Passive Sampling Techniques for Groundwater and Sediment Sites

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RITS 2013

Presentation Overview

- ► Introduction
- Groundwater (GW) Samplers
- Transition to Passive Samplers
- Sediment Porewater/Surface Water Samplers
- Summary

2 RITS 2013: Passive Sampling Techniques

Today's talk will include a brief introduction to the many varieties of passive sampling that exist and will review some of the groundwater samplers that are currently available. We'll talk about how to transition from using traditional well sampling to passive sampling, if you decide that passive sampling could be useful for your site. There are several sites that have deployed passive sampling for groundwater monitoring, and we'll discuss a few of these. I understand that passive sampling technology for groundwater was the topic of recent RITS, so our discussion of specific groundwater passive sampling technologies will be brief. For porewater and surface water passive samplers, I'll introduce the chemical concepts that make these methods work and will discuss the types and quality of data you get from these samplers, the basics of deploying them, cost estimates relative to other sampling methods, and some of the limitations of these samplers that you should be aware of. As I mentioned, these have not been used widely, but we'll talk about 2 case studies where they have: Hunters Point, San Francisco Bay, and Palos Verdes Shelf, Los Angeles.

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Acronyms

- HOCs: hydrophobic organic contaminants
- PE: polyethylene
- PED: polyethylene device
- POM: polyoxymethylene
- RPPS: rigid porous polyethylene sampler
- SPMD: semi-permeable membrane diffusion (aka "fat bag")
- SPME: solid-phase micro extraction

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Some key terms that we use in this presentation are provided here.

Definition of Passive Sampling

- **Broad definition – Any sampling technique that does not require power, a constant operator, pumping & purging, etc., or more generally that reduces the amount of effort required to take a sample relative to "traditional" methods**
  - **In groundwater: A passive sampler is one that is able to acquire a sample from a discrete location without the active media transport induced by pumping or purge techniques (ITRC, 2006).**
  - **In surface water and sediment porewater: Any device or material that accumulates contaminants through diffusion when placed in contact with an environmental phase.**

5 Introduction RITS 2013: Passive Sampling Techniques

The term passive sampler seems to have been applied to any new technology that gets us out of doing something annoying. Traditional sampling methods often require the constant vigilance of a skilled operator, often they require electricity, and in some cases they introduce sample handling "artifacts" into the data collected. Passive samplers have been developed to address some of these issues in a great variety of environments.

It's worth noting here that for groundwater, porewater, and surface water, these samplers are not new technology. Some of the samplers that will be discussed today have been around for more than 20 years and generally well accepted for at least 10 years, but the Superfund program and federal remediation programs have been slow to adopt them. I will discuss some of the reasons for this during the talk, but I want to point out that there are very few Navy sites or, more generally, Superfund sites, that have deployed passive samplers. In light of recent changes in program funding and efforts at optimizing and improving the sustainability of clean ups, RPMs and other stakeholders are showing more interest in passive sampling techniques.

Groundwater Samplers

3 Volume Purge

Low Flow

Photos courtesy U.S. Navy

On the left is a traditional groundwater sampling method, 3 well volumes etc.; on the right is the newer, low flow method, which still generates purge water and is fairly complicated.

Groundwater Samplers (cont.)

