga blooms. The HAB known as brown tide ( <i>Aureococcus anophagefferens</i> ) has plagued the estuary since 1985. Excessive nutrients, metals, and possibly pesticides from groundwater seepage are thought to contribute to the onset and proliferation of HABs in the System	
<b>9) Monitoring Methods:</b>		
<b>Physical Measurements</b>	<b>Geochemical Parameters</b>	<b>Bioassays</b>
Installation of monitoring well and mini-piezometers with percussion drill and hollow augers; geophysical measurements using logging techniques including natural gamma, induction and resistivity logging; direct contact resistivity measurements of bay bottom to map out groundwater seepage faces; groundwater seepage measurements using time	Field parameters (conductivity, temperature, dissolved oxygen, chlorophyll, pH); nutrient species including inorganic and organic forms of nitrogen; metals; volatile organic compounds; pesticides	Brown tide ( <i>Aureococcus anophagefferens</i> ) cell counts

**10) COMMENTS:**

The Peconic Estuary System is a large estuary system on Long Island, New York that received National Estuary Status in 1994. Associated with the estuary program are numerous ongoing investigations and studies. These investigations include studies on the ecological, chemical and physical properties of the Peconic Bay Estuary. One property being studied is the effect of groundwater seepage on the chemical and biological conditions in the bay. Direct measurements of groundwater seepage along with the chemical analysis of coastal groundwater and bay bottom pore water in the estuary are being made. This information is being used to develop a surface water model and a groundwater model for the estuary system. The modelling results are being used to develop guidelines for nutrient loading to the bay especially as they pertain to chlorophyll and dissolved oxygen levels in the bay.

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**9) Monitoring Methods:**

***Physical Measurements***

***Geochemical Parameters***

***Bioassays***

Velocity and tracer-dilution gaging of stream discharge; in-stream solute-tracer experiments to determine surface and hyporheic-zone water exchange; in-stream auto-samplers; USGS mini drivepoint sampler; seepage meters; stainless-steel drivepoints; conventional wells; identification of ground water source areas using water stable isotopes; age-dating of ground water using CFCs.

pH, DO, temperature, alkalinity, major ions, dissolved metals, particulate and colloidal metals, dissolved organic carbon, nutrients

**10) COMMENTS:**

USGS and the University of Arizona have identified natural attenuation processes that remove metal contaminants due to interactions between surface water and ground water. Hydrologic exchange between the stream that receives the contaminated ground water and the hyporheic zone beneath the stream delays the downstream movement of contaminants, and also exposes the contaminants to unique microbial processes that enhance removal of contaminants in the hyporheic zone. USGS and the University of Arizona have published more than fifteen journal papers and reports on this topic. Interested readers are encouraged to contact the lead scientists listed above for reprints and more information.

<b>871) SITE NAME: St. Joseph, Michigan</b>		
<b>2) City/State:</b> Stevensville, Michigan	<b>5) Surface Water Body:</b> Lake Michigan	<b>8) Contaminants:</b>  <b>Ground Water</b>  Chlorinated VOCs (TCE; <i>cis</i> -1,2-DCE; <i>trans</i> -1,2-DCE; 1,1-DCE, VC, ethene)  <b>Soil</b>  Not sampled  <b>Surface Water</b>  None detected  <b>Pore Water</b>  Chlorinated VOCs (TCE; <i>cis</i> -1,2-DCE; <i>trans</i> -1,2-DCE; 1,1-DCE, VC, ethene)  <b>Sediment</b>  Not sampled
<b>3) Regulatory Authority:</b>  CERCLA/State	<b>6) Range of Tidal Variation:</b>  <1ft	
<b>4) Contact:</b>  John M. Lendvay Research Fellow University of Michigan 217 EWRE Building 1351 Beal Avenue Ann Arbor, MI 48109-2125 Phone: 734-764-6350 lendvay@engin.umich.edu  Peter Adriaens Associate Professor University of Michigan 181 EWRE Building 1351 Beal Avenue Ann Arbor, MI 48109-2125 Phone: 734-763-1464 adriaens@engin.umich.edu	<b>7) Risk:</b> <b>Human Health</b> Contact    <b>Ecological</b> Fish Shell Fish	
<b>Monitoring Methods:</b>		
<b>Physical Measurements</b>	<b>Geochemical Parameters</b>	<b>Bioassays</b>
Multi-level sample points, cores, field chemistry tests	Cations / Anions, dissolved hydrogen gas, dissolved iron, dissolved nitrogen, dissolved oxygen, dissolved sulfide, field parameters (O <sub>2</sub> , E <sub>h</sub> , pH, temperature, specific conductance)	Laboratory cultures

**10) COMMENTS:**

Spatial and temporal studies conducted to evaluate the effect of storm activity on the transformation potential of contaminants.

