Evaluating the Groundwater/Surface Water Interface

U.S. Geological Survey

RITS Fall 2009

Presentation Overview

- Introduction
- Overview of Hydrology at the Groundwater/Surface Water (GW/SW) Interface
- Overview of Contaminant Chemistry at the Interface
- Techniques for Studying Hydrology at the Interface
- Tools for Investigating Contaminated Groundwater Discharge to Surface Water
- Alternate Concentration Limits in Mixing Zones
- Summary/Take-Home Messages

Purposes

- Equip Remedial Project Managers (RPMs), investigators, and regulators:
  - To better understand the physical and chemical effects on groundwater contamination discharging to surface water;
  - To become familiar with techniques and tools used to evaluate the hydrology and the chemistry of groundwater/surface water interfaces, including understanding the strengths and weaknesses;
  - To make informed decisions regarding directions of project field activities;
  - And to better evaluate the results of field investigations regarding the groundwater/surface water interface.

Take-Home Messages

- Numerous methods exist to measure GW/SW interaction at the interface
  - Generally the best answer is obtained by using multiple approaches because all methods have limitations
- Different geomorphic settings can have different GW/SW interactions
  - Rivers: Don't forget to consider the hyporheic zone, if present
  - Tidal zones: Constantly changing GW/SW interaction
  - GW discharge to SW can be very localized in fractured-rock and Karst systems and where there are discontinuities in low-permeability zones beneath surface water
- Substantial natural attenuation can take place at the GW/SW interface
- Consider application of mixing zones and ACLs as a remediation alternative

Selected Definitions

- GW/SW: groundwater/surface water
- Hyporheic zone: subsurface zone beneath and adjacent to surface water where groundwater and surface water mix
- Karst: limestone in which groundwater flow is through solution cavities, such as caverns
- VOC: volatile organic compounds
- Mixing zone: an area where effluent discharge is diluted and concentrations meet water quality criteria at its boundary
- ACLs: alternate concentration limits

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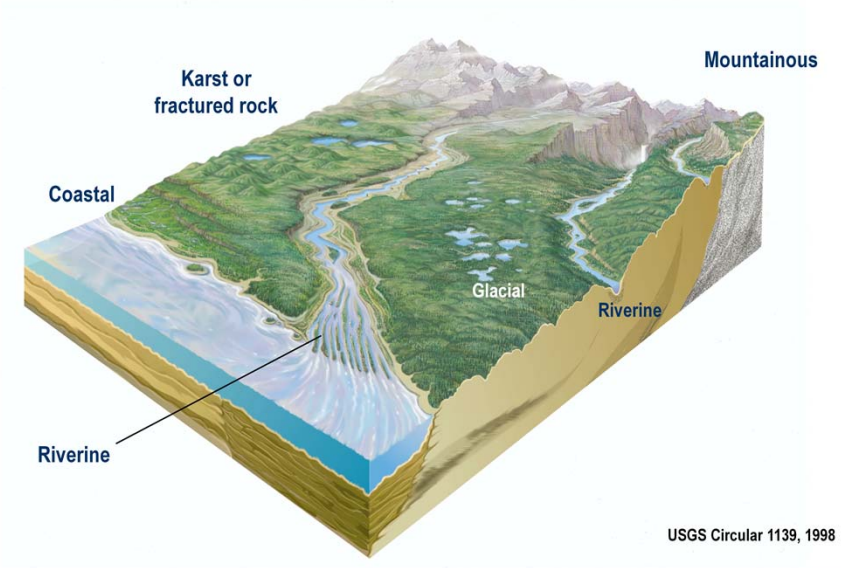
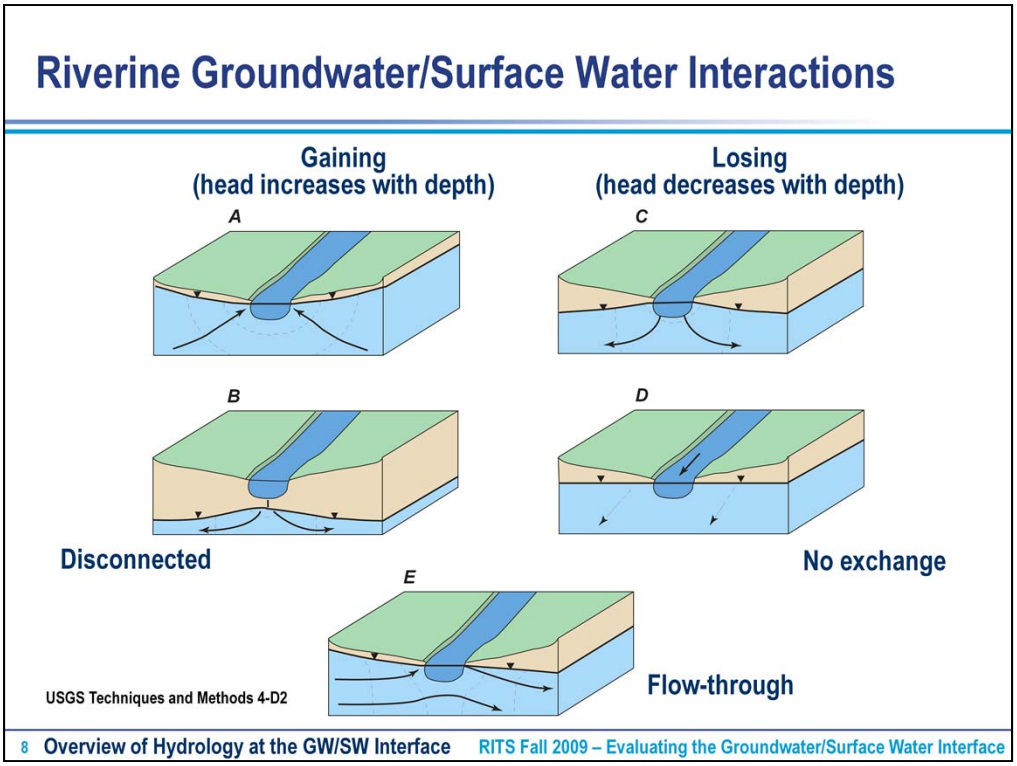
Differing Geomorphic Landscapes Produce Differences in the Nature of Groundwater Discharge



7 Overview of Hydrology at the GW/SW Interface RITS Fall 2009 – Evaluating the Groundwater/Surface Water Interface


Riverine Groundwater/Surface Water Interactions
Gaining
(head increases with depth)
Losing
(head decreases with depth)
A
C
B
D
Disconnected
No exchange
E
Flow-through
USGS Techniques and Methods 4-D2
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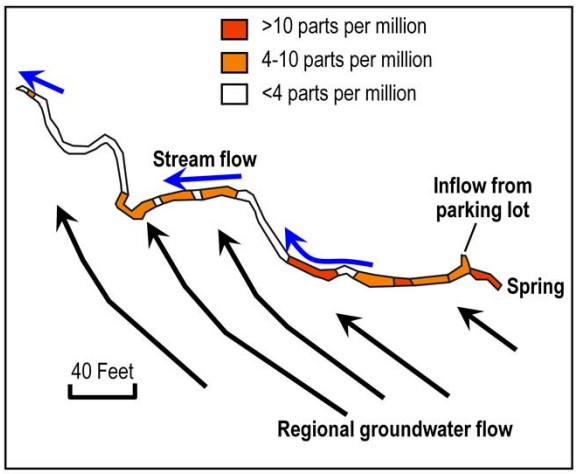
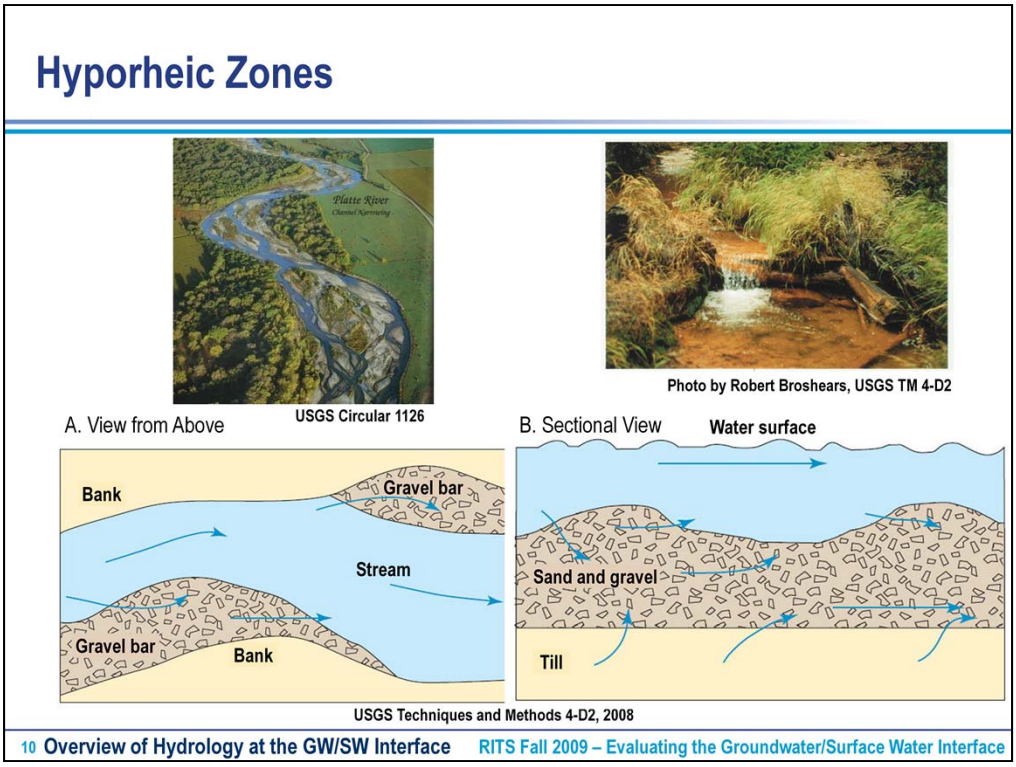
Groundwater VOC Discharge to a Meandering River, Greenville, South Carolina