- **Passive Sampler – Passive Diffusion Bag (PDB)**

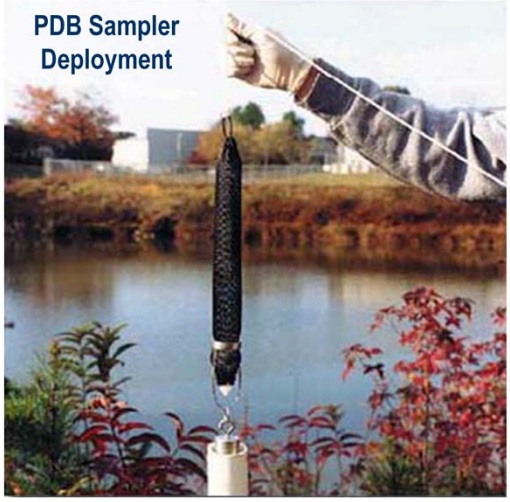

Photo courtesy ITRC

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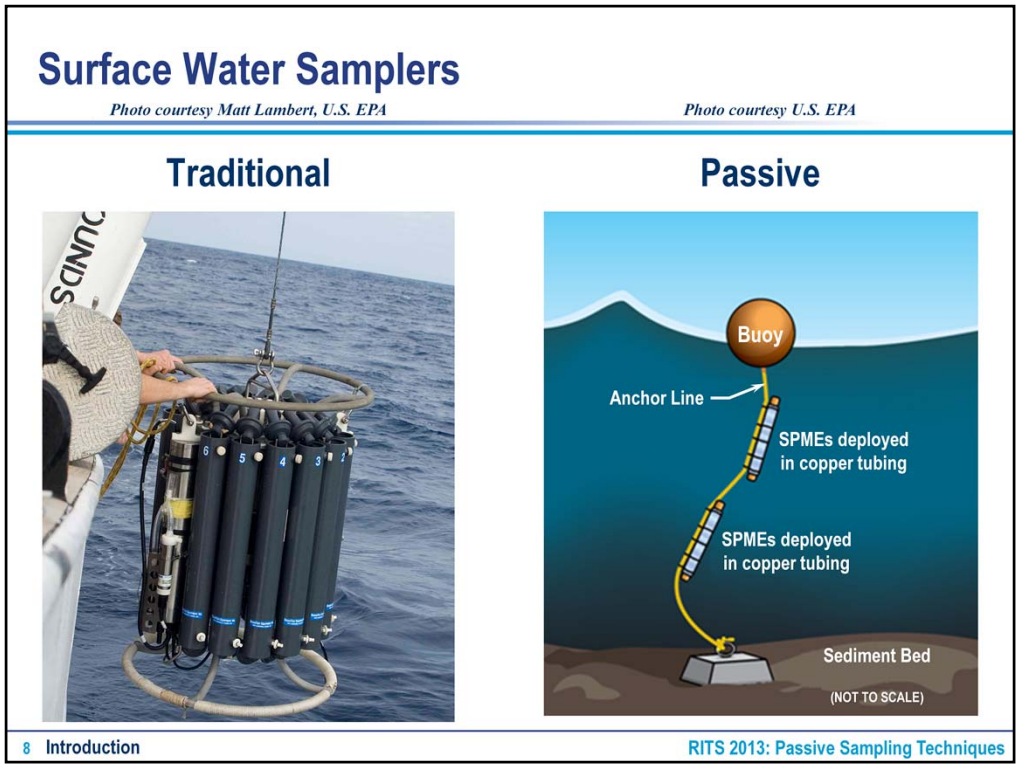
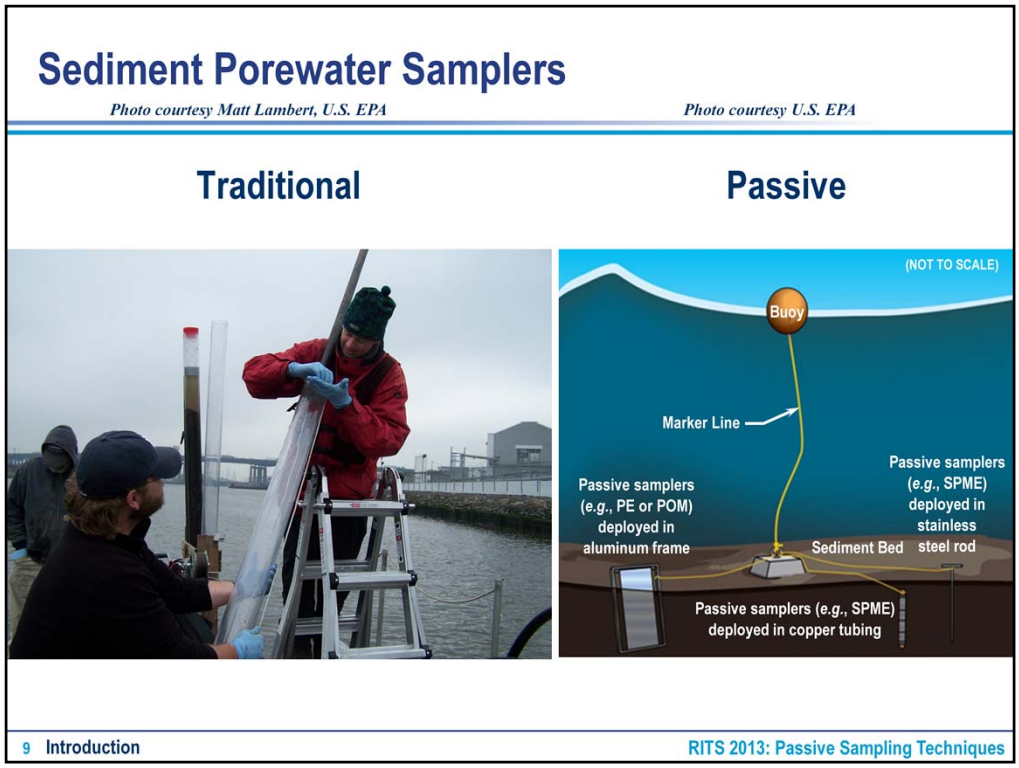
This is an image of a Passive Diffusion Bag. It's simple- no pumps, no generator, much less purge water, and less investigation derived waste (IDW). The sampler is lowered slowly into the open screened (or open borehole) well and left in place to come to equilibrium, for about 2 weeks in the case of the PDB. It is then retrieved and the sample water is transferred from the sampler to a container for shipment to a lab. The passive samplers themselves and attachment cable/string are IDW after deployed. The weights can be reused.