<b>1) SITE NAME: Union Pacific Railroad Laramie Tie Plant Site</b>		
<b>2) City/State:</b> Laramie, Wyoming	<b>5) Surface Water Body:</b> None- The Contaminant Isolation System prevents releases to the Laramie River	<b>8)Contaminants:</b>  <b>Ground Water</b>  Residuum oil, PAHs, pentachlorophenol (PCP), benzene, ethylbenzene, toluene, xylene, DNAPL  <b>Soil</b>  PAHs, PCP, dioxin, furans  <b>Surface Water</b>  Not applicable  <b>Pore Water</b>  Residuum oil, PAHs, pentachlorophenol benzene, ethylbenzene, toluene, xylene  <b>Sediment</b>  Not applicable
<b>3) Regulatory Authority:</b>  RCRA, CERCLA, State	<b>6) Range of Tidal Variation:</b>  Not applicable	
<b>4) Contact:</b>  Marisa Latady Wyoming Department of Environmental Quality/Soil & Hazardous Waste 122 West 25 <sup>th</sup> Street Cheyenne, WY 82002 Phone: 307-777-7752 mlatad@missc.state.wy.us  Felix Flechas US EPA Region VIII 999 18 <sup>th</sup> Street Denver, CO 80202 Phone: 303-312-6014 felix.flechas@epa.gov	<b>7) Risk:</b> <b>Human Health</b> Dermal contact Incidental ingestion Inhalation of particulates  <b>Ecological</b> Direct exposures via soil ingestion Direct exposures via dermal contact with soil Indirect exposures via ingestion of contaminated food items Inhalation of particulate dust (considered less significant the others described above)	
<b>9) Monitoring Methods:</b>		
<b>Physical Measurements</b>	<b>Geochemical Parameters</b>	<b>Bioassays</b>
Monitoring wells; piezometers; sediment sampling; monitoring of the containment systems for hydraulic control; DNAPL thickness	Field parameters	WET testing of the water treatment plant effluent under an NPDES permit

# **10) COMMENTS:**

UPRR operated the Laramie Tie Plant Site for the treatment of railroad ties and other wood preserving operations on an intermittent basis from 1886 to 1983. The site borders the Laramie River just south of the city of Laramie, Wyoming. Waste management practices, such as allowing treated ties to drip dry onto the ground and discharging wastewater generated in the treating process to an unlined surface impoundment, are believed to be the causes of contaminated soils and ground water at the site. The primary contaminants identified at the site include creosote, pentachlorophenol and other residuum oils.

Contamination at the site was discovered in 1981, and in 1983 the Environmental Protection Agency (EPA) and UPRR signed a CERCLA Administrative Order on Consent (AOC) to continue the remedial investigation already in progress and to conduct site cleanup. The investigation identified contamination in surface soils and ground water contamination, including the presence of oil in the subsurface [i.e., Dense Non-Aqueous Phase Liquid (DNAPL)]. Some of the early activities conducted by UPRR to address the contamination identified include:

1. In 1983, UPRR decommissioned the facility, including demolition of on-site buildings and shipment of unused wood treatment materials to another facility.
2. In 1984, UPRR partially closed the unlined Surface Impoundment that received wastewater. The Surface Impoundment is a regulated unit as defined by the WDEQ/HWRR Chapter 10, Section 6(a) .
3. In 1987, UPRR installed the Contaminant Isolation System (CIS) to prevent migration of contaminants to the Laramie River. The CIS consists of relocation of the Laramie River to an uncontaminated channel; construction of a cutoff wall; installation of a water management system consisting of horizontal drain lines along the exterior and interior of the cutoff wall to maintain an inward hydraulic gradient; construction of a water treatment plant to remove dissolved contaminants and implementation of a monitoring program to ensure the effectiveness of the CIS.
4. In 1988, UPRR installed ground water extraction wells, referred to as the Morrison Contaminant Withdrawal System (MCWS), outside the western site boundary to address a small area of contaminated ground water in Morrison bedrock.

In 1991, EPA and UPRR entered into an AOC under RCRA that required UPRR to conduct a Corrective Measure Study (CMS) to identify long-term remedies for implementation at the site, including pilot tests of various techniques to remove DNAPL from the subsurface.

In 1994, EPA selected the remedy to address contamination at the site. The remedy included continued operation of the CIS and MCWS systems, removal of DNAPL using the waterflood oil recovery method, covering a portion of the site with topsoil to address contaminated surface soils, installing a RCRA cap over the former Surface Impoundment area, and maintaining restricted access to the site. Nine criteria were selected to evaluate the performance of the final remedy. Detailed descriptions of these criteria can be found in EPA's September, 1994, "Final Decision and Response to Comments.

In 1995, the RCRA AOC was amended to require UPRR to submit an application for a RCRA Permit for post-closure care and corrective action by September 1, 1995. UPRR submitted an application for a post-closure care and corrective action permit on September 1, 1995, and revised that application in May 1996, August 1997 and March 1998. The amendment to the AOC also required UPRR to implement the final remedy selected by EPA in 1994. The final remedy was amended in 1995 to include the use of a Corrective Action Management Unit (CAMU) to consolidate contaminated

concrete debris and soils in the partially closed unlined Surface Impoundment. The CAMU currently has an interim soil cover of six inches.