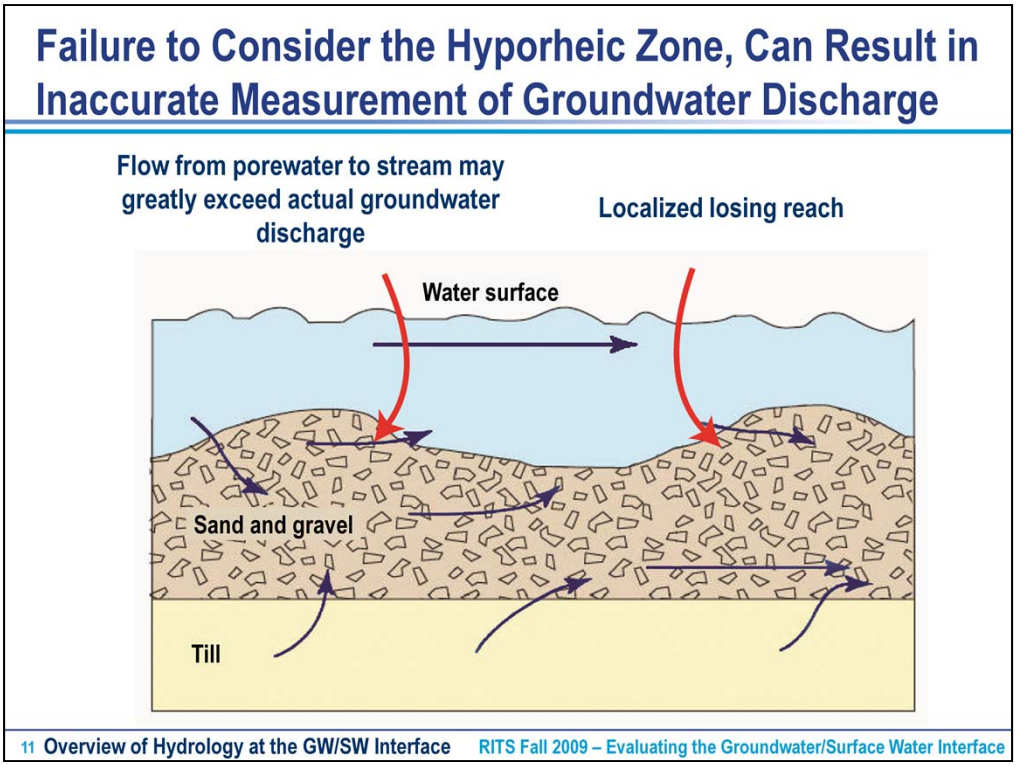


- Higher VOC discharge took place where the meander was perpendicular to the major direction of GW flow than where the meander was parallel to the major direction of groundwater flow

2000, EPA/542/R-00/007, p. 143-147

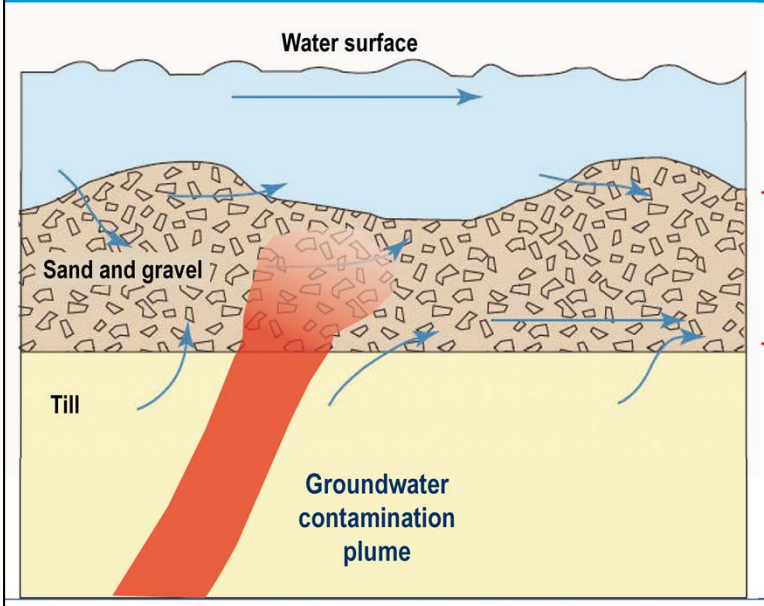


Hyporheic zones can be defined as the zone beneath and lateral to a stream where groundwater and surface water mix



If your investigation is too localized, you may get grossly inaccurate measurements of groundwater discharge

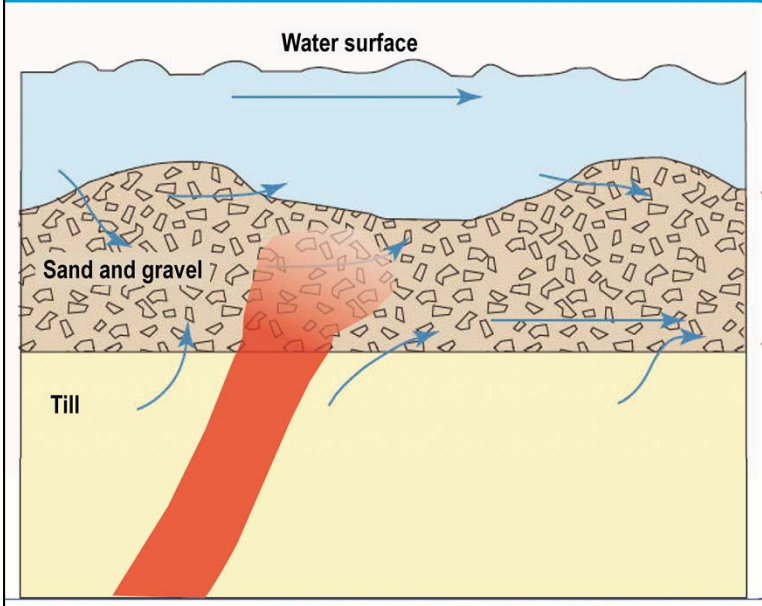
Importance of the Hyporheic Zone for Contaminant Attenuation



Substantial natural attenuation over a short distance:

Dilution, Biodegradation, Sorption

Case Study: Long Island, NY



Concentrations decreased by 34% to 95% over 5 ft

Primarily by mixing in the hyporheic zone, but also included biodegradation

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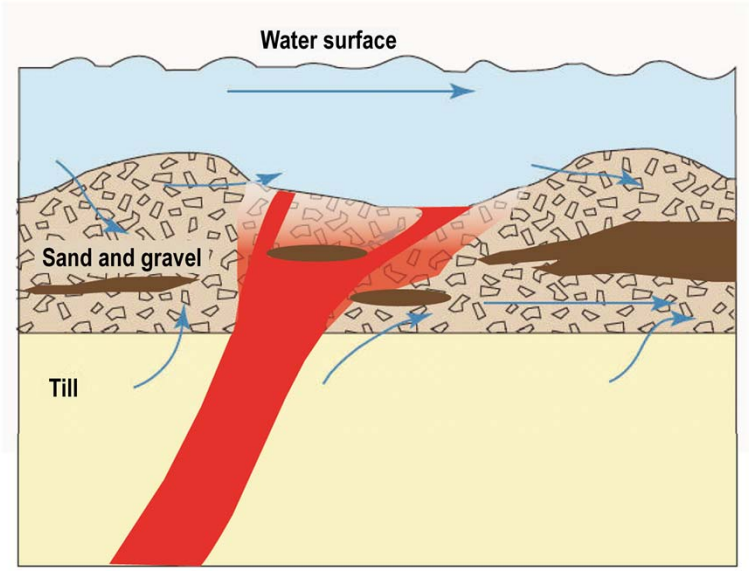
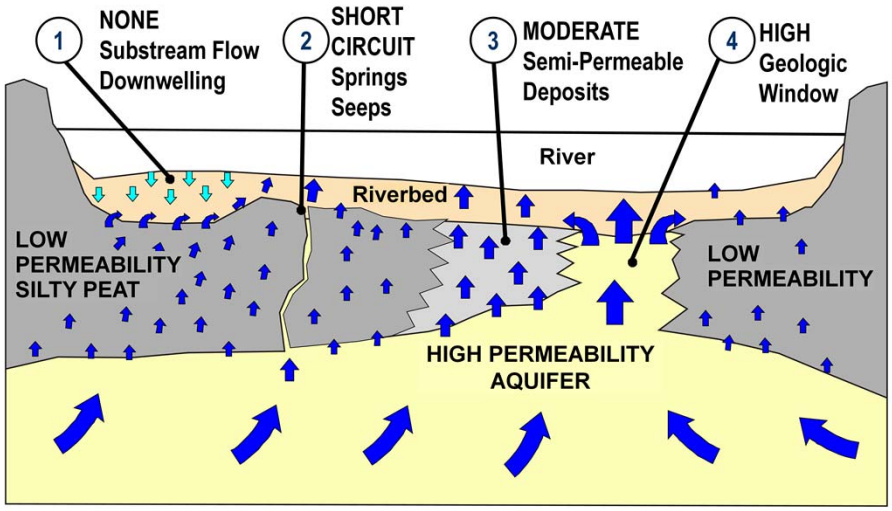
Effect of Heterogeneity of Contaminant Discharge