On the left is a carousel with twelve 2 liter Niskin bottles for sampling ocean water; on the right is the passive sampling method. You would need to collect 10 – 100 liters of surface water to obtain the same detection limits as the passive sampler on the right. The traditional method captures the concentration at one point in time. The passive sampling method gives a concentration integrated over the time of deployment. Both methods can be used to “grab” a sample from any location in the water column, but, as you’ll see on the next slide, the passive samplers also can be used to measure the sediment porewater and the porewater/surface water interface.



We should define what we mean by porewater here, particularly as to how it differs from groundwater. In reality, there is a gradient between groundwater and porewater; no strict delineation exists. For the purpose of this talk, the term porewater will apply to the interstitial water of particulate matter that has been deposited by sub-aqueous (or sub-marine) processes and has not been significantly weathered since deposition or may reasonably be expected to experience sub-aqueous (or sub-marine) erosion. In other words, the porewater of particles that have recently experienced movement or may experience movement. In groundwater, the surrounding particle matrix is unlikely to be transported and has not been transported for a substantial length of time. This is a useful definition when discussing passive samplers for groundwater and porewater because the key risk drivers in contaminated groundwater are hydrophilic and dominantly transported in dissolved form, while the key risk drivers in contaminated porewater are hydrophobic and dominantly transported by particle movement.

In situ passive sampling of porewater is shown on the right. This allows a direct measurement of porewater concentrations without the complications associated with coring or sediment grabs, such as upsetting the redox conditions, mixing the sample, or the lack of natural advective forces. This type of sampling will never replace coring or sediment grabs because we run many types of analyses on such samples, but can be a useful and more accurate measure of porewater concentrations and may be a proxy for bioavailability or bioaccumulation. There are also ex situ passive sampling methods that can take sediment core or grab samples and measure the dissolved porewater concentrations with much greater accuracy than the traditional methods used. We'll talk about this more later.

