**Groundwater-Surface Water Workshop - Summary of Discussion**
RTDF/Sediments Remediation Action Team
Fall Meeting, October 29, 2002

# 1.0 Introduction

## 1.1 Background

Current interest in groundwater (GW), surface water (SW), and sediment interaction in the transition zone is fostered by:

- Recent compliance requirements with RCRA Environmental Indicators and potentially future development of Ecological Indicators;
- Increased interest in the GW-SW transition zone as a potentially important ecological habitat;
- Increased interest in the interplay of groundwater and surface water for resource management and conservation;
- Unique considerations the interaction of GW-SW may present when evaluating remedial alternatives.

## 1.2 Purpose of this Document

The purpose of this document is to capture the valuable discussion that took place at the workshop and condense the ideas in an organized and usable format. A summary and the presentations made during this workshop may be found on the RTDF website (**http://www.rtdf.org/public/sediment/minutes/103002/summary.html**). The document highlights the issues upon which there was general agreement and issues for which consensus has not yet been reached. As a result of the on-going dialogue among the sub-team members and comments from the RTDF membership, additional information and useful tools are also included in this document.

## 1.3 Scope of the Document

The document attempts to address the GW-SW interaction on a number of technical levels. While addressing policy issues and providing technical guidance were not goals of the workshop or this document, RTDF reviewers raised two issues:

1. The Designated Use of the water body under the Clean Water Act (e.g. swimmable, fishable, or drinking water source) must be considered when designing an investigation.
2. The local input of a groundwater plume may not incrementally increase risk in a surface water system wherein ambient conditions are already above the water quality standards. Such scenarios are not uncommon and may call for a broader risk management strategy that addresses the inputs to the system on a watershed level. This would allow for a more efficient use of resources to control significant on-going sources to the watershed and restore water quality to its appropriate use.

## 1.4 Goals of the GW-SW Workshop:

- Goal 1. <u>Develop conceptual models that can be used for risk-based assessment and remediation</u>
  Although models were not developed during the workshop, there was considerable discussion of models and consensus was reached that development of a sound conceptual model is crucial to the evaluation of the system. **Attachment A** includes highlights of the CSM development discussion.

- Goal 2. <u>Identify pragmatic tiered approaches to evaluate impact</u>
  An approach was presented at the workshop and identified for further discussion by the subgroup. The results are included in **Attachment B** which presents "A Tiered Approach to Data Evaluation for Weight of Evidence Screening of Groundwater Impact on Surface Water & Sediments." A number of specific technologies for assessment of the transition zone were presented at the workshop.

- Goal 3. <u>Identify areas of consensus among disciplines</u>
  Several areas of consensus were identified during the workshop (see Section 2.1).

- Goal 4. <u>Identify remediation technologies</u>
  Discussion in this area was limited (see Section 2.1F).

An important premise of this workshop was that the effects of a contaminated groundwater plume on "clean" sediments or the effects of contaminated surface water quality on "clean" sediments were examined. In the case of contaminated sediments, other potential contaminant sources to the system must be considered.

Areas for further discussion were identified for follow-up by a smaller group of workshop participants (see Section 2.2.A-C).

## 1.5 Technical Needs

The following list of technical needs was derived by considering the background discussion, the workshop notes, how well each of the workshop goals was met, and issues from each of the expanded discussions.

- Ecological Characterization
  - Ecosystem Characterization: Basic ecology of the potential zone of impact (i.e., the GW-SW transition zone) and strength of ecological links (trophic and functional) within and outside this transitional ecosystems.
  - Indicators of Potential/Actual Effects: Method and supporting data on how to develop environmental/ecological indicators for the GW-SW ecosystem.
- Development of Remedial Alternatives
  - System dynamics and how they impact remedial action selection.
- Toolkit Development:
  - Other characterization approaches
  - Real-time screening methods for hydrologic and physiochemical properties
  - Monitoring tools to evaluate success

- Examples, case studies, and pilot studies on:
  - Evaluation approaches at large scales
  - How assessments have been tied to decision-making.
  - Conceptual models successfully applied for assessment and remediation decisions
  - Remedial technology (e.g., multiple stressors that involve the GW pathway as a source to or through sediments and the role of GW in mobilizing contaminants in sediments)

# 2.0 Technical Issues Identified during Workshop Discussions

## 2.1 Technical Issues with Consensus

A. Development of a sound conceptual model is key to the evaluation of the system. The conceptual model incorporates the important physical, biogeochemical, and biological (fauna and flora) parameters and integrates those parameters with consideration of the dynamic environment in space and time as well as the ultimate remedial goals. See Attachment A for highlights of the CSM development discussion.

B. In many cases, the GW-SW interaction is not an interface but rather a transition of the two waters.

C. Several conditions and processes affect the fate and transport of contaminants from groundwater aquifer to surface water. Groundwater discharge to a surface water body does not automatically equate to plume discharge to a surface water body. Some important parameters to consider include: plume geometry, hydrostratigraphy, physiochemical behavior of the constituents of concern, the hydraulics of the system, permeability of the sediments, sediment bedforms, geochemical environment, biotic and abiotic processes, and the "residence" time of contaminants within the transition zone.

D. Specific areas of groundwater or plume discharge are not always obvious. A number of both non-invasive and intrusive tools may be used to determine areas of discharge. Various tools were presented during the workshop (see workshop presentations by Pardue, Lorah, Chadwick, Adraiens, Conant and Greenberg).

E. Because of the potential spatial variability of the GW-SW transition environment (e.g. up-welling areas vs. down-welling areas, areas of no flow), the scale of investigation is important. Defining the question that one is trying to answer (problem formulation) and a developing a preliminary conceptual model aid in determining the scale of the investigation. For example, is the receptor (or in a regulatory context, the point of compliance):
   a) In the water column some distance from the groundwater seep,
   b) In the surface water column near the seep, or
   c) In the biologically active zone of the sediment?

F. Groundwater as a source of contamination may be an important consideration when evaluating and implementing remedial activities at a contaminated sediment site.