Preferential pathways can lead to localized areas of contaminant discharge

Effects of Streambed Heterogeneity



USEPA/542/R-00-007

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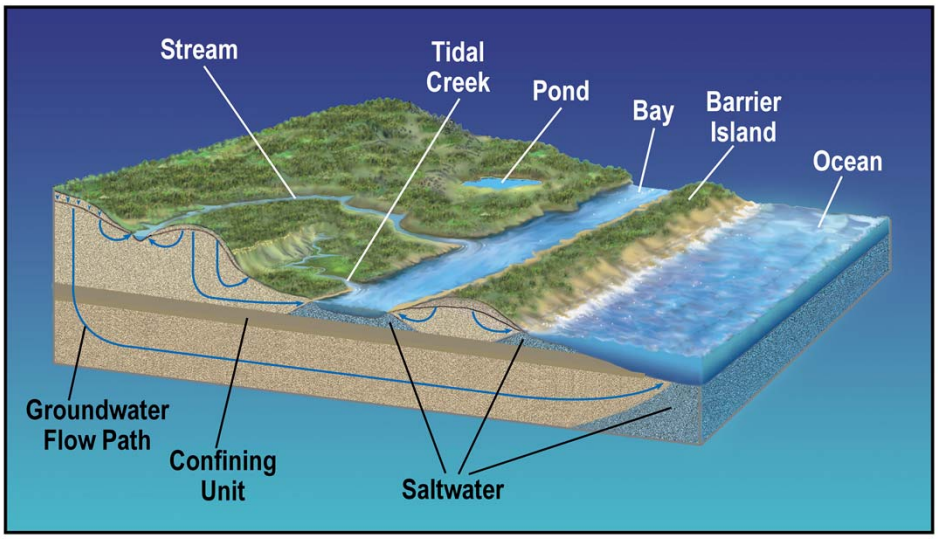
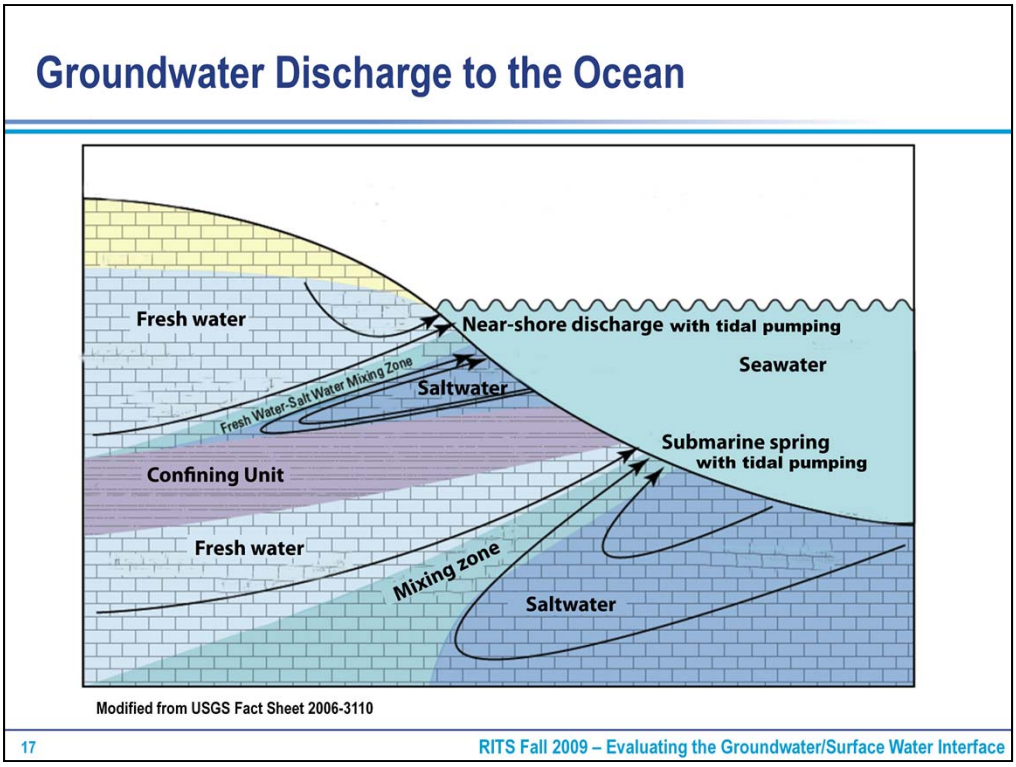
Coastal Terrain



Modified from USGS Circular 1262



Tidal pumping: At high tide, saltwater, which is denser than fresh water, washes into the groundwater-saturated sediments

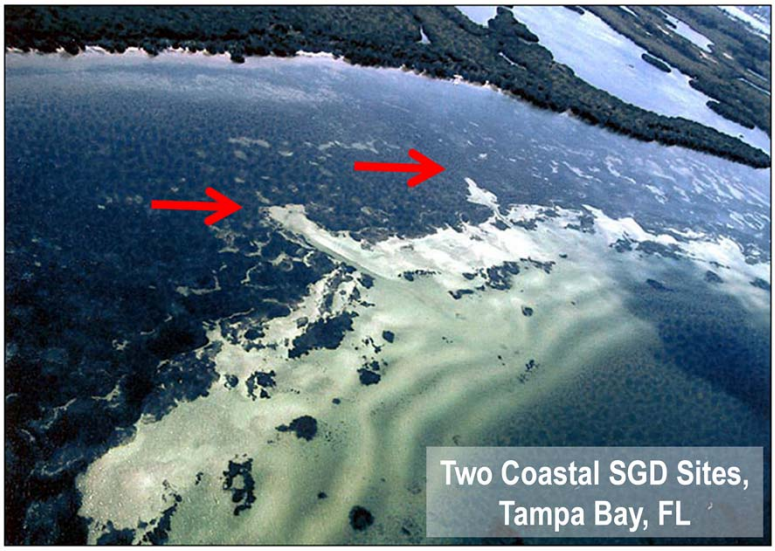
This produces an overheight in the water table.

When the tide ebbs, the brackish seawater and groundwater mixture is sucked into the ocean

New groundwater then flows into the sediment and is pumped out on the next tide.

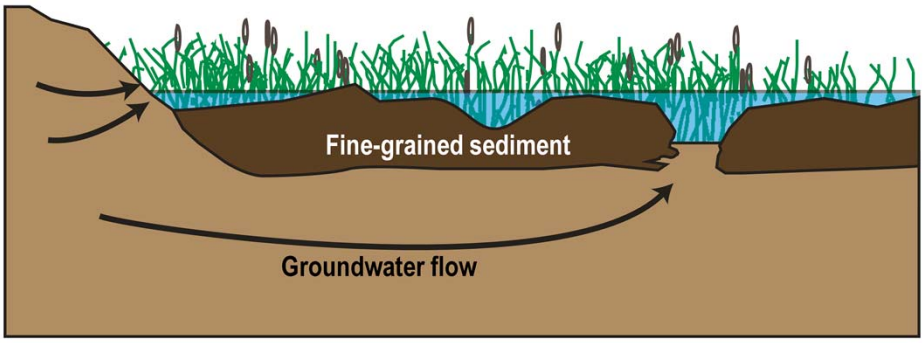
Thus, substantially more groundwater is pumped out to sea than if there were no tidal pumping.

Localized Submarine Groundwater Discharge (SGD)

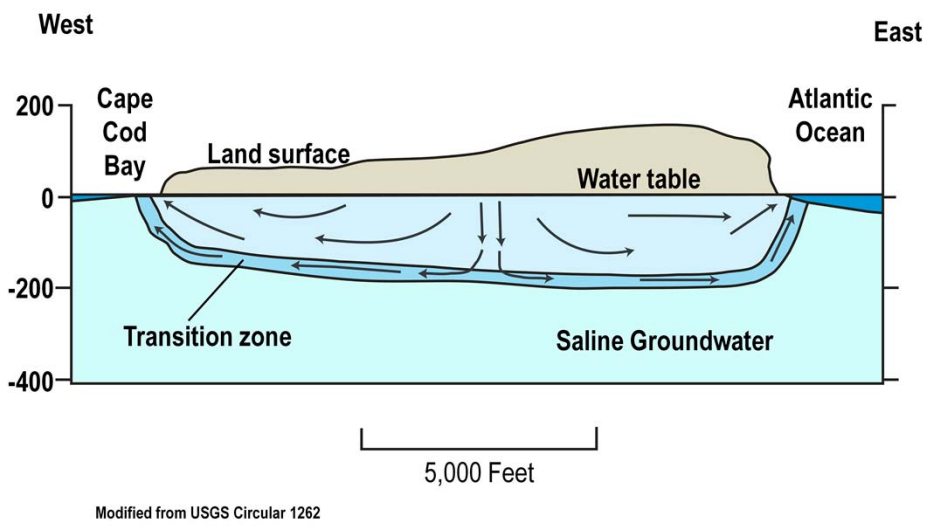


USGS OFR 2004-1226; Aerial photo courtesy of C. Kovach, Florida DEP

Groundwater Discharge to a Salt Marsh

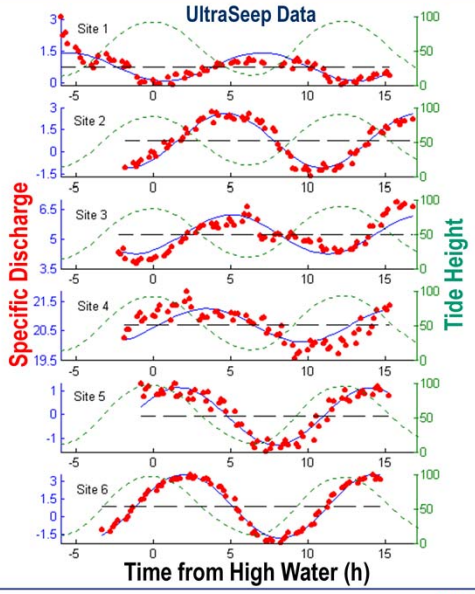


Outer Cape Cod; Groundwater Flow



Modified from USGS Circular 1262

How Does the Tidal Cycle Affect Sample Timing? Anacostia River, Washington D.C.

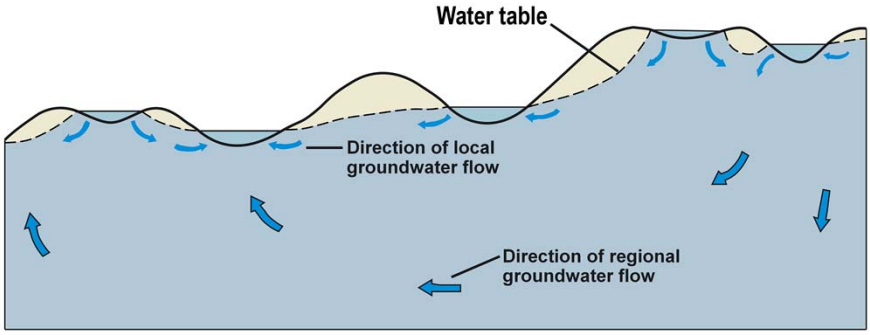


- At some places, even in the same surface water body, the maximum groundwater discharge is at low tide; some places it is not
- You may need to sample at multiple times through a tidal cycle