That portion of the final remedy that requires closure (i.e., installation of a RCRA cap) and post-closure care of the Surface Impoundment, as described in Section A of this Fact Sheet, is deferred to allow implementation and evaluation of phytoremediation, an innovative technology, designed for in-situ remediation of waste, contaminated soils and contaminated ground water. Phytoremediation test plots will be established over a portion of the Surface Impoundment and the western portion of the facility to determine the effectiveness of this technology. Review of this corrective action program will be conducted every five (5) years as part of the technical impracticability (TI) determination. The TI determination is made when ground water restoration to applicable cleanup standards is unattainable from an engineering perspective. If WDEQ determines, based on the five (5) year review process, that phytoremediation does not meet the remediation criteria specified in the Permit, UPRR will be required to implement the closure and post-closure care requirements established in the Permit. Those portions of the final remedy that are not deferred include continued oil recovery operations in the Surface Impoundment area until all recovery units have achieved the endpoint criteria, and implementation of the ground water corrective action program.

As of December 1998 UPRR has recovered approximately 1,500,000 gallons of oil from the subsurface through the waterflood oil recovery method.



<b>1) SITE NAME: West Branch Canal Creek, Aberdeen Proving Ground</b>		
<b>2) City/State:</b> Edgewood, Maryland	<b>5) Surface Water Body:</b> Wetland and stream	<b>8)Contaminants:</b>  <b>Ground Water</b>  Chlorinated VOCs Possible DNAPL  <b>Soil</b>  None  <b>Surface Water</b>  Infrequently detected, low concentrations of chlorinated VOCs  <b>Pore Water</b>  Chlorinated VOCs  <b>Sediment</b>  Chlorinated VOCs in wetland sediment
<b>3) Regulatory Authority:</b>  CERCLA	<b>6) Range of Tidal Variation:</b> About 2 ft change in stage in creek; affects ground-water flow direction and plume distribution	
<b>4) Contact:</b>  Michelle Lorah U.S. Geological Survey 8987 Yellow Brick Road Baltimore, MD 21237 Phone: 410-238-4301 Fax: 410-238-4210 mmlorah@usgs.gov	<b>7) Risk:</b> <b>Human Health</b> Air transport of VOCs   <b>Ecological</b> Air transport of VOCs Possible exposure of benthic organisms to VOCs in water and sediment	
<b>Monitoring Methods:</b>		
<b>Physical Measurements</b>	<b>Geochemical Parameters</b>	<b>Bioassays</b>
Nested piezometers, diffusion samplers, cores, field chemistry tests, salinity, pressure transducers and tide gage	VOCs; ethane; ethene; dissolved organic carbon; total organic carbon redox species- methane, sulfide, Fe(II)/Fe(III), manganese, dissolved oxygen, nitrate, ammonia; field parameters (pH, alkalinity, temperature, conductance, salinity, turbidity); major cations and anions; selected trace metals	Microcosms to measure biodegradation rates and daughter products; DNA/RNA analysis of microbial communities in wetland sediment

**10) COMMENTS:**

USGS WRIR 97-4171: Report on project results through 1997 available online:  
<http://md.usgs.gov/publications/online.html>

<b>1) SITE NAME: Wyckoff Eagle Harbor</b>		
<b>2) City/State:</b> Bainbridge Island, Washington	<b>5) Surface Water Body:</b> Eagle Harbor Puget Sound	<b>8)Contaminants:</b>  <b>Ground Water</b>  Creosote compounds, PAHs, pentachlorophenol, fuel oil, LNAPL, DNAPL  <b>Soil</b>  Creosote compounds, PAHs, pentachlorophenol  <b>Surface Water</b>  Rarely detected  <b>Pore Water</b>  Creosote compounds, PAHs,  <b>Sediment</b>  Creosote compounds, PAHs, DNAPL
<b>3) Regulatory Authority:</b>  CERCLA	<b>6) Range of Tidal Variation:</b>  14 ft	
<b>4) Contact:</b>  René Fuentes Hydrogeologist U.S. EPA, Region 10 1200 Sixth Avenue Seattle, WA 98101 Phone: 206-553-1599 fuentes.rene@epa.gov  Hahn Gold Remedial Project Manager U.S. EPA, Region 10 1200 Sixth Avenue Seattle, WA 98101 Phone: 206-553-0171 gold.hahn@epa.gov	<b>7) Risk:</b> <b>Human Health</b> Contact Inhalation Fish consumption  <b>Ecological</b> Fish Shell fish DNAPL contact	
<b>9) Monitoring Methods:</b>		
<b>Physical Measurements</b>	<b>Geochemical Parameters</b>	<b>Bioassays</b>
Monitoring wells, mini-piezometers, sediment probe (temperature and electrical conductivity), seepage meter, off-shore cores, diver surveys (NAPL), water level surveys, LNAPL and DNAPL studies	Field parameters, LNAPL and DNAPL studies, salinity	Biomonitoring of treatment plant effluent

**10) COMMENTS:**

## **Appendix D: MHE Push Point Sampling Tools**

by Mark A. Henry\*

A new tool and sampling methodology have been devised for collecting pore water samples from beneath beaches and surface water bodies. The use of this technology enables a single investigator or small team to rapidly gather pore water samples at or near the interface between groundwater and receiving bodies of water. From a research perspective, the information gained in analyzing these samples may be very helpful in understanding the geochemical nature of this transition zone and the biological processes at work.