G. Groundwater that poses an unacceptable risk to surface water systems may be managed in a number of ways. Appropriate technologies include both conventional methods , e.g., upland groundwater containment and treatment and innovative technologies, e.g., enhanced bioremediation of groundwater, constructed wetlands, and amended (treatment) caps at the seep or discharge areas (designed to attenuate or prevent breakthrough) were discussed.

## 2.2 Technical Issues Needing Further Discussion

A. How to approach evaluation of a site where no apparent impact is evident and the only data are site groundwater plume concentrations and flow direction (see Section 3.1).

B. How to approach evaluation of groundwater contamination input to an urban river where multiple inputs to the system are likely (e.g., outfalls, historical spills, etc.) and how to readily assess the incremental risk presented by groundwater (see Section 3.2).

C. How to find and assess groundwater discharge areas of concern in large tidal and estuarine settings where the scale of the sediment issues may occur on a watershed scale (see Section 3.3).

# 3.0 Expanded Discussion of Selected Technical Issues

## 3.1 Evaluation of a Site Approaching from Upland to the Surface Water

### 3.1.1 The Problem

Visual evidence of seeps that contain non-aqueous phase liquid (NAPL) or seeps that are obviously stressing the environment facilitates a targeted investigation approach. However, how does one approach evaluation of a site where no apparent impact is evident and the only data are site groundwater plume concentrations and flow direction?

### 3.1.2 Discussion

In cases where there is no evidence of impact, a preliminary CSM should be developed using available information. Simple analytical models or more complex numeric models (see workshop presentation by Mohsen) may be used to help frame the magnitude of the potential risk. Using a weight of evidence approach to determine whether more investigation and fieldwork are needed was discussed at the workshop. It is important that the evaluation team understand what decision needs to be made and how their information will be used in the decision process. The following approach was offered (see workshop presentation by Grosso).

**First Level Screening for Evaluation of Groundwater Impact on Surface Water**:

1. Formulate the problem and identify the management decisions to be made.
2. Determine constituents of potential concern (COPCs) by selecting appropriate screening criteria and comparing plume values. Appropriate screening criteria may be based on ecological or human health receptors depending upon the designated use of the surface water system. Review fate and transport characteristics of COPCs within groundwater, porewater, sediments, and surface water.
3. Determine whether these COPCs are expected to accumulate in sediments. This step helps to determine the sampling medium that may be relevant in future phases of evaluation.
4. Evaluate whether these COPCs present a problem in the system on a local or regional scale (apart from the local groundwater plume being evaluated).
5. Determine whether there is a sensitive receptor(s) or habitat(s) in the area (habitat mapping), besides the receptor identified in the problem formulation.
6. Estimate the concentration of relevant COPCs and estimate average surface water concentration based on realistic evaluation of the hydraulics of the system.
7. Compare resulting average surface water constituent concentrations attributable to GW discharge to surface water screening criteria for an indication of potential significance of GW plume discharge to surface water. Determine whether the "size" of the potential impact would be significant in degrading the ecosystem.
8. Compare resulting average surface water constituent concentrations attributable to GW discharge to ambient background.
9. Compile information and integrate into the conceptual model. If the weight of evidence indicates additional evaluation is warranted - plan investigation strategy.

See Attachment B for more details on this procedure. The way in which the lines of evidence are weighted would be determined on a site-by-site basis. For instance, concern over a sensitive habitat may carry more weight than the transport and fate characteristics of a particular COPC. See Attachment C for a summary of physiochemical properties that affect sorption of inorganics to sediment.

## 3.2 Assessing Groundwater Impact in Settings with Potentially Multiple Sources

### 3.2.1 The Problem

How does one approach evaluation of groundwater contamination input to an urban or multi-use river where multiple potential sources to the system are likely (e.g. outfalls, historical spills, agricultural runoff, etc.)? How can one readily assess the incremental risk presented by groundwater?

### 3.2.2 Discussion

Although this is a complex problem, there are logical ways in which to approach assessment of an urban river. Whether or not the incremental risk that groundwater poses can be readily assessed depends upon the complexity of the system and what is already known about it. An important consideration is that groundwater cannot be assessed on its own in a system; it must be assessed as one of many potential ongoing sources to a surface water system. In addition, the use designation of the water body will help to define whether the groundwater plume poses a risk to the resource.

*Principles for Managing Contaminated Sediment Risks at Hazardous Waste Sites,* issued by USEPA (OSWER Directive 9285.6-08) in February 2002, provides valuable guidance for systematically evaluating and addressing contaminated sediment sites that may include other significant sources. Specific technical principles that apply to this GW-SW problem are:

- *Develop and refine a CSM:* A conceptual model should identify all known and suspected sources of contamination, the types of contaminants and affected media, existing and potential exposure pathways, and the known or potential human and ecological receptors that may be threatened. (Principle no. 4)
- *Control sources early:* As early as possible, all direct and indirect continuing sources of significant contamination to sediments (surface water system) should be identified. Examples of sources include discharges from industries or sewage treatment plants, spills, precipitation runoff, erosion of contaminated soil from stream banks or adjacent land, contaminated groundwater and NAPL contributions, discharges from storm water and combined sewer overflows, and upstream contributions and air deposition. These sources should be prioritized in terms of their relative contribution to site risks. Continuing sources should be assessed in terms of which ones can be controlled and by what mechanisms. (Principle no. 1)
- *Use an iterative approach in a risk-based framework*. The use of an iterative approach is encouraged, especially at complex contaminated sites. An iterative approach is defined broadly to include approaches that incorporate testing of hypotheses and conclusions and foster re-evaluation of site assumptions as new information is gathered. Each iteration might provide additional certainty and information to support further risk-management decisions, or it might demonstrate the need for a course correction. (Principle no. 5)

- *Carefully evaluate the assumptions and uncertainties associated with site characterization data and site models.* Assumptions made in constructing conceptual models and numeric models should be documented and revisited if new data do not support these assumptions (Principle no. 6)
- *Select site-specific risk management approaches that will achieve risk-based goals* (Principle no. 7)
- *Ensure that sediment (system) cleanup levels are clearly tied to risk management goals* (Principle no. 8)

The following approach applies some of these principles to the evaluation of groundwater impact on a surface water system. There may be a series of phases that are necessary to resolve the question.