See RITS Spring 2003:
Coastal Contamination Migration Monitoring

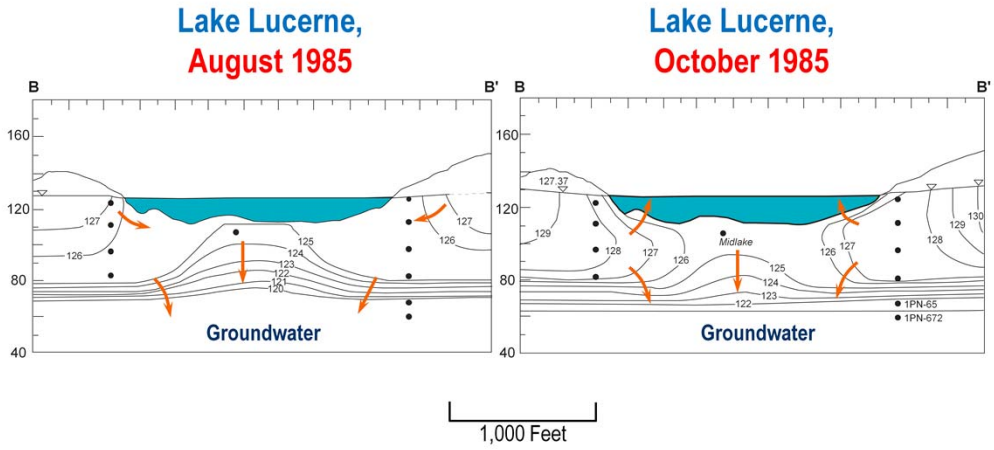
Hummocky Terrain

- Small fundamental hydrologic landscape units superimposed at random on large fundamental hydrologic landscape units
- Examples: glacial and dune



USGS Circular 1139, 1998

Groundwater Flow into Lakes Can Change Seasonally



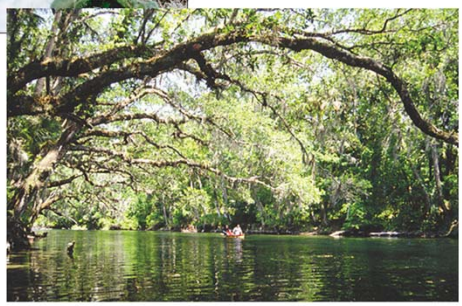
USGS Techniques and Methods 4-D2, 2008

Variety of Outlets for Karst Springs

Orangeville Rise, Southern Indiana

USGS Techniques and Methods 4-D2, 2008

Whistling Cave Spring, Southern Indiana



Volusia Blue Spring, Florida
USGS Fact Sheet 2008-3035

Fractured-Rock Aquifers

- Discharge from groundwater to surface water is along discrete fractures or fracture zones
- Can be very localized

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Potential Redox Changes Near or At the GW/SW Interface

- If the GW/SW interface is at a different redox state than the discharging groundwater, then changes can occur in the discharging contamination plume
  - Organic-rich bottom sediment and mud typically produce highly reducing conditions and a high sorption capacity for organic contaminants
  - Surface water flow through sandy bed material sometimes can maintain aerobic conditions in the hyporheic zone even when discharging groundwater is anaerobic

Potential Changes in Dissolved Metals Concentrations at the GW/SW Interface

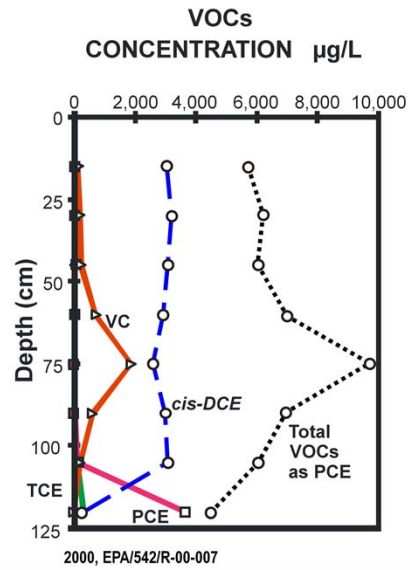
- Most metals=dissolved at low pH and anaerobic conditions, precipitate at high pH or aerobic conditions
- Anaerobic groundwater discharging into an aerobic hyporheic zone or stream can result in precipitation of metals
- Particularly common in petroleum hydrocarbon plumes in which dissolved iron is abundant

Differences in Biodegradation of Organic Compounds under Differing Redox Conditions

- Anaerobic degradation
  - TCE, PCE
  - PCB
  - Creosote, phenols
  - Perchlorate
  - Nitrate
- Aerobic degradation
  - Petroleum hydrocarbons
  - Vinyl chloride
  - *cis*-1,2-DCE
  - MTBE
  - Chlorobenzene
- Individual chlorinated solvents can degrade with differing efficiencies depending on the specific anaerobic redox condition (i.e., Iron reduction, sulfate reduction, methanogenesis)
- So it can be important to identify the specific redox condition

Enhanced Biodegradation at the GW/SW Interface: Pine River, Angus, Ontario, Canada

- No biodegradation of PCE upgradient of stream
- Extensive anaerobic biodegradation of PCE in the few cm of streambed



2000, EPA/542/R-00-007

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PCE concentrations dropped from 3,700 µg/L to <5 µg/L over a vertical distance of 15 cm, with a corresponding increase in daughter products, primarily cDCE.

Tidal Pumping

- Can deliver oxygenated water to the aquifer
- Potentially enhancing oxidation of petroleum hydrocarbons in the groundwater prior to discharge. (i.e., Pensacola Bay)
- Potentially, if the groundwater is characterized by low pH and high dissolved metals, infiltration of high pH of seawater could cause precipitation and removal of metals from solution
- However, tidal pumping can accelerate nutrient flushing from groundwater to surface water

See RITS Spring 2003

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Injecting Dye into a Karst Aquifer to Determine Flowpaths

A. Sodium fluorescein into sinkhole

B. Rhodamine into a sinking stream

- Useful for Karst because groundwater flow can be very fast

C. Rhodamine into observation well

USGS Techniques and Methods 4-D2, 2008

Dye Study: Boxelder Creek, SD

Dye disappearing down a sinkhole

- Field fluorometers can detect the dye at concentrations lower than you can actually see

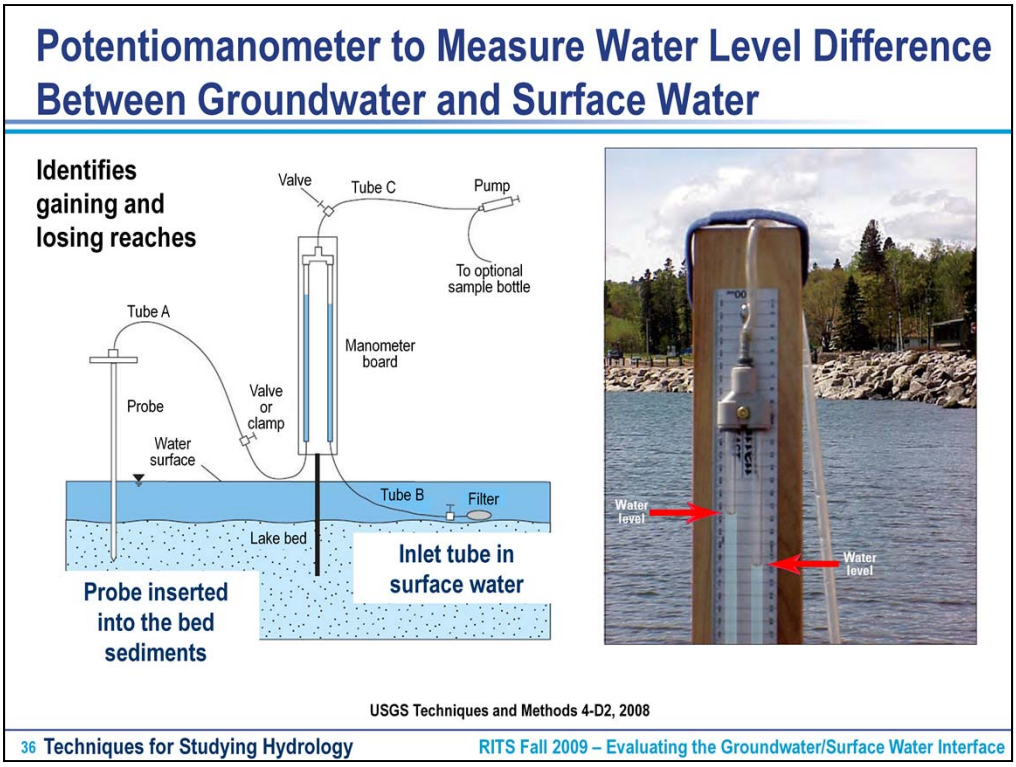
Dye reappearing 671 meters downstream

USGS Techniques and Methods 4-D2, 2008

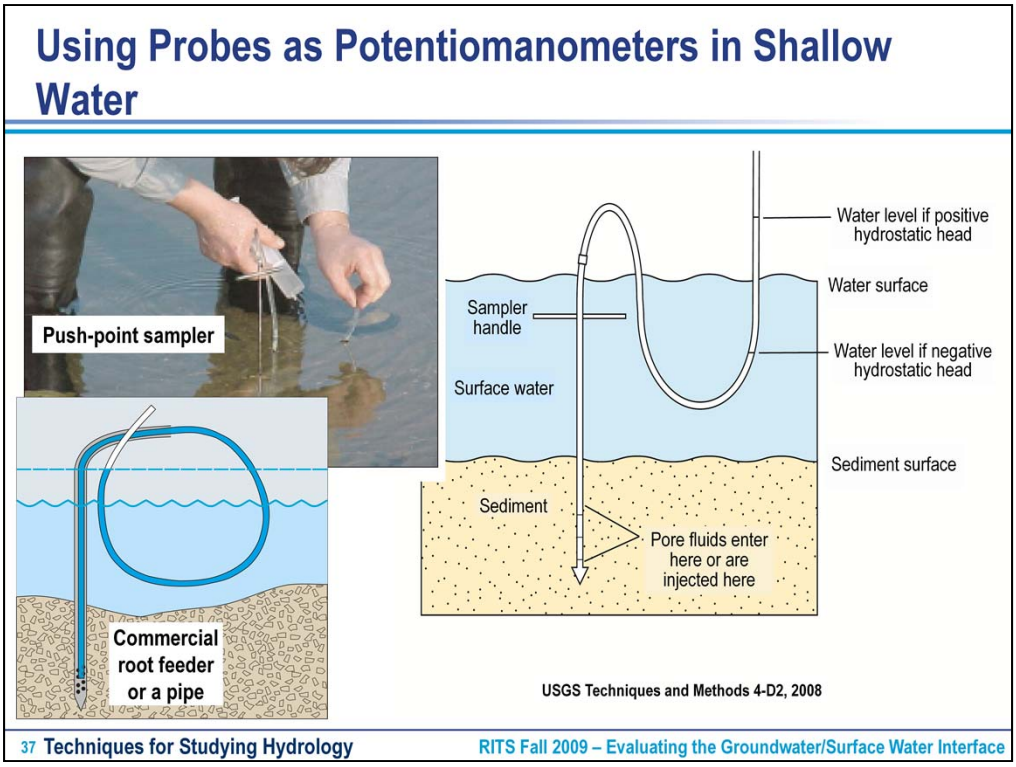
Groundwater Constituents as Tracers

Examples of groundwater constituents that sometimes have been used to investigate GW/SW interactions

- Common dissolved constituents
  - i.e., Major cations and anions
- Oxygen (^{18}O) and deuterium (^{2}H) isotopes
  - Ratios vary depending on affects of rainfall, evaporation, temporal changes
- Radon (^{222}Rn)
  - Half-life of only 3.83 days
  - Several studies documented its use in identifying GW-discharge to coastal environments
  - Groundwater is usually enriched in Rn relative to surface water



Remember that we can identify gaining and losing reaches by head decreasing or increasing with depth. In this case, we can compare the porewater head to the surface water stage



Can also use a simple steel pipe. Attach a lag bolt loosely in the bottom end of the pipe with some masking tape so the bolt stays in place until it touches the stream bottom. Then pound the pipe a couple of feet into the sediment. Put a steel rod down the middle and pound out the lag bolt. Then give it some time to equilibrate and measure the difference in head between the inside (groundwater) and outside (surface water) of the pipe.