This methodology has been used very successfully to locate the expression of contaminated groundwater venting into several lakes in Michigan. The technique involves the use of an MHE 27-inch push-point sampling device (PP27), ¼-inch outer diameter by ⅛-inch inner diameter Tygon tubing, and 50 ml, 100% polyethylene syringes or a peristaltic pump. The PP27 is a rigid ⅛-inch diameter stainless steel probe that is screened at one end and ported at the other to allow the collection of pore water with a syringe or peristaltic pump. In this method's simplest form, the investigator would walk along a beach or in shallow water paralleling the beach, and at periodic intervals push (by hand) a decontaminated PP27 into the sand or sediments with a twisting motion until refusal (usually 6-18-inches). Then the screened zone is exposed and pore water samples are withdrawn at "low-flow sampling" collection rates using a disposable syringe connected by a length of Tygon tubing. Usually, only 30-50 ml of water withdrawal is necessary to develop this miniature well; this equates to approximately 20-35 volume exchanges through the PP27. Subsequently drawn water is usually non-turbid and suitable for dispensing directly into sample containers or instruments. A 3-dimensional sampling array is possible within the sediments and the water column. The PP27 is easily decontaminated in the field but if the investigator has several of the inexpensive sampling devices on-hand, sample collection along a transect can be very rapid. When 100% polyethylene syringes are employed, samples may be collected and stored temporarily within the syringe by placing the full, sealed syringe in a cooler. Once the sample collection has been completed, the investigator can process the samples in a controlled environment. As an added benefit, it is possible to use the sample-filled syringes for on-site headspace analysis of VOC's using a field GC—information that be used to direct an investigation in real time. If the syringe is half-dispensed and refilled with air, resealed, and agitated, the headspace in the syringe above a known volume of water can be quickly analyzed.

The Michigan Department of Environmental Quality (MDEQ) uses an enhanced variation of this method. As samples are being collected, some of the pore water is immediately dispensed into field analytical equipment for measurement of "stabilization parameters" such as dissolved oxygen, pH, conductivity, redox, and temperature, or analytes such as dissolved iron, sulfide, etc. The MDEQ investigators were able identify and map the expression of a groundwater plume venting into Lake Michigan and several inland lakes using this methodology and/or these techniques and SCUBA gear. Furthermore, the MDEQ couples its sampling with location information obtained using sub-meter accuracy global positioning system (GPS) equipment. Plotting the geochemical data onto an accurate GPS representation of the sampling locations and predominant local features produces a precise plume expression map. GPS technology allows investigators to reliably relocate previous sampling locations for additional study and accurately combine and compare data from multiple sampling events.

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\* Editor's Note: Mark Henry presented this material at a meeting of the Ground Water Forum in April 2000.

*What follows is found in the MHE PP-27 sampler instruction manual. It is presented as additional information about the sampler and to provide a few practical hints.*

## MHE PP27" Push-Point Sampling device (Patent Pending) Operators Manual, Ver. 1.02, May 13, 2000

### INTRODUCTION

The groundwater/surface water interface has been a research interest of mine for the past decade. This transitional zone is usually rich in biomass and may play a predominant role in the bioattenuation of contaminated groundwater entering surface water bodies. Usually these biologic processes have limited effectiveness in attenuating highly contaminated groundwater, leaving a plume of parent contamination and metabolic byproducts that eventually expresses itself in receiving waters—usually classified as non-point sources of pollution because of the uncertainty of the discharge area. Part of the problem in the detection and study of these plumes is that there were no devices on the market for the rapid, discrete collection of pore water samples. Reliance on conventional technology and techniques to perform a detailed investigation required extensive effort and burdensome equipment.

Through several iterations, I have evolved a simple device for collecting pore water samples from beneath surface water bodies or the beach areas surrounding them. Pore water sampling using the PP27 becomes a simple and efficient process, generating a wealth of information and very little waste. The effective working depth is up to 26 inches below the land or sediment surface. If one collects groundwater samples in a transect perpendicular to groundwater flow in the suspected area of plume discharge to an open water body, their analysis yields information about the areal extent of contaminant discharge to the water body. At this point, additional sampling can complement the initial data and provide the information necessary to map the plume expression in both magnitude and areal distribution. This is becoming increasingly important to regulators as they decide the ecological impacts of discharging contaminant plumes.