Uses of Passive Samples – Site Characterization and Monitoring

- Site Characterization
  - At groundwater sites: Generally not used for site characterization, but may be used to understand the vertical distribution of contaminants.
  - At sediment sites: Used to characterize the freely dissolved concentration, the bioavailability, and the net flux of contaminants.
- Monitoring
  - At both groundwater and sediment sites: used for long-term monitoring of progress towards meeting RAOs and clean-up levels.
- One line of evidence in addition to traditional sampling
- IR and MRP

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Passive samplers may be used throughout the Superfund process. Although groundwater passive samplers are generally not used for site characterization, they have been used at this stage to understand the vertical distribution of contaminants or estimate the chemical flux. At sediment sites, they may be used to measure time integrated freely dissolved concentrations to be used in a Human Health Risk Assessment or an Ecological Risk Assessment, to characterize the bioavailability of contaminants to benthic organisms, or to calculate the flux chemicals into or out of the sediment. The ease of passive sampling field work and the associated cost savings make them excellent tools for long-term monitoring.

The particular use of passive sampling depends on Data Quality Objectives and the needs of the site. Sediment porewater and surface water passive samplers are much better measures of freely dissolved concentrations and are useful in understanding bioavailability. Thus, they are better at explaining toxicity and food chain effects, but they do not provide information on the mass of contaminant in a sediment bed and are not useful in designing a dredge project based on mass removal.

Why Consider Passive Samplers in Remediation?

- EO 13423 Consider "use of passive samplers where feasible"
  - The Aug 10 2009 DoD memo on Consideration of GSR in Remediation specifically called out the use of passive samplers where feasible.
  - Specifically: Deputy Under Secretary of Defense Installations and Environment asked that DoD components report back regarding their use of various GSR practices, including passive samplers where feasible.

Optimization Guidance, GSR Metrics

- **2012 Navy Environmental Restoration Program Monitoring and Management Approach (MMN)**
- **2012 DON Guidance on Green and Sustainable Remediation (GSR)**
  - **GSR metrics:**
    1. Energy Consumption
    2. Greenhouse Gas Emissions
    3. Criteria Pollutant Emissions
    4. Water Impacts
    5. Ecological Impacts
    6. Resource Consumption
    7. Worker Safety
    8. Community Impacts
- **2010 DON Guidance for Planning and Optimizing Monitoring Strategies**

Key Point — **Passive samplers generally use less resources and less energy is consumed in using them**

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Eight GSR metrics identified in the Navy Fact Sheet (2009)

Energy consumption**

Greenhouse gas (GHG) emissions**

Criteria pollutant emissions**

Water impacts

Ecological impacts

Resource consumption**

Worker safety

Community impacts

**(the ones I believe are most important to passive samplers)

There are tools, such as SiteWise™, that will help you calculate these GSR Metrics. On most of these metrics, passive sampling technologies score better than traditional methods. How much better depends on the sampler selected and the manner of their use.

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- ► Groundwater Samplers
  - Grab Sampling
  - Passive Diffusion Sampling
  - Passive Diffusion/Sorption Sampling
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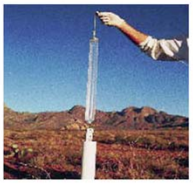
Available Technologies for Passive GW Sampling

- **Grab Sampling**
  - ***e.g.*, HydraSleeve™ and Snap Sampler™**
- **Passive Diffusion Sampling**
  - ***e.g.*,**
    - Low-Density Polyethylene (LDPE) Membrane
    - Regenerated-Cellulose Dialysis Membrane (RCDM)
    - Rigid Porous Polyethylene Sampler (RPPS)
- **Passive Diffusion/Sorption Sampling**
  - ***e.g.*, GORE® Module (screening tool)**



Photos courtesy ITRC

14 Groundwater Samplers RITS 2013: Passive Sampling Techniques

Props have been briefly shown here, by way of describing the types of samplers available, but details of each technology are not discussed.