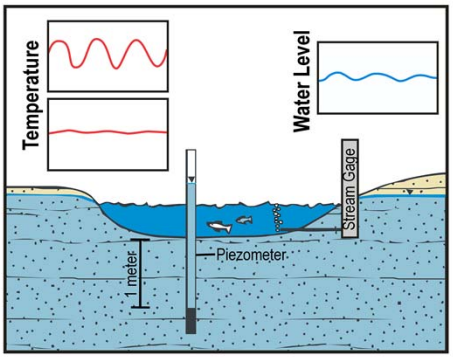
Head Gradient Measurements: Sources of Error

- **Improper seal in sediment = loss of gradient**
  - **Particularly a problem in:**
    - Rocky or gravelly sediment
    - Where the probe is rocked back and forth during insertion
    - Where the probe is inserted a very short distance into the sediment
- **Large bubbles entrained in the tubing**
  - **Gas can change volume with temperature, thereby corrupting the difference in measured head**
- **Waves**
  - **Enclose the surface water tube in a stilling well, or pipe, or even a coffee can for shallow water, to cut down on the waves**
- **Sometimes can require hours to equilibrate in low-permeability formations**

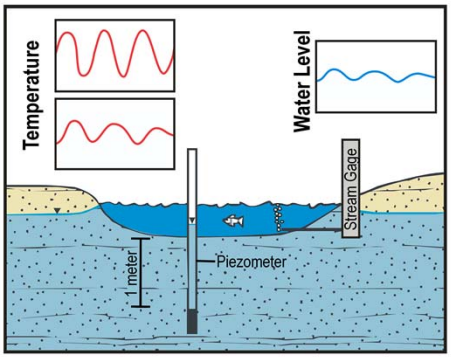
Comparison of Temporal Temperature Changes in Surface Water and Underlying Groundwater

Identifies gaining and losing reaches

Gaining stream



Losing stream



USGS Techniques and Methods 4-D2, 2008

Quantifying Discharge Flux Using Streambed Temperature (Pine River, Angus, Ontario, Canada)

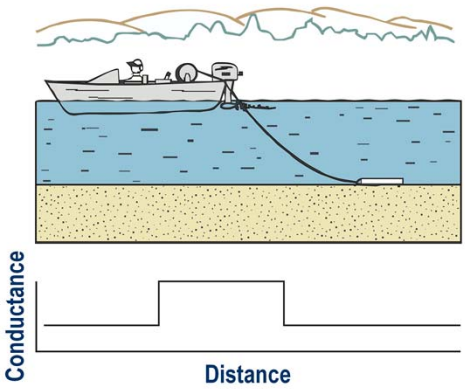
1. Used traditional methods to calculate GW discharge to SW flux
2. Determined relation between discharge and temperature
3. Mapped discharge using streambed temperature

Streambed temperature mapping, minipiezometers, and geochemical analysis were used to delineate groundwater-discharge zones. Conant used an empirical model to relate fluxes from minipiezometer data to temperatures, so temperature mapping could be used to get a detailed picture of groundwater flux to surface water.

Infrared Photography

- Areal infrared photography has been used to locate areas of groundwater discharge to surface water
- Only effective if there is a sharp temperature contrast between groundwater and surface water

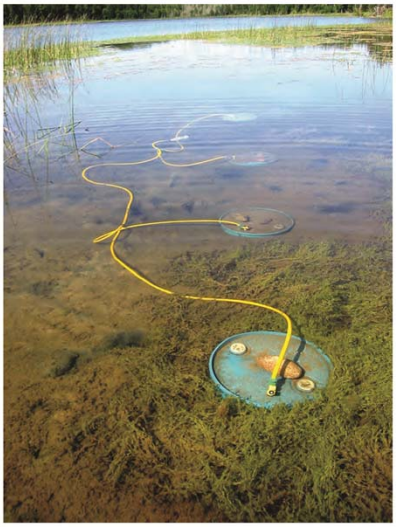
Specific Conductance Probes to Identify Gaining Reaches



USGS Techniques and Methods 4-D2, 2008

- Specific conductance probe is towed from a boat
- Depends on a conductance difference between groundwater and surface water
- Conductance changes also may reflect lithology changes, so this is only a reconnaissance method
- Electrical resistivity can be used in a similar way

Seepage Meters to Quantify Rate of Groundwater Discharge to Surface Water



USGS Techniques and Methods 4-D2, 2008

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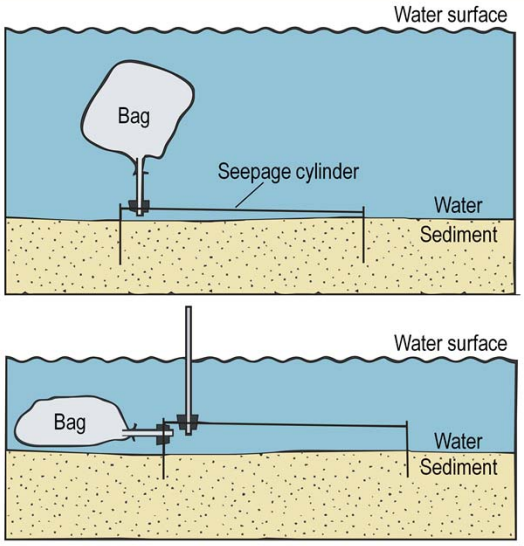
Multiple seepage drums connected to a single discharge-collecting bag

Diagram of Half-Barrel Seepage Meter

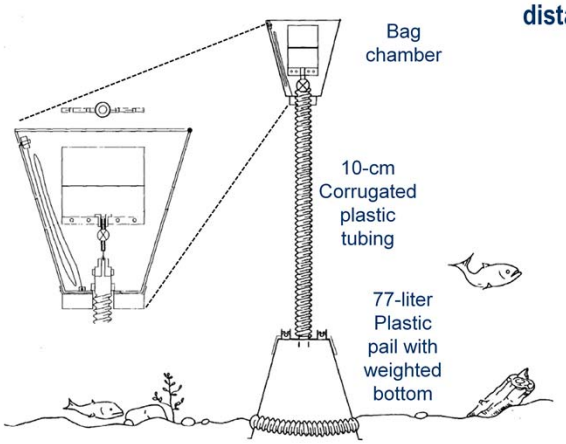


1. Push into sediment open-end down
2. Tilt it slightly so that the vent hole will allow gas to escape
3. Prefill the bag with about 1 L
4. Deployment period is hours to days

USGS Techniques and Methods 4-D2, 2008

Deep-Water Seepage Meter

- The collection bag can be floating or suspended a short distance below the surface



USGS Techniques & Methods 4-D2

Seepage Meter Measurements to Quantify Groundwater Flux to Surface Water

- Well-suited for:
  - Direct measurement of seepage flux
  - Areal distribution of seepage flux
  - Measurements in clayey silt to medium gravel
  - Calm water
  - Shallow
- Poorly suited for:
  - Areas with wave action, strong currents, or fast water (can collapse the bag or erode around the meter
  - Very soft, low-density sediment
  - Rocky sediment
  - Beds with dense vegetation
- Stepping near it can induce flow

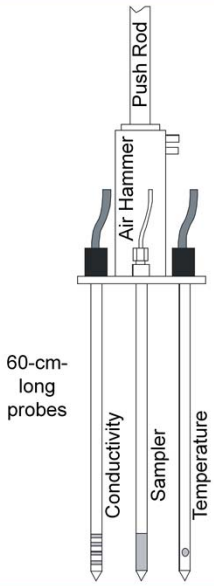
Recent Improvements in Seepage Meters

- Low-profile seepage meters made from drums, even garbage-can lids, can be used, with the flow diverted by a tube to a shelter for the bag that is protected from the current
- One device used a magnet on the collection bag. When the bag fills, the magnet closes a switch, which records the time on a data logger and empties the bag. The cycle then automatically starts over.

Additional Approaches to Flow Velocity Measurement

- Ultrasonic meter: based on the relationship between water-flow velocity and travel time of an ultrasonic signal
- EM meter: the voltage induced by movement of water perpendicular through a magnetic field is proportional to velocity
- Dye dilution: the dilution rate of a dyed solution is proportional to the rate of water flow through the solution
- Heat pulse: time of travel of a generated heat pulse

Trident Probe to Locate Discharge Zones and Collect Samples



- Direct-push system with temperature, conductivity, and water-sampling probes
- Uses contrasts between GW and SW temperature and conductivity to locate GW-discharge areas
- Then uses water-sampling probe to collect water samples
  - Vacuum pump or syringe is used to extract a sample
- GPS coupled to system records the sampling location

SPAWAR Tech. Rpt. 1902, June 2003

See Spring 2003 RITS

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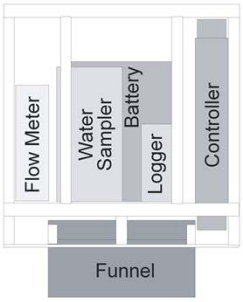
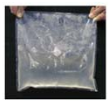
This unit combines the concept of temperature and conductivity differences to locate GW-discharge areas.