Sampling at each location usually takes five minutes, allowing a small crew to collect dozens of samples in an afternoon. These samples can be analyzed in the field for real-time information useful in directing field investigations and research. The work that I have conducted at several contamination sites indicates that many groundwater plumes discharge in surface water bodies in 2-3 feet of water depth—accessible to investigators wearing hip boots or waders. Many plumes, especially light non-aqueous phase liquid (LNAPL) plumes can be delineated by collection of samples in very shallow water or from under beaches. My initial experience has shown that dense non-aqueous phase liquid (DNAPL) contaminant plumes express themselves in the shallow, near-shore water as well, even though the onshore depth of the contaminant mass was deep in the aquifer.

### DIRECTIONS

As shown in Figure 1, the PP27 device is a very simple, precisely machined tool consisting of a tubular body fashioned with a screened zone at one end and a sampling port at the other. The bore of the PP27 body is fitted with a guard rod that gives structural support to the PP27 and prevents plugging and deformation of the screened zone during insertion into sediments. The PP27 is made of 316 stainless steel assuring compatibility with most sampling environments. The screened zone consists of a series of interlaced machined slots which form a short screened zone with approximately 20% open area.

Operation of the PP27 is not difficult. Simply hold the device in a manner that squeezes the two handles towards each other to maintain the guard rod fully inserted in the PP27 body during the insertion process (as shown in Figure 2). Holding the device in this manner, push the PP27 into the sediments or beach to the desired depth using a gentle twisting motion. When the desired depth or refusal is reached remove the guard rod from the PP27 body without disturbing the position of the deployed sampler. Once the guard rod has been removed from the PP27, it **SHOULD NOT** be reinserted into the device until the bore of the PP27 has been thoroughly cleansed of all sand, silt, etc.

Attach a syringe or (peristaltic) pump to the PP27 sample port (see Figure 3) and withdraw water at a low-flow sampling rate (50-200 ml/min.). Once non-turbid aliquots have been withdrawn, representative samples can be collected for on-site and off-site analysis.

#### HELPFUL HINTS, INFORMATION, AND CAUTIONS

- Multiple depths can be sampled in one hole if samples are collected from deepest to shallowest. Insert the sampler using a twisting motion until you reach refusal. Remove the guard rod. **Do not push the sampler further into the sediments once the guard rod has been removed as this may damage the screened zone and plug the PP27 with sediment.** Once sampling has been completed at this deepest depth, the PP27 can be partially pulled from the hole to a new sampling elevation. Remember not to insert the PP27 into the sediments without the guard rod inserted to prevent screened zone damage. Alternately, multiple holes can be used to collect samples from multiple depths at a particular sampling location. It is recommended that some type of device be used to prevent lateral movement and slippage of the PP27 as sampling is conducted near the top of the hole (see Figure 3). This offsets the leverage of the instrument and reduces hole degeneration. MHE offers an 8-inch diameter, heavy-duty steel sampling platform engineered for precise sampling depth requirements of field research. A plate of steel with a 3/16-inch diameter hole through its center would serve the fundamental purpose of maintaining a rigid hole opening. If repeated shallow sampling is to be conducted, it may be more convenient to use a shorter sampler (MHE - PP15").
- If you wish to reuse the PP27 sampler at a particular sampling location and want to clean the bore quickly while you're there so that the guard rod may be safely reinserted, you can use a syringe filled with surface water or deionized water to backflush the bore several times before reinserting the guard rod. Use at least 100 ml of water. If you have too much trouble reinserting the guard rod (e.g., due to grit), it will be necessary to use the standard cleaning procedures with cleaning rod and soap solution.
- If the screened zone of the PP27 becomes plugged while inserted in the sediments, it is frequently possible to hydraulically/pneumatically shock the screened zone free of adhering material while it is inserted into the sediments. Attach a large-volume syringe to the sampling port. In a quick motion, pull the syringe plunger most of the way back (creating a vacuum) and then immediately release the plunger—the plunger will slam to a neutral position, sending a shock wave through the bore of the PP27 and may alleviate the problem.
- The PP27 can be used as a piezometer to determine the static head of the groundwater and hence, the potential direction of groundwater movement. To do this, a tube is connected to the sample port as shown in Figure 5. A continuous stream of water is established from the syringe (or pump) to the screened zone by pumping out any air remaining in the PP27 and tubing. When the tube is

disconnected from the syringe, the static water level in the tube will represent the static water level at the depth that the screened zone occupies.