1. Identify the management decisions that may be made.
2. Identify the risk assessment endpoint for your site with consideration of the designated use of the water body and develop a CSM.
3. Identify and prioritize known or suspected sources in the watershed or near your site. Existing data and system models (numeric or conceptual) will help. Developing a mass balance is also important for estimating concentrations of COPCs in surface water. Although often difficult to construct mass balance estimates are needed to help understand potential exposures and relative risk contributions .
    1. Control identified significant sources that can be readily addressed in a straightforward manner.
    2. Choose appropriate parameters and monitor the response of the system.
    3. If the system does not respond as expected within the time frame expected, incorporate new data into the CSM and refine understanding of potential sources.
    4. Conduct additional investigation as necessary and incorporate into the conceptual understanding of the system.

## 3.3 Some Tools and Technical Approaches in Large Tidally Influenced Waterways

### 3.3.1 The Problem

Many useful techniques were presented for mapping groundwater discharge zones and assessment techniques in small rivers or marine coves. Most of the techniques shown (peepers, mini-peizometers), however have not yet been established for application in large tidally influenced waterways. How does one find and assess groundwater discharge areas in large tidal and estuarine settings where sediment issues may occur on a watershed scale?

### 3.3.2 Discussion

It is recommended that the CSM be developed  to incorporate and integrate existing data. How to integrate information across large scales will be tied very closely to decision-making process for the waterbody as a whole, as well as specific sites with overlapping issues. For most, it is a matter of trade-offs. The risk consequences of missing a hotspot and the consequences of over-sampling (and possibly still missing a hotspot) should be analyzed individually and then compared.

In general, first areas of groundwater discharge are identified. Then, flux of the contaminants (at the anticipated location of the plume) may be measured. While the major rivers of the world are reasonably well gauged and analyzed, evaluating the extent and chemical mass flux of freshwater discharge, and submarine groundwater discharge (SGD) remains difficult due to the size of discharge area under consideration, and the complexity of the hydrologic system.

A comparison of various SGD assessment methods in different hydrogeologic environments was conducted by a working group supported by the Scientific Committee on Oceanic Research (SCOR), the International Geosphere-Biosphere Program and UNESCO's Intergovernmental Oceanographic Commission (IOC). The first experiment was conducted on the coastline of the northeast Gulf of Mexico (20,000 $m^2$). The site was chosen based on information on seepage along the coast out to a few hundred meters offshore.

The quantitative assessment was based on modeling (e.g. radon), direct physical measurement (e.g., seepage flux meters, piezometers), and tracer techniques (e.g., radon, radium). Lessons learned are shown below.

1. Seepage meters ("Lee-type"):
   - Meters worked well where flux rates are relatively high (> 2cm/day; 1.6-2.5 $m^3$/min).
   - Measurement improved dramatically when automated meters using heat pulse or acoustic Doppler techniques were used instead of manual collector bags.
   - Highest flux rates occurred during transition from highest to lowest tide.
   - Agreement between manual and automated meters should be evaluated using geochemical tracers.
   - Meters require significantly more work than tracer studies.

2. Radon 222:
   - Radon 222 is a good natural tracer, behaves conservatively, and is easy to measure.
   - Continuous radon measurement was integrated over 1-hour intervals.
   - Corrections were required for atmospheric and mixing (difficult to estimate) losses.
   - There was good agreement with automated seepage measurements (1.7-2.5 $m^3$/min).

3. Radium Isotopes (long-lived: 226 and 228; short-lived: 223-223):
   - Long-lived isotopes (226 and 228) from SGD are the main source in coastal waters.
   - Short-lived (half-life of 11 days) isotopes (223 and 223) can be used to determine mixing rates in SGD.
   - The combination of all four isotopes provides the flux of radium to the open ocean.
   - The average seepage flux estimated in the 100-m wide study domain was 1.5 $m^3$/min.
   - Since sharp gradient of $^{223}Ra$ exists within first 3 km off shore, the spatial density of the sampling was adjusted accordingly.

4. Hydrogeologic modeling:
   - Modeling results indicate fluxes 8-10 fold lower than those estimated from the measurements.
   - The discrepancy was caused by simplifying model assumptions (e.g. no tidal pumping and wave action, focus on onshore-to-offshore hydraulic gradient and density-dependent recirculation within the salt-water wedge).

<u>Note</u>: Other large scale SGD measurements have been performed in the southeastern United States, based on radium tracers.

For more detail on these techniques the reader is referred to the following:

Burnett, et. al 2002. Assessing methodologies for measuring groundwater discharge to the ocean. EOS, Transactions, American Geophysical Union, 83 (11), 117-122.

Moore, W.S. 1996. Large groundwater inputs to coastal waters revealed by 226Ra enrichments. Nature 380: 612-614.

Burnett, W.C., G. Kim , and D. Lane-Smith. 2001. A continuous radon monitor for use in coastal ocean waters. J. Radioanal. Nucl. Chem. 249: 167-172

Cable, J.E., W.C. Burnett, and J.P. Chanton. 1997. Magnitude and variations of groundwater seepage into shallow waters of the Gulf of Mexico. Biogeochem. 38: 189-205.