UltraSeep System to Quantify Flux and Collect Samples



- Used for longer-term deployment to determine discharge rate (ultrasonic flowmeter) and collect samples
- Lowered to the bottom from a boat or by divers
- Divers check the seal
- Can run for a few days
- Seepage is continuously monitored
- Multiple water samples can be automatically collected



Sampling bag

SPAWAR Tech. Rpt. 1902, June 2003

See Spring 2003 RITS

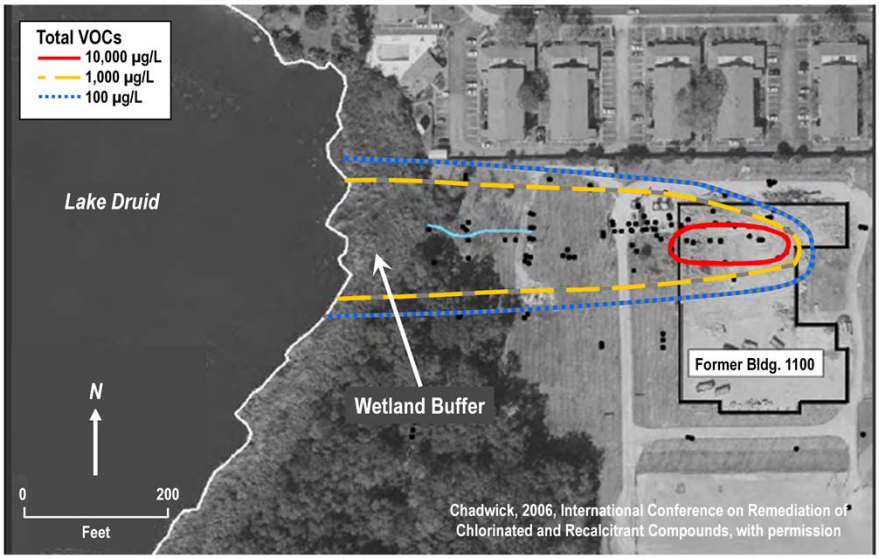
Advantages of the Trident Probe and UltraSeep System

- Allows mapping of the GW-discharge zone
- Allows collection of multiple pore-water and seepage-water samples over a tidal cycle
- Allows continuous measurement of discharge flow rates

Limitations of the Trident Probe and UltraSeep System

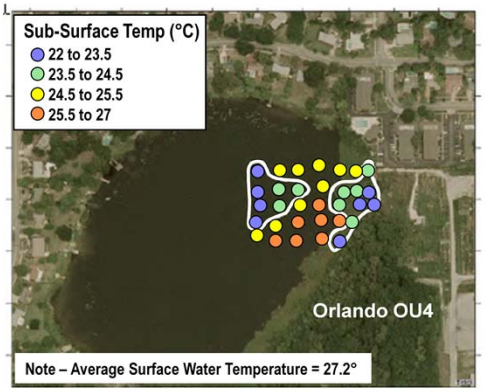
- Trident limited to water depths of about 40 ft for push-pole deployment
  - Need divers for deeper deployment
- Conductivity contrast can be affected by geology
- Pore water collection is difficult in fine-grained sediment
- The probe may be hard to insert in some hard sediment
- They do not work well in rocky, coral, or otherwise hard sediment
- Low flow rates may preclude collection of water samples
- Water samples may include surface water because the funnel initially captures ~5 L of surface water

Former NTC Orlando OU4
Trident and UltraSeep Demonstration



Temporarily turned off pump system to allow Trident and UltraSeep demonstration

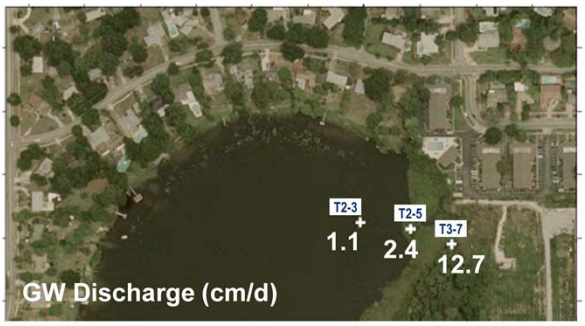
Trident Was Used to Map GW and VOC Discharge Areas and Identify Ultraseep Stations



- Identified two zones of groundwater discharge (~3-5°C cooler than SW)
  - 50-100 ft offshore
  - 200-300 ft offshore

Chadwick, 2006, International Conference on Remediation of Chlorinated and Recalcitrant Compounds, with permission

UltraSeep: Orlando OU4



- Three UltraSeep stations were selected for flowrate and discharge sampling based on Trident
- Deployed for 24 hrs
- GW discharge strongest nearshore

Chadwick, 2006, International Conference on Remediation of Chlorinated and Recalcitrant Compounds, with permission

Groundwater Flow Models

- MODFLOW
  - River package: simulates flow from or to a river
  - Streamflow routing packages have been developed to simulate fluxes between groundwater and surface water
  - Reservoir package
  - Lake package
  - Many of these require a determination of the transmissivity at the GWSW interface
  - Some level of field validation is needed for many applications

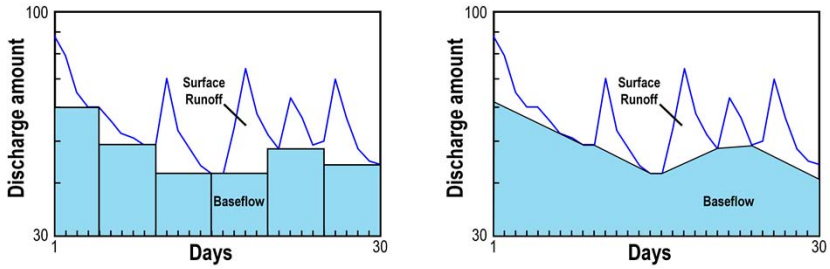
Comparison of Streamflow at Multiple Locations to Locate Groundwater Discharge to Streams

- Seepage Run
- Measurements of stream discharge at different reaches can show whether the stream is gaining or losing water
- Requires that all tributaries along the reach of interest be measured and subtracted from the downstream discharge
- Withdrawals for irrigation, etc., must be added to the downstream discharge
- Works best for small streams

Hydrograph Separation to Quantify Groundwater Discharge to Surface Water in a Stream

- **HYSEP: Computer program for hydrograph separation**

French Creek, Near Phoenixville, PA



April 1992
Hydrograph separation using the fixed-interval method

April 1992
Hydrograph separation using the local minimum

USGS WRI 96-4040

There are a variety of methods for calculating baseflow from hydrographs of streamflow. Two are illustrated here. HYSEP is a USGS computer program that can be used for hydrograph separation.

Choice of Appropriate Method Depends on the Objective of the Research (High Resolution vs. Low)

- High resolution
  - Seepage meters
  - Potentiomanometers
  - Temperature
  - Trident
  - UltraSeep
- Low resolution
  - Hydrograph separation
  - Modeling

Many methods are available. They all have advantages and limitations. Choose the appropriate method based on the objective of the research. Use multiple methods to provide better answers.

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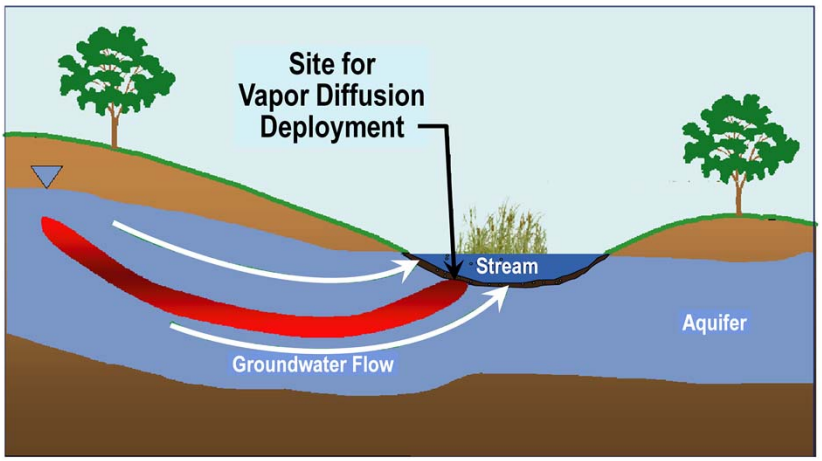
Methane Bubbles as a VOC-Mapping Tool

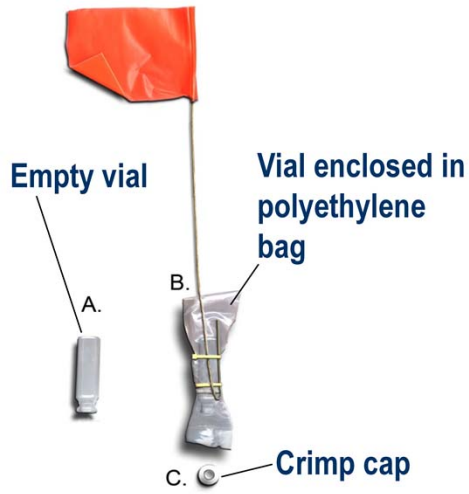
VOCs from groundwater transported into bubble-filled bottom sediment

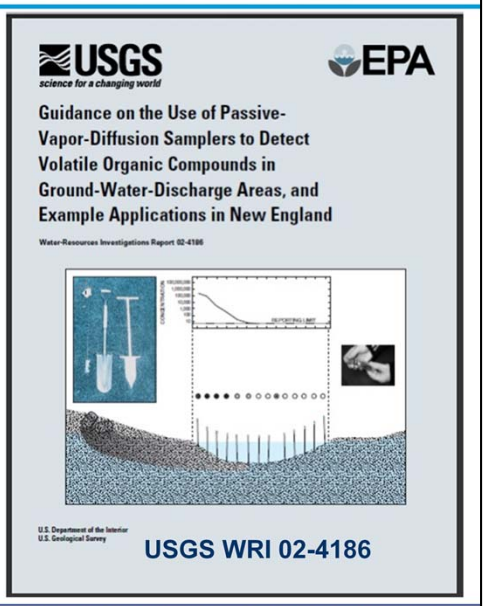


Floating Device for Capturing Methane Bubbles

- Captured methane bubbles from bottom sediment
- Analyzed with field GC
- Found VOCs in the methane bubbles at discharge areas of groundwater contamination
- Found high VOCs in background area (Later found out that it was a formerly unknown plume discharge zone)
- Not all sites have methane bubbles, so you can make an artificial bubble

Passive Vapor Diffusion (PVD) Sampler





Generalized Distribution of VOCs in Fractured-Rock Aquifer, Little Rocky Creek, Greenville, SC