- It is frequently possible to push the PP27 through thin lenses of low-permeability material and collect samples from below them and gather valuable geochemical samples. At many of the sites where the PP27 has been used, sampling from just below a layer of fine sand, silt, or clay, one occasionally encounters seemingly large pockets of gas that seem to have coalesced and collected under this less permeable stratum. Analysis of these pockets may provide additional insight to predominant biological processes. It may true that the concentration of volatile organic compounds (VOCs) in the groundwater has equilibrated with these bubbles (i.e., steady state), which means that their presence in a sampling stream or syringe would not significantly affect the concentration of dissolved VOCs. In fact, if one assumes that steady-state conditions exist, the concentration of VOCs in the bubbles is directly related the concentration in the surrounding groundwater. An alternate condition may exist if the groundwater is supersaturated with bacterial metabolic waste gases and the negative pressure exerted by the pump (or syringe) is initiating a degassing of dissolved gases from the groundwater. In this instance, VOCs would partition from the groundwater to the bubbles as they are formed in the sampling tubing (this is fairly evident if occurring). The consequence is that part of the dissolved contaminant mass has partitioned into the gas phase; unless the gas-phase is captured, quantified, and accounted for, the native VOC concentration of the groundwater is not reflected by analysis of the groundwater alone. If this condition exists, the degassing effect can be minimized by decreasing the sampling rate to a rate more easily yielded by the sampled formation. With experience, it is easy to distinguish which of these conditions (or combination of conditions) exist and to what extent they affect sample quality.
- The internal volume of a PP27 is approximately 1.5 ml. A 50 ml syringe full of distilled water, decontamination water, methanol, etc. will push about 33 volumes through the bore.
- When straightening the screened zone it is sometimes helpful to wash out the bore of the device and then insert the guard rod or the cleaning rod to the area of the bend in the screened zone. Gently unbend the portion of the screened zone nearest the rod and carefully advance the rod to the next bend. After the rod has been fully inserted into the screened zone perform the final screened zone straightening fine-tuning until the guard rod slides freely through it.
- If the sampling port of the PP27 is above the static level of the water body, each time you remove the syringe or pump from the PP27 sampling port, air will fill the bore of the PP27 allowing the water level in the bore to reach its static head. To avoid this plug of air from entering the subsequent syringe, attach a clamp adapter and or a three-way valve between the sampling port and the syringe or pump inlet as shown in Figure 7.
- I have conducted dye tests by injecting concentrated uradine dye under a perforated 1.5-foot diameter disk through which the PP27 was inserted 3-12-inches into sediments. The goal of these tests was to determine whether or not surface water and dye is drawn into samples collected in near surface sediments (i.e., whether a cone of depression is formed). The results indicated that no surface water is drawn into samples even though sampling was conducted with a peristaltic pump at a rate of 600 ml/min.
- I usually couple my field investigations with GPS location of the sampling point. If conditions permit, a pin flag can be placed at the sampling point for later location by GPS. I usually use sub-

meter grade GPS for this surveying; GPS can then be used to relocate previously sampled point even if certain site physical characteristics have changed (eroding shorelines, etc.).

- Sampling by syringe has many advantages. This is my preferred field method due to its simplicity and versatility. It is useful to be able to collect several 50 ml syringes full of groundwater, store them on ice, and perform the sample transfer to a VOA vial, etc. under more controlled conditions. To transfer sample to a VOA vial, place the end of the transfer tube (Figure 8) to the bottom of the VOA vial. Dispense sample into the VOA vial and slowly withdraw the transfer tube from the vial maintaining the mouth of the transfer tube just below the sample surface. When the transfer tube is almost out of the vial, continue to dispense sample and leave an “anti-meniscus” of sample above the rim of the vial. Add several drops of HCl (which will displace a few drops of sample) and cap. If VOC samples are to be collected and stored temporarily in a syringe, I recommend using 100% polyethylene (“two piece”) syringes such as those made by Henke Sass Wolf GMBH (NormJect®, 50 ml) configured as shown in Figure 8. From personal experience I have found that small amounts of aromatic compounds (BTEX) can leach from the rubber parts of the rubber-tipped plunger found in common medical syringes. Rubber-tipped plunger syringes have less side-wall resistance and work much smoother than the 100% polyethylene syringes so I use medical syringes for “development” of the PP27. Standard medical syringes also work well for collecting samples for non-VOC analysis. I utilize handheld meters for pH, conductivity, redox, dissolved oxygen, etc. One can dispense sample from the syringe into these types of instruments for field measurements.
- The 50 ml, 100% polyethylene syringes mentioned above can be purchased directly from MHE, configured with tubing as was the example syringe included with your order, or customized to suit your individual needs. If you would to make your own, the syringes that I am currently using are purchased from National Scientific Company. The tubing is Tygon ¼-inch outer diameter and ⅛-inch inner diameter. Be sure to use some type of clamp at the tubing mouth to ensure a good seal at the sampler port.
- Headspace GC analysis of VOCs can be easily accomplished using 100% polyethylene syringes. Dispense all but 20 ml of the sampled groundwater from the syringe. Refill the syringe to the 40 ml mark with ambient air (and heat the syringe in a water bath if desired) as shown in Figure 9. Insert a GC syringe needle through the transfer tube into the syringe headspace and withdraw a sample for GC analysis.
- Occasionally a small amount of sand and silt is withdrawn into the syringe or pump sampling stream, even after proper development of the PP27. This may be due to the nature of the geologic formation. This fine material is probably already at equilibrium with the surrounding groundwater and should not influence analysis of VOCs in the groundwater sample. The sample can be transferred to its shipping container without this silt if the syringe is dispensed in a way that lets the solid material settle out in the syringe and not carry over to the shipping vial.
- The PP27 has been used very successfully for underwater investigations using SCUBA equipment and a series of 100% polyethylene syringes. Once again, GPS equipment was used for location of the position that the divers collected groundwater samples of contaminant plume expression in the lake. Underwater notes (temperature, depth, observations, etc.) can be written directly on the sample syringes if they are pre-prepared with a strip of Scotch Magic Transparent Tape applied down the syringe body and writing is done with a soft pencil.