The following individuals contributed to the preparation of this document:
Peter Adriaens, University of Michigan
Bruce Duncan, USEPA Region 10
Robert Ford, USEPA Robert S. Kerr Environmental Research Center
Nancy Grosso, DuPont
Bob Maxey, USEPA Region 3
Farukh Mohsen, Gannett Fleming
Ralph Stahl, DuPont
Bernie Zavala, USEPA Region 10

Comments were provided by the RTDF membership

**Attachment A**

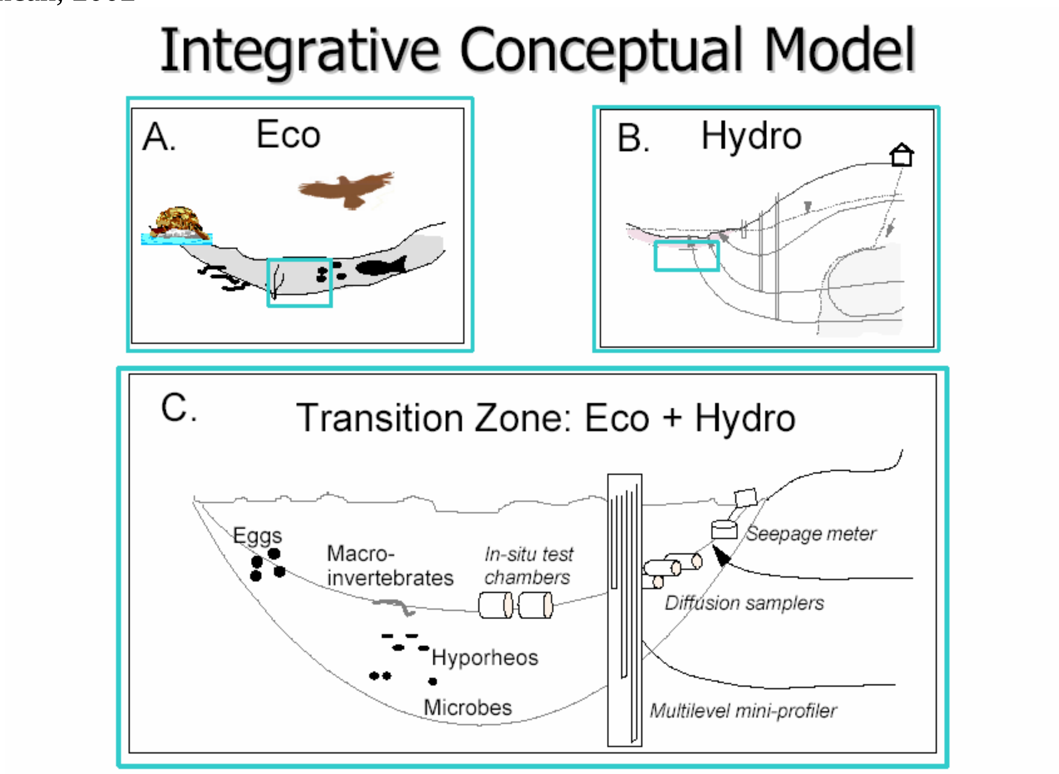
## Highlights of the CSM Development Discussion

Development of a sound CSM is crucial to the evaluation of a surface water system. The conceptual model incorporates the important physical, biogeochemical, and biological (fauna and flora) parameters and integrates those parameters with consideration of the dynamic environment in space and time. A process for developing a CSM is to collect and integrate knowledge of physical, chemical and biological processes, and then to superimpose and integrate contaminant behavior. A CSM is developed with a view toward the remedial actions that may be taken. A CSM helps to:

- Define the resource that is being protected
- Determine if an unacceptable risk is present
- Determine what can be done to reduce risk

A model for integrating the ecological, hydrologic, and hydrogeologic elements of the CSM where benthics and transition zone processes are of interest was presented by Duncan.

Duncan, 2002




As a start to developing the CSM, a generic conceptual understanding of the physical setting or geologic landscape (see workshop presentation by Conant) may be used. Physical settings that may be used as a basis for the CSM were presented at the workshop. These included stream/rivers (Pardue, Conant, and Greenberg); tidal rivers (Mohsen); high-energy lakes (Adraiens), marine setting (Chadwick), tidal freshwater wetlands (Lorah).

CSM Elements:

- Properties of the groundwater environment, e.g., nature and rate of groundwater flow.

- Factors that influence rates of groundwater discharge to surface water features, e.g., tidal effects, seasonal variation, variation due to rainfall events, sediment type in discharge zone.
- Subset of groundwater constituents that should be considered COPCs in surface water.
- Contaminant concentrations of COPCs in groundwater.
- Factors that affect contaminant discharge mass and concentration, e.g., biological and physiochemical attenuation effects in the discharge zone.
- Properties of the surface water body and temporal variations, e.g., size variable flow rate and stage.
- Properties of the sediment, e.g., nature of the sediment (sand, silt, clay), organic carbon content, redox potential characterized by iron or sulfur species.
- Receptor characteristics, e.g., use classification, habitats, and contaminant sensitivities.
- Physical, chemical, and eco-toxicological properties of the COPCs.
- Other current and historical sources of surface water and sediment contamination.
- Comparison of surface water and sediment sample results with available and appropriate surface water and sediment criteria.
- Observed effects on receptors, such as from bioassays, benthic surveys, or other site-specific ecological evaluations.

In many cases, much can be gleaned from the chemistry of the groundwater plume.

- Hydrophobic constituents are not likely to be seen dissolved in groundwater at significant concentrations. As a result, they would not be expected to be carried and discharged to the surface water body. For example:
  - Volatile organic compounds tend to occur at low concentrations.
  - PCBs are rare in groundwater. PAHs are also rare in groundwater, unless there is a co-solvency effect from other compounds.
- NAPL behavior, specifically the way in which the contamination migrates, should be considered differently than dissolved plume behavior.
- Metals behave differently depending upon the metal and the physiochemical environment. Some metals are not as common in a dissolved form as others . For example, lead is often associated with particulates in groundwater rather than with the dissolved phase.