- PVD samplers as a tool to understand contaminated discharge from a fractured-rock aquifer

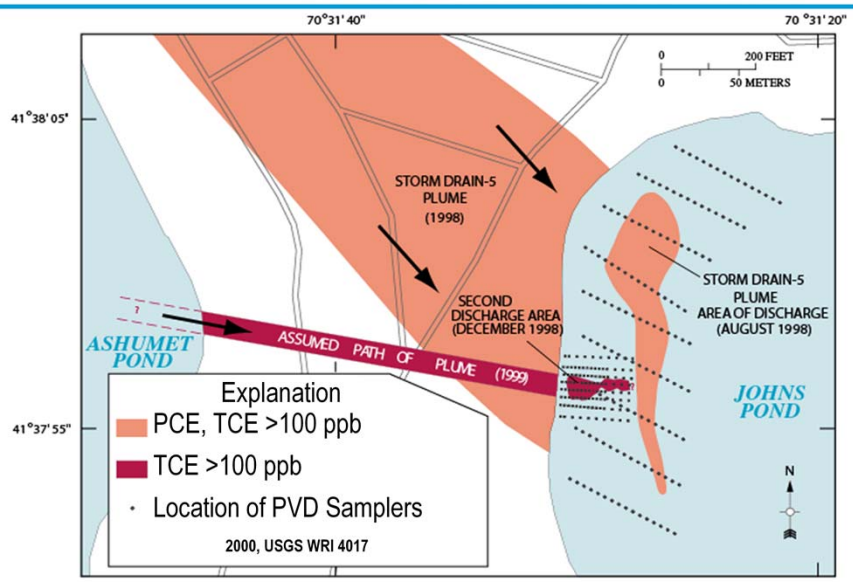
VOCs in Diffusion Samplers at Little Rocky Creek, SC

VOCs in Diffusion Samplers at Little Rocky Creek, SC (cont.)

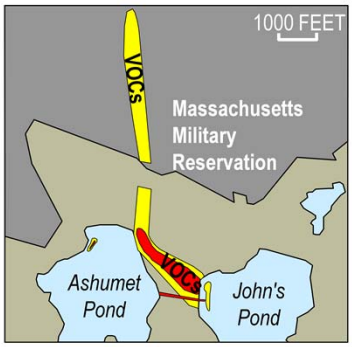
- Diffusion samplers show primary VOC discharge zones are at intersection of creek and fractures

When the VOC concentrations were overlain on electromagnetic anomalies identified in surface geophysical surveys as fracture zone, they matched up. Thus, the PVD samplers identified specific fracture zones contributing VOCs to Little Rocky Creek.

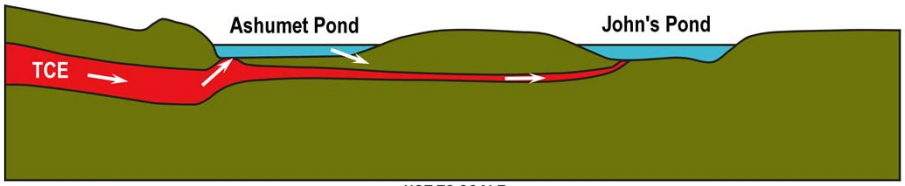
Plumes 1 and 2, Johns Pond, Massachusetts Military Reservation



Massachusetts Military Reservation – Cape Cod



2000, USGS WRI 4017



NOT TO SCALE

Other Passive Samplers

- Passive diffusion bags: water-filled polyethylene
  - Great for VOCs, not good for inorganics
  - Advantageous over pumped samples in organic-rich or low-yield sediment
- Regenerated-cellulose diffusion bags
  - Good for all solutes, but the bag biodegrades if deployed too long

Peepers

- Rigid body with openings that typically hold about 1 to 20 mL of water
- Cons:
  - Some membranes are subject to biofouling (i.e., cellulose)
  - Requires hours to days for equilibration
  - Must deoxygenate the materials used for construction
  - Only small volumes are collected
- Pro:
  - You sometimes can get very small-scale resolution of the contaminant distribution and processes

USGS SIR-2004-5220

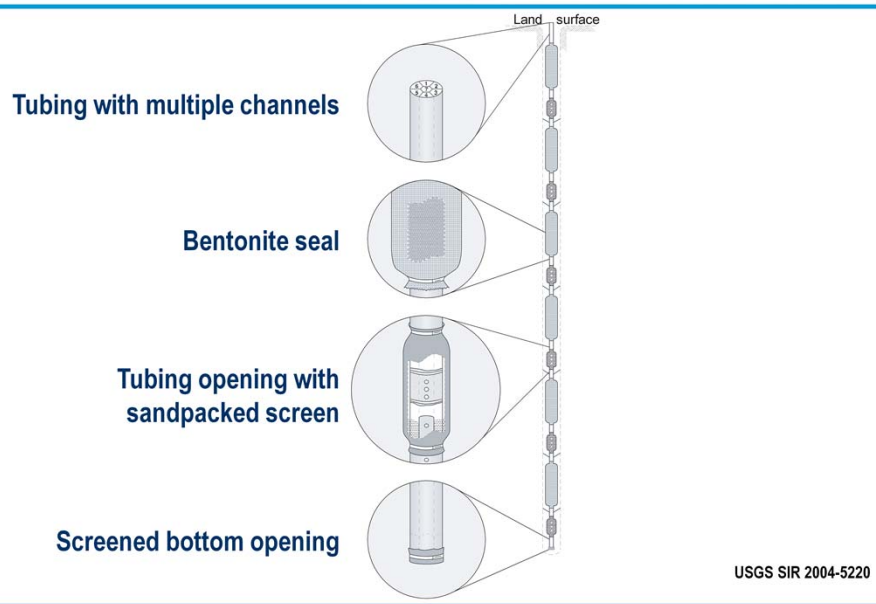
Push-Point Samplers

- Great sampling method for shallow sandy streams
- Less useful in fine-grained and organic-rich sediment because of clogging
  - This also can apply to other probe samplers with no sandpack

USGS Techniques and Methods 4-D2, 2008

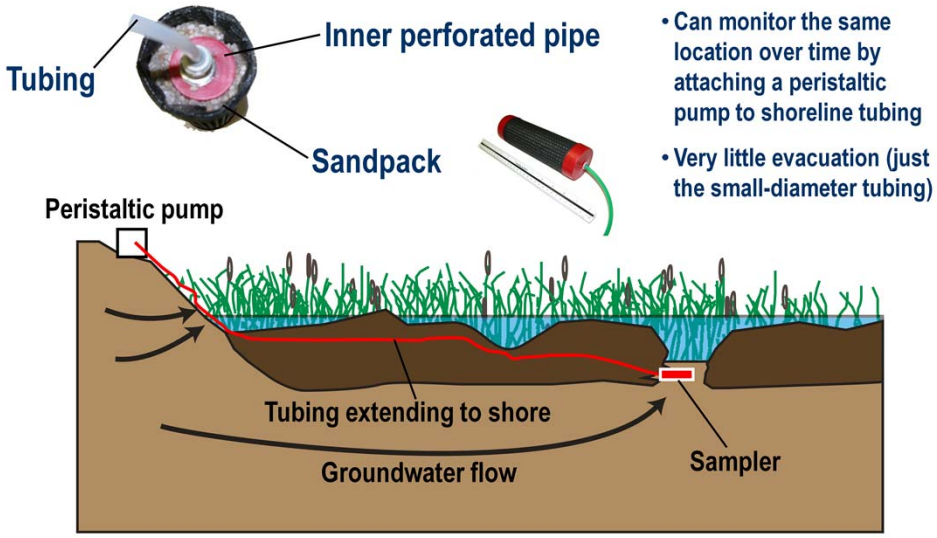
These are great for sampling in sandy material. There is no need for two trips (deployment and recovery). They do have some clogging problems in organic-rich and low-permeability sediment. Diffusion samplers sometimes are better in those situations.

Multilevel Sampling Ports



USGS SIR 2004-5220

Long-Term Porewater Sampler



- Can monitor the same location over time by attaching a peristaltic pump to shoreline tubing
- Very little evacuation (just the small-diameter tubing)

USGS SIR 2007-5154

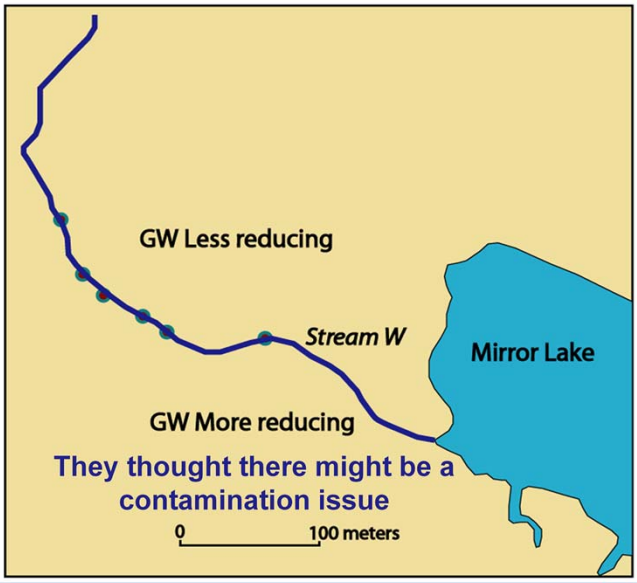
Determining Redox Condition at the GW/SW Interface

Because contaminants degrade differently under differing redox conditions, it sometimes is useful to determine the redox condition in the bottom sediment

Dissolved H_2 in pore water can be used as an indicator of the terminal electron accepting process (TEAP)

Predominant TEAP	H_2 Concentration (nM)
Nitrate reduction	<0.1
Mn reduction	0.1-0.2
Fe(III) reduction	0.1-0.8
Sulfate reduction	1-4
Methanogenesis	5-30