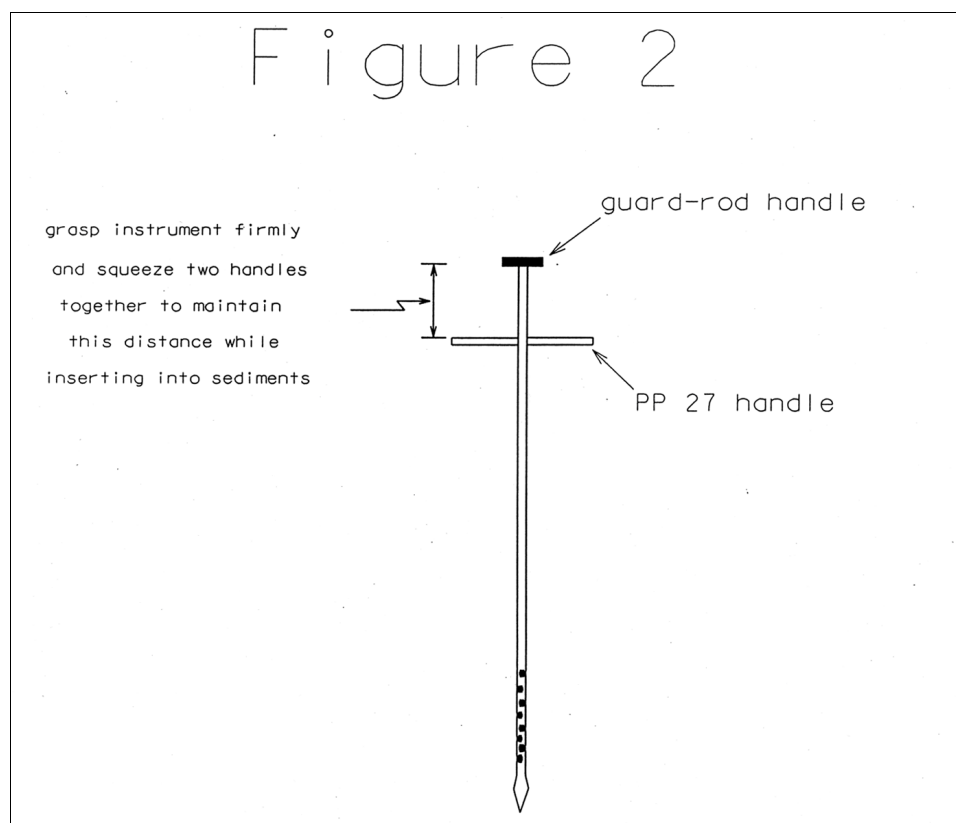
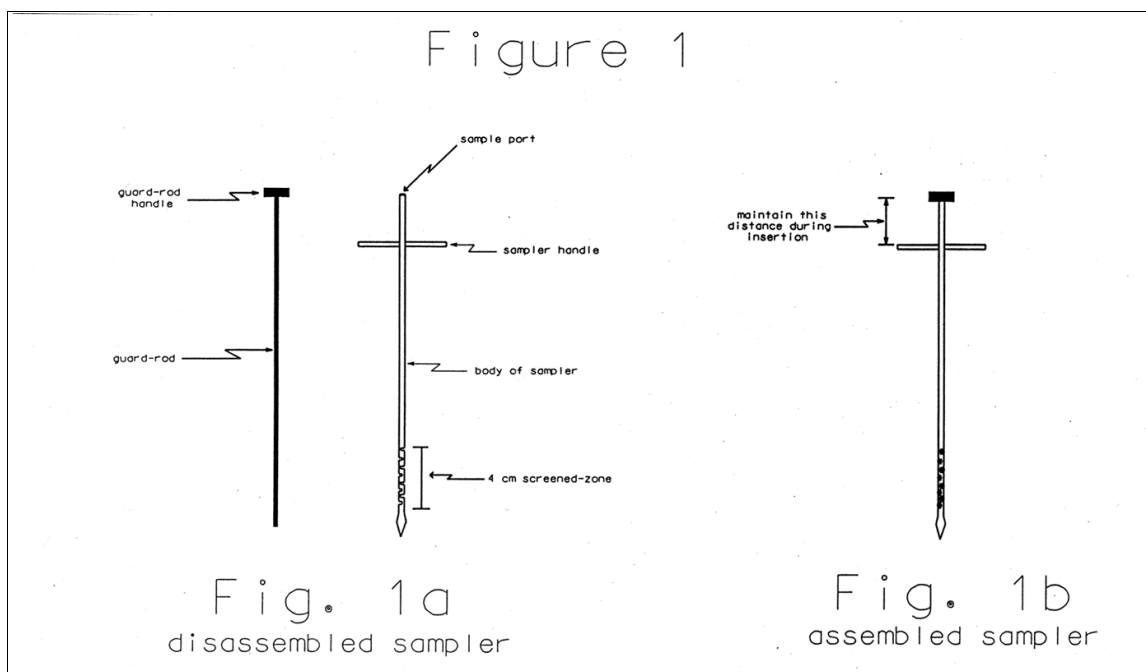
- The PP27 may be used to inject nutrients or dyes into the sediments for field trials of biologic or geochemical testing or tracing groundwater paths. Simply insert the PP27 to the desired depth and after the guard rod has been removed, connect a syringe or pump and slowly inject the desired fluid into the sediments, perhaps followed by a small amount of native groundwater to flush the instrument.
- These devices can be dedicated as semi-permanent underwater monitoring devices. If a PP-27 is inserted to the desired depth through a plate (such as the sampling platform mentioned earlier) that can lock the sampler at the correct insertion depth, a vinyl cap can be placed over the mouth of the sampler, and the sampler can be dedicated to that location so that future samples can be withdrawn when desired.
- It has been useful to carry several samplers in “quivers” made of 2-inch PVC tubing: one tube for 10-15 clean and assembled samplers, and one tube for used samplers and their separated guard rods. This arrangement protects both the investigators and the instruments.