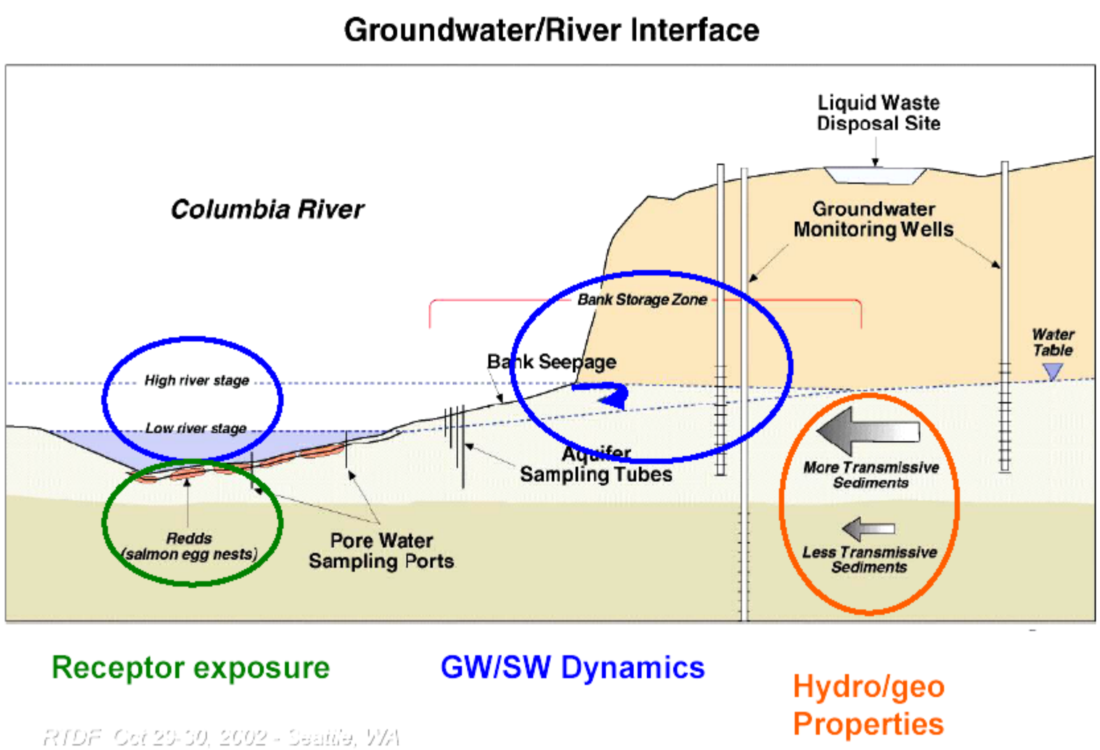
All aspects of the CSM (physical, biogeochemical, and biological) are interdependent and affect the system characteristics. It is important to include the interaction of the various environmental compartments and to consider the spatial and temporal variations (daily/ seasonally, areas of deposition and ecology) when collecting and evaluating field data. For shallow groundwater systems, variations in precipitation rates can significantly impact groundwater hydraulic flux and must be considered when measuring flux. In addition, consider the physiochemical and biogeochemical processes as well as possible contaminant transformation/degradation as a result of these processes (see workshop presentations by Chadwick, Conant and Lorah).

To help focus an investigation and evaluation of the data, the problem must be formulated early in the CSM development process. Some fundamental questions may be posed to help clarify the objective of the activities that will be conducted at a site.

To help formulate the problem consider the following:

1. Is the habitat unique, e.g. Hanford Site and salmon spawning grounds? Prepare habitat map and prioritize areas (see figure below).
2. Are the critical receptors present at only specific times/seasons of the year?
3. Is the contaminant persistent, bioaccumulative, and toxic (PBT)?
4. What are other potential sources besides groundwater?
5. What is the incremental risk that the groundwater plume adds to the system?
6. Where will resources and time best be spent to improve the quality of the system?
7. What is the risk assessment endpoint? Is the concern human health, ecological health, or both? If the concern is ecological, is it a community, a population, or an individual?
8. What is the appropriate scale for evaluation (meter scale, reach, or watershed)? What are you willing to "miss"? Is the initial scale of the investigation appropriate for the receptors of concern?

These are examples of considerations that arose during the workshop discussion, but there are doubtless many others. The exercise of formulating the problem for the site early in the process will help to streamline the CSM development. Below is an example where salmon egg nests are the receptors of concern (workshop presentation by Duncan).



### *Detailed Data Evaluation Steps for Surface Water*

The following evaluation steps are intended to help guide evaluation of potential impacts of current groundwater discharges on surface water quality. They present a step-wise, weight-of-evidence approach to focus on groundwater hydrogeology, surface water hydrology, and physiochemical attributes of the constituents of concern. The usefulness of this approach allows evaluation of potential surface water impacts of current groundwater discharges using existing or readily available hydrogeological and hydrologic information. As noted previously, it is important for the evaluation team to understand the decision being made and how their information will be used in that decision.

1. **Determine which constituents in the discharging groundwater are COPCs that should be carried forward for further evaluation based on their physiochemical properties.**
   - Consider screening out constituents whose average discharge concentrations are below relevant surface water comparison criteria (e.g., Ambient Water Quality Criteria, MCLs for drinking water supplies). Due to mixing that occurs in surface water and the mobility of surface water receptors, average discharge concentrations should generally be considered unless specific characteristics of the receiving water suggest otherwise. The weighting of this factor should be based on the quality of the data.

   - Consider the environmental fate of the constituents—particularly Henry's Law constant (propensity of the constituent to partition from water to air) and the soil/water partition coefficient, $K_{d,}$ (propensity of the constituent to sorb to sediment)—to evaluate whether the constituent is likely to be present in surface water (vs. air or sediment). Constituents that are not likely to be present or to persist in surface water can be significantly weighted and screened out from further evaluation for surface water impacts. Note that a similar evaluation for their potential sediment impacts should be made (see p.19). These evaluations should be made based on readily available data such as published or typical values. These parameters may also be estimated using spreadsheet models, such as the fugacity model developed by Utah State University, which is accessible at http://www.engineering.usu.edu/uwrl/www/faculty/fugacity/fugacity.html. Data for use in evaluations include:
     - Henry's Law constant (H) — an indication of the propensity of a chemical to volatilize from the aqueous state. If H is $<10^{-7}$ atm-m$^3$/mol, the constituent will not volatilize rapidly and would be expected to persist in water. If H is $>10^{-3}$ atm-m$^3$/mol, the constituent will tend to volatilize rapidly from the aqueous state and would not be expected to persist in the water (Montgomery, 1996; Dragun, 1988).
     - The propensity for constituents to preferentially partition to sediments can be evaluated based upon partitioning coefficients, including their soil/water

partition coefficient ($K_d$), octanol-water partitioning coefficient ($K_{ow}$), organic carbon-water partitioning coefficient ($K_{oc}$) and the fraction of organic carbon in the sediments ($f_{oc}$).