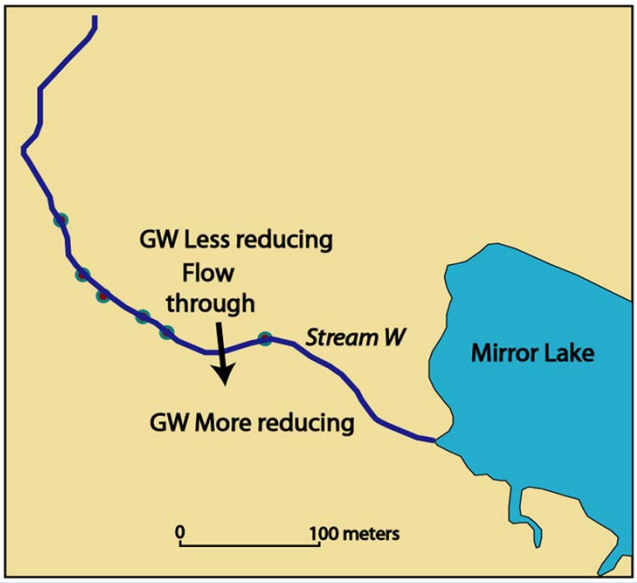
Flow-Through Stream, Mirror Lake, NH



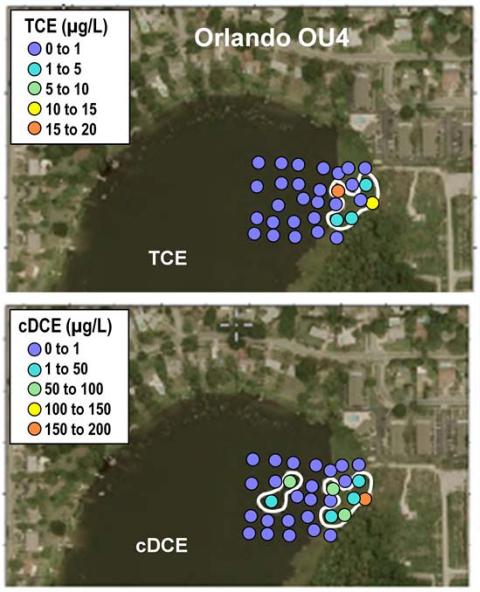
75 Tools for Investigating Contaminated Discharge RITS Fall 2009 – Evaluating the Groundwater/Surface Water Interface

New Hampshire

Flow-Through Stream, Mirror Lake, NH (cont.)



Trident Mapping for VOCs



- Successfully mapped VOC distribution at 2 ft below ground surface
  - VOCs concentrated in nearshore zone
  - Previously unknown offshore zone of VOC discharge
  - The VOC detections were within the temperature zones detected by Trident

Chadwick, 2006, International Conference on Remediation of Chlorinated and Recalcitrant Compounds, with permission

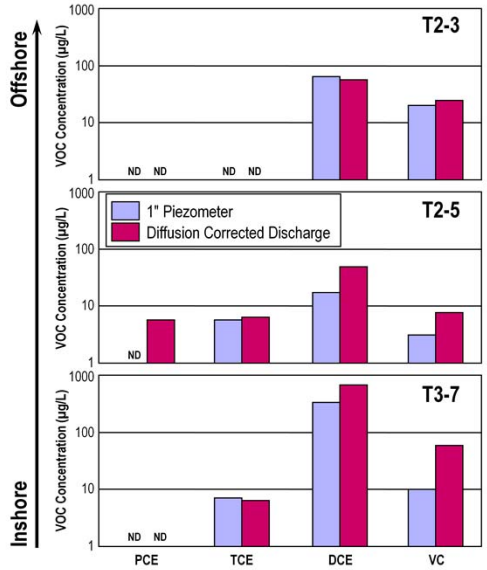
77 Tools for Investigating Contaminated Discharge RITS Fall 2009 – Evaluating the Groundwater/Surface Water Interface

VOCs from UltraSeep: Orlando OU4

- Three UltraSeep stations selected based on Trident

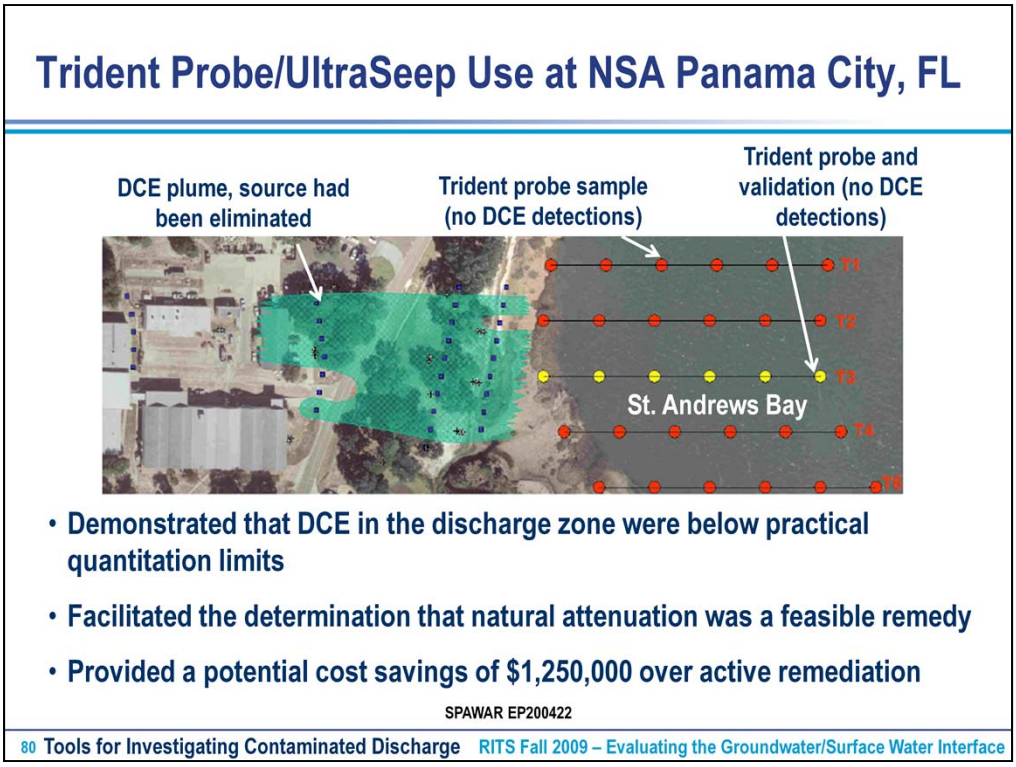
Chadwick, 2006, International Conference on Remediation of Chlorinated and Recalcitrant Compounds, with permission

UltraSeep VOC Discharge Concentrations



- **Most UtraSeep VOC stations showed good agreement to VOCs from piezometers**

Chadwick, 2006, International Conference on Remediation of Chlorinated and Recalcitrant Compounds, with permission



For 1,1-DCE at AOC 1, a Direct Push Technology (DPT) investigation in 2001 and monitoring well sampling in 2002 and 2003 showed exceedences near St. Andrews Bay of the Florida Marine SWCTL of 3.2 µg/L. The DPT investigation indicated that 1,1-DCE is completely depleted in the source zone, but it has migrated laterally to the edge of St. Andrews Bay at concentrations slightly above the SWCTLs. Since there are no wells or DPT locations in the bay, it was unknown where the discharge to surface water would occur.

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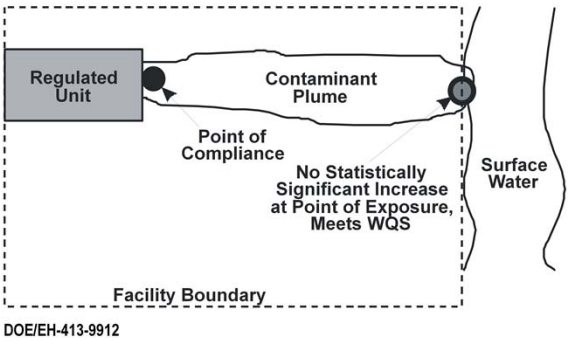
Mixing Zones

- Mixing zone: An area where an effluent discharge is diluted and mixes with surface water
  - Water quality criteria must be met at the edge of a mixing zone, but not necessarily within it
  - No acutely toxic conditions are allowed in the mixing zone
- Alternate concentration limits (ACLs) may be established where:
  - Contaminated GW is a point discharge to SW
  - There is no statistically significant increase of contaminants in SW
  - Enforceable measures exist that will preclude human exposure or ecorisk

Mixing Zone is Between POC and POE



- Point of compliance (POC): vertical plane at the downgradient edge of the waste-management unit
- Point of exposure (POE): where a potential receptor can contact the contamination

EPA Requirements for Mixing Zones

- Must be as small as practical
- The shape must be a simple configuration, like a circle or rectangle
- Must avoid biologically important areas
- Can't be used for "shore hugging" plumes
- The criterion maximum concentration (CMC) must be met within a short distance of the discharge

(EPA-823-R-92-004)

Mixing-Zone Adoption by Regulatory Programs

- Many state regulatory programs allow for mixing zones for NPDES-permitted discharge to surface water
- Not commonly used for point-source groundwater discharge, but the same principles apply
- Individual states decide whether to accept mixing zones and specify their dimensions

When Can ACLs be Used?

- They are particularly useful for addressing contamination of groundwater in situations where
  - It is impracticable or impossible to achieve the existing groundwater protection standards, and
  - When, given the exposure pathways that exist, ACLs can be shown to be protective of human health and the environment

  (DOE/EH-413-9912)

ACL Example

Amnicola Dump, Chattanooga TN:

- Contaminants were above Regulatory levels in GW
- BUT, there were no GW users at or down gradient
- AND, the GW discharge to the Tennessee River would not result in statistically significant increases in contaminant levels in the river
  - There were no ecological risks
- Groundwater cleanup was not required
- ACLs were set as the final cleanup standard

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Take-Home Messages

- Numerous methods exist to measure GW/SW interaction at the interface
  - Generally the best answer is obtained by using multiple approaches because all methods have limitations
- Different geomorphic settings can have different GW/SW interactions
  - Rivers: Don't forget to consider the hyporheic zone, if present
  - Tidal zones: Constantly changing GW/SW interaction
  - GW discharge to SW can be very localized in fractured-rock and Karst systems and where there are discontinuities in low-permeability zones beneath surface water
- Substantial natural attenuation can take place at the GW/SW interface
- Consider application of mixing zones and ACLs as a remediation alternative

Key References/Links

- Field Techniques for Estimating Water Fluxes at the Interface: USGS Techniques and Methods 4-G2
- Ground Water and Surface Water, A single resource: USGS Circular 1139
- USGS 2002, Guidance on the use of passive-vapor-diffusion samplers to detect volatile organic compounds in ground-water-discharge areas, and example applications in New England: U.S. Geological Survey Water-Resources Investigations Report 02-4186, 79 p.
- Department of the Navy Guidance for Planning and Optimizing Monitoring Strategies: August 2008. User guide UG-2081-ENV.
- USEPA Use of Alternate Concentration Limits in Superfund Sites