I hope that users will find many useful and innovative uses for this device. If you have other helpful information, uses, and advice concerning these samplers, please write or e-mail suggestions to me for inclusion in future manual revisions. I will be forming a website soon, and posting much of my GSI research with links to as much GSI field research and related topics as I can find.

Thanks.

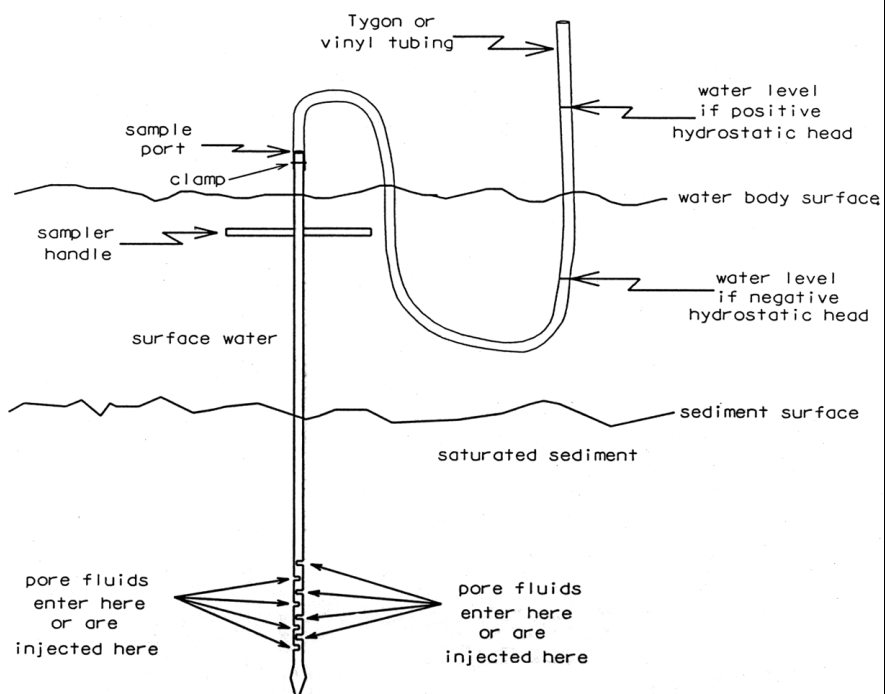
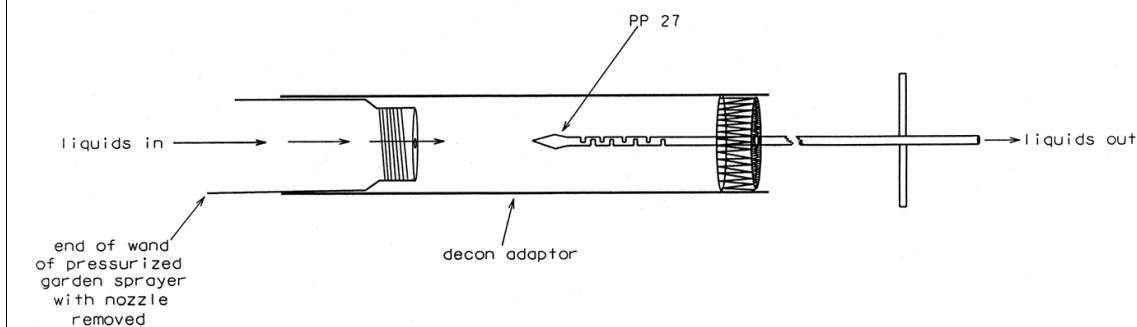
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# Figure 4

attachment of decon adaptor



# Figure 5