- For organics, $K_d = K_{oc}$ x $f_{oc.}$ In general, compounds with $K_d$ >10 are considered immobile, typically sorb to sediment, and would not be expected to persist in surface water. Constituents with $K_d$ <1generally are mobile in water and would not be expected to sorb to sediment (Montgomery, 1996; Dragun, 1988).
- The nature of sediments in the discharge zone is important for determining the likelihood of a constituent accumulating in sediments. Primarily granular sediments or sediments with $f_{oc} <$ 0.2% (DiToro *et al*, 1991) generally do not accumulate constituents, but finer and more organic sediments are more likely to accumulate constituents. Typical values of $f_{oc}$ for common sediments are available in the literature. Constituents having a large $K_{oc}$ may still appreciably sorb to sediments with low organic content, however. Therefore, $K_d$ should be used to assess the tendency for a constituent to accumulate in sediments. Another source of information to guide decisions for sediment parameter measurements can be found at: http://www.epa.gov/rpdweb00/cleanup/partition.htm
- Constituents with log10 $K_{oc}$ or log10 $K_{ow}$ < 3 are generally unlikely to accumulate in sediments and would be expected to enter the water column where they may or may not volatilize to the atmosphere depending upon their Henry's Law constant.
- Where more detailed evaluations of sediment metal accumulation and potential bioavailability are warranted, the acid volatile sulfide-simultaneously extracted metal (AVS-SEM) approach can provide a measure of bioavailability for Cd, Pb, Ni, Zn and Ag. The approach is not currently applicable to other metals. While AVS-SEM approach may not always be predictive of the presence of toxicity due to these metals, it is generally predictive of the lack of toxicity due to them. In addition, the AVS content of sediments may be used to evaluate the mobility of metals within sediments. Other factors that influence form and fate of metals in the environment, such as pH, temperature and $K_d$, should also be taken into account.
- Other mechanisms that may affect the fate of constituents in the discharge zone or surface water environment are co-solvency effects, biodegradation (biological attenuation), hydrolysis (reaction with water), and photodegradation (reaction with light). Information on these qualities of a constituent can often be found in common reference sources. (Howard *et al*, 1991.)

- Use of sorption criteria for screening is an attempt to account for the retardation of COPC movement through the sediment. The impact of retardation will vary depending on characteristics of the sediment such as depth and organic carbon content. In some cases, constituents with log $K_{oc}$ < 3 will be so retarded that they cannot reach the biologically active surface layer of the sediment or the water column, which could seem contrary to the discussion above. Therefore, estimation of whether or not penetration of sediments has occurred is important as a screening criterion. If the COPC has not penetrated the sediment, at a screening level one can assume groundwater discharge does not impact surface water. This assumption may need to be revisited if more detailed evaluation suggests groundwater contribution of this constituent is significant.

These evaluations should be used to develop enough evidence to determine if COPCs can be screened out so further evaluation can be focused on the remaining COPCs.

2. **Once COPCs have been determined, develop an estimate of the constituent mass flux to the surface water body.** Generally, this involves a simple combination of the groundwater mass flux and average plume concentrations at the point of discharge with consideration of any significant attenuation mechanisms. If warranted, more detailed evaluations can be performed via sensitivity analysis and/or computer calculations and modeling, assuming that sufficient data exist. It may be important in some cases to estimate both nearfield (at the plume discharge point(s)) and farfield concentrations (downstream) particularly when the constituent is known to be bioaccumulative or readily transported on particulates in the water column.

   - Average concentration of COPCs in the plume at the point of discharge should be determined by weight-averaging concentrations over the plume at the discharge area (assuming that there are enough data). If data are not sufficient to determine flux accurately, the next phase of the investigation can be focused to collect the required information. In addition, sensitivity analyses and watershed mass balance approaches can be used to determine the sensitivity of the analysis to these parameters.
     - ➢ Where COPC attenuation mechanisms (e.g. microbial attenuation in the discharge zone) are expected to be significant, they should be factored into the mass flux estimate.
       - — In estimating groundwater volumetric flux to the surface water body, first evaluations should be based upon Darcy's equation (Q=KiA) where K= hydraulic conductivity, A = the discharge area (cross-section of the contaminant plume at the discharge point), and i = the hydraulic gradient at the point of discharge. If necessary, more detailed evaluations can be made through sensitivity analysis and/or computer modeling.
     - ➢ Hydraulic factors that can affect groundwater volumetric and/or constituent mass flux, such as tidal variations in the receiving water, should also be considered. In tidal receiving waters groundwater discharge varies with tidal cycle. Tidal fluctuations have an effect of flushing the aquifer, thereby reducing concentrations entering the surface water body as compared to similar conditions in a non-tidally influenced system (Yim and Mohsen, 1992). However, this enhanced mixing associated with near-shore tidal action (termed "tidal pumping") may cause the constituent to break through into the surface water system earlier than in a non-tidal system. The degree of mixing is a function of the amplitude and period of the tides and the aquifer storativity and hydraulic conductivity (Johnston, 1998). Therefore, it should be examined on a site-specific basis.

       Shallow groundwater systems can fluctuate significantly with variations in precipitation events and rates. This variation may be significant for aquifers and sediments with high hydraulic conductivity.

3. **Evaluate the resulting effect of COPC mass flux on surface water concentrations.** This involves calculating concentrations after mixing with the surface water. Unless specific aspects of the surface water body suggest otherwise, the contaminant mass flux may be calculated to mix with a readily available flow estimate within a calculated mixing zone for the water body. Mixing zones should be approximated on a site-specific basis. Some sites' hydraulics may justify using the entire width of a surface water body, while at other sites only a small fraction of the fresh water flow in a surface water body may be needed. In some cases a groundwater plume will hug the bank for a distance downstream of the discharge area. A site-specific approach is recommended when determining the use and size of a mixing zone.

    - Appropriate surface water flow rates are generally available from US Geological Survey gauging stations.
        - For acute effects (ecological and, if appropriate, human water use) the appropriate flow estimate is generally the 7Q10 value, an estimated 7-day low-flow period anticipated to occur in a 10-year period.
        - For chronic effects (such as carcinogenic effects), a long-term average flow represented by the harmonic mean is most appropriate.
    - Tidal effects in a surface water body should be taken into account where they occur. Tidal fluctuations can result in significant attenuation of COPCs in the bank storage area. Tidal effects in surface water can be accounted for by adding a dispersion term (through application of a simple mixing model) to the calculation of water column concentrations . However, effects on subsurface chemical processes should also be considered for tidal water bodies. The chemical makeup of seawater differs from groundwater— e.g., ionic strength, concentrations of dissolved organic matter (DOM) and colloidal matter, redox potential, pH, and buffering capacity are higher. As a result, chemical fate processes of a constituent in groundwater may be affected. There processes include chemical equilibrium and partitioning, complexation and precipitation (especially for metals), and reaction kinetics. Note that the natural chemistry of groundwater may be altered by the presence of a contaminant plume.

4. **Compare the estimated surface water constituent concentrations attributable to groundwater discharges to relevant surface water screening levels to evaluate their potential significance, i.e., which should be viewed in light of background water quality.**

    - There are various sources of appropriate screening values, including:
        - EPA's National Ambient Water Quality Criteria (NAWQC),
        - Maximum Contaminant Levels (MCLs), where the surface water is a drinking water source,
        - State ambient water quality criteria,
        - Water quality-based effluent limits (WQBELs) in a facility's NPDES permit, and
        - Toxicological values (e.g., derived from EC50, LC50).

5. **Consider potential background sources of contaminant loading and their relative effects on surface water quality to help determine whether potential groundwater discharges are significant.** This step is meant to put the current groundwater discharge in context with other discharges both past and current.

- Potential loading sources include:
  - Current upstream (and, in tidal waters, downstream) point source loadings such as National Pollutant Discharge Elimination System (NPDES) discharges.
  - Current upstream (and downstream in tidal waters) non-point source loadings, e.g., storm water runoff, combined sewer outfalls, agricultural runoff, atmospheric deposition, etc.
  - Historical use and impact to the surface water body (i.e., history of sediment contamination).

***Summary***

These steps should allow the project team to use readily available data to:

1. Narrow the focus of the evaluation to constituents most likely to present potential impacts.
2. Estimate COPC mass flux into a surface water body.
3. Estimate COPC concentrations in the surface water body.
4. Evaluate the significance of those concentrations.
5. Determine whether the surface water impact of discharging groundwater is likely to be discernible from “background” impacts and the significance relative to other discharges.

If this initial evaluation suggests that current groundwater discharges may be causing measurable surface water impacts above background and above applicable screening criteria, consider more detailed evaluation .

*Data Evaluation Steps for Sediments*

The following steps are intended to guide evaluation of the potential impact of current groundwater discharges on the sediment ecosystem in the receiving water. They begin with a weight-of-evidence screening process to determine which constituents may be screened out as potential concerns for sediment-based ecological receptors. This allows additional evaluations to be focused on COPCs. This evaluation is intended to be performed with existing or readily available data and to guide any further evaluations or data collection. It should be noted that evaluation of the sources and significance of sediment contamination is a rapidly developing field. As with surface water, potential impacts on the sediment ecosystem need to be considered in relation to background sediment conditions and impacts.

1. **Determine which constituents in the discharging groundwater are COPCs based on the eco-toxicity, and evaluate the environmental fate of constituents present in the discharging groundwater.**

    - There is a range of aquatic/sediment ecological toxicity screening criteria, including the National Ambient Water Quality Criteria and Sediment Guidelines, state water quality criteria, and toxicity benchmarks.
        - There are relatively few sediment quality guidelines available at this time. These values should be used with caution to ensure they are appropriate to the nature of the sediment ecosystem under consideration.
        - Constituents with relatively low eco-toxicity (based on both aquatic and sediment characterizations) can be weighted heavily and screened out from further consideration. Constituents present in discharging groundwater at concentrations below relevant surface water criteria generally can be screened out unless specific characteristics (e.g. significant accumulation in sediment) suggest further evaluation. Generally, average groundwater concentrations should be evaluated unless specific factors of the site suggest use of some other concentration value . It is important to review other information on COPCs for their ability to bioaccumulate or persist in the environment. Even COPCs considered to have high acute toxicity may not pose a significant hazard if they also have a short half-life in the environment (short = 5 days or less) or are readily biodegrade.

    - The environmental fate of constituents in discharging groundwater should be evaluated to determine whether the constituent is likely to present the potential for significant impacts on the sediment ecosystem.
        - Environmental fate can be evaluated based on factors such as Henry's Law constant, biodegradation potential, tendency to hydrolyze, photodegradation potential, and effects of oxidation and reduction. Information on these factors is available in common references.
        - Henry’s Law constant (H) is an indication of the propensity of a chemical to volatilize from the aqueous state. If H $<10^{-7}$ atm-m$^3$/mol, a constituent will not tend to volatilize rapidly and may persist in the aqueous environment or accumulate in sediments. If H $>10^{-3}$ atm-m$^3$/mol, the constituent will tend to

volatilize rapidly from the aqueous state and is unlikely to persist in water or sediment (Montgomery, 1996; Dragun,1988).

- ➢ Other mechanisms that may affect the fate of constituents are biodegradation (biological attenuation), hydrolysis (reaction with water), photodegradation (reaction with light), and the affects of oxidation and reduction. The rate at which these reactions occur can sometimes be found in literature or estimated. (Howard *et al*, 1991).
- ➢ Consider screening out constituents that are unlikely to persist in the sediment environment (e.g. highly volatile or highly biodegradable materials).

2. Evaluate the propensity of a constituent to accumulate in or migrate through sediments as well as to partition from sediments to sediment pore water, where it can become bioavailable.
   - The propensity of a constituent to accumulate in and migrate through sediment can be characterized by partitioning coefficients, including the soil/water partitioning coefficient ($K_d$), octanol-water partitioning coefficient ($K_{ow}$) and organic carbon-water partitioning coefficient ($K_{oc}$). These coefficients are available for many constituents in common references.
     - ➢ For organics, $K_d = K_{oc}$ multiplied by the fraction organic carbon in sediment, or $f_{oc.}$ If $K_d$ >10, the constituent is generally immobile and will tend to sorb to sediment. If $K_d$ <1, the constituent is generally mobile in water and will tend not to sorb to sediment.
     - ➢ Constituents with log10 $K_{oc}$ or log10 $K_{ow}$ <3 are generally considered unlikely to accumulate in sediments.
     - ➢ The nature of sediments in the discharge zone is important for determining the likelihood of a constituent accumulating in sediments. Primarily granular sediments or sediments with $f_{oc}$ <0.2% (Di Toro *et al*, 1991.) generally do not accumulate constituents, while finer and more organic sediments are more likely to accumulate constituents. Typical values of $f_{oc}$ for common sediments are available in the literature. Constituents having a large $K_{oc}$ may still appreciably sorb to sediments with low organic content, however. Consequently, $K_d$ should be used to assess the tendency for a constituent to accumulate in sediments.
     - ➢ Similar to *Step 1* of the surface water evaluation, an analysis should be performed to determine whether the COPCs might have penetrated the sediments into the biologically active zone.
     - ➢ Constituents that appear unlikely to have penetrated the sediments or those that are unlikely to accumulate in sediment <u>and</u> are not expected to present significant aqueous toxicity in the sediment ecosystem should be screened out from further evaluation.
     - ➢ Where more detailed evaluations of sediment metal accumulation and potential bioavailability are warranted, the acid volatile sulfide-simultaneously extracted metal (AVS-SEM) approach can provide a measure of bioavailability for Cd, Pb, Ni, Zn and Ag. The approach is not currently applicable to other metals. While AVS-SEM approach may not always be predictive of the presence of toxicity due to these metals, it is generally predictive of the lack of toxicity due to them. In addition, the AVS content of sediments may be used to evaluate the mobility of metals within sediments.

Other factors that influence form and fate of metals in the environment, such as pH, temperature and $K_d$, should also be taken into account.

3. **Evaluate the sensitivity of potential ecological receptors/habitats in the surface water/sediment environment to constituents that have been determined to be COPCs.**
   - This should include evaluating the various natural and manmade stressors affecting that environment, and whether the potential stress of COPCs in discharging groundwater is likely to be discernible against this background. Evaluations should focus on receptor populations rather than individual receptors unless threatened or endangered species are affected.
     - The sensitivity of the receiving water ecosystem should be considered. A small, relatively pristine upland stream or an undisturbed wetland, for example, would be expected to be relatively sensitive and, as a result, the impacts of groundwater discharge may be significant. A historically industrialized river, or a river subjected to periodic dredging is likely to be less sensitive, and effects of groundwater discharge would be less significant.
     - Natural factors potentially affecting receptor species richness and diversity also should be considered to understand the likely sources of any observed impacts. Numerous natural factors, many of which vary over time, have potentially significant impacts. These include the availability of prey species/food sources, sediment type (e.g., sandy vs. silty), turbidity, water temperature, oxygen content and other water chemistry factors, sediment dynamics, and salinity.

4. **Evaluate the potential for significant effects, taking into account the ability of the materials to accumulate in sediments or up the food chain and the sensitivity of the habitat.** Biological effect concentrations in sediments may be estimated for non-polar organic chemicals and other divalent metals based on equilibrium partitioning theory, knowledge of the water-only effects concentrations for the chemicals of concern, and concentrations of important binding phases in sediments (e.g., AVS-SEM, organic carbon).

5. Consider the relative effects of potential background sources of contaminant loading on sediment and environmental quality to help determine whether potential groundwater discharges are significant .
   - Potential sources of loading include:
     - Current upstream (downstream in tidal waters) point source loadings such as NPDES discharges.
     - Current upstream (downstream in tidal waters) non-point source loadings such as storm water runoff, combined sewer outfalls, agricultural runoff, atmospheric deposition, etc.
     - Historical use and impact to the surface water body (i.e., history of sediment contamination).

**ATTACHMENT C**

**Physicochemical Properties That Affect Inorganic Sorption to Sediments**

1. Charge on predominant aqueous specie :

   Arsenic: May exist as $H_2AsO_4^{2-}$ or $HAsO_4^{3-}$ in typical oxic waters; valence of arsenic is defined as V or +5 (note that valence does not directly indicate charge of ion).

   Lead: May exist as $Pb^{2+}$, $PbCl^-$, or $PbCO_3^0$ in typical oxic waters depending on the relative abundance of complexing anions (chloride and carbonate in this case); valence of lead is defined as II or +2.

2. Oxidation state of contaminant specie:

   Arsenic: Predominantly exists as As(V) ($H_nAsO_4^{n-}$) in oxic systems and As(III) ($H_nAsO_3^{n-}$) in anoxic/reduced systems. Arsenite is predominantly present as an uncharged anion ($H_3AsO_3^0$) in anoxic natural waters.

   Chromium: Predominantly exists as Cr(V) ($H_nCrO_4^{n-}$) in oxic systems and Cr(III) ($Cr^{3+}$) in anoxic/reduced systems.

3. Net (or average) charge on sorbent phase, which depends on a) permanent charge (such as found with clay minerals) and b) pH-dependent charge (common to oxides, carbonates, sulfides, and organic matter).

4. Water pH, which predominantly determines factors (1) and (3) above.

5. Sediment composition, e.g., organic carbon, inorganic carbon, Fe content, S content and clay mineral content.

Predominant contaminant aqueous species that may occur in water can be determined through use of several computer-based commercial and share-ware chemical equilibrium programs (see http://www.epa.gov/ceampubl/minteq.htm). A fairly comprehensive database that documents the chemical constants needed for input into these programs is available through the National Institute of Standards and Technology (NIST Standard Reference Database 46: NIST Critically Selected Stability Constants of Metal Complexes Database). The referenced EPA program also has an attached database.

Since the variability of factors controlling contaminant sorption to soil/sediment solids is high, one typically determines an empirical sorption coefficient by measuring uptake of the contaminant of concern onto soil/sediment materials collected from site. This is a reasonable approach provided the in-place characteristics of the soil/sediment material are preserved.