Advantages of Passive GW Samples

- Reduces labor costs
- Significantly reduces or eliminates purge water production and disposal
- Reduces field sampling variability
- Potential cost savings of up to 70% compared to low-flow sampling
- Typically more green and sustainable
- Enables sampling from discrete intervals
- Can be used for vertical profiling

15 Groundwater Samplers RITS 2013: Passive Sampling Techniques

Well screen issues: A large well screen interval may result in sample variability, although this issue can be minimized by collecting multiple representative passive samples throughout the well screen interval, or by collecting samples from the same screened interval using both the passive and purging sampling methods. Vroblesky (2001) noted that stratification of certain chemicals has been observed over vertical distances of as little as 3 ft.

Lithology issues: The presence of interlayered, discontinuous lithology suggests the potential for preferential flow pathways within the well screen and chemical stratification. This is captured in three purge volume or low flow by averaging, but results from passive sampling techniques may differ due to discrete level samples.

Limitations of Passive GW Samples

- Must be submerged in screened intervals throughout deployment
- Requires aquifer be in hydraulic communication with well screen
- Sample volume/analyte limitations
- Requires consideration of contaminant stratification
- Cannot be used if there is significant vertical flow
- Potential for in-well mixing
- Multiple site visits may be required for deployment and retrieval

16 Groundwater Samplers RITS 2013: Passive Sampling Techniques

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Potential Cost Savings

Per-Well Passive Sampling Method Cost Comparison

Traditional 3-Volume Purge	$310
Low-Flow Purge	$280
Snap Sampler™	$155
RPPS	$104
RCDM	$80
PDB LDPE	$68
HydraSleeve™	$63

(USACE and AFCEE, 2005)

- Passive sampling costs per well generally 1/5 to 1/3 of conventional sampling
- Need to consider costs of transition sampling event
  - Labor and materials
  - Analytical costs (can be double or more)

17 Groundwater Samplers – Costs RITS 2013: Passive Sampling Techniques

Emphasize that a concurrent sampling event is pretty expensive, especially if multiple passive samples (*i.e.*, PDB or Snap Samplers) are collected per location where only one conventional sample was previously collected. Analytical costs can soar.

Presentation Overview

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- Groundwater Samplers
- ► Transition to Passive Samplers
  - Desktop Review
  - Comparative Evaluation
  - Case Studies
  - Groundwater Passive Sampler Selection Tool
- Sediment Porewater/Surface Water Samplers
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Transition to Passive Sampling

- **A fact sheet on transitioning is available**
- **Transitioning or incorporating passive sampling methods:**
  - **Requires careful site-specific evaluation and an understanding of the Conceptual Site Model (CSM)**
  - **Engage stakeholders/partnering team initially and throughout the evaluation process**
  - **Involves a 2-step site-specific evaluation**
    - *Step 1*: Desktop Review
    - *Step 2*: Comparative Evaluation

19 Transition to Passive Sampling RITS 2013: Passive Sampling Techniques

A concise fact sheet on transitioning is available. It was prepared by the ARTT with input from the Optimization work group. It is perfect to use with your whole stakeholder team.

Converting to passive sampling means going from average concentrations to point concentrations. You may wind up with higher concentrations which may not be favorable to stakeholders. This further supports the development of DQOs and understanding the CSM.

For bullet 2, a good take home point is “what passive sampling concentrations will be acceptable and comparable to previously collected data”. Again – must meet DQOs.

Transition to Passive Sampling – Desktop Review

- **Evaluate regulatory program**
- **Understand/update the site CSM**
  - **Physical**
    - Geology/hydrogeology
  - **Chemical**
    - Chemicals of Concern (COC)s, time-series concentration data
- **Current monitoring program**
  - **Types (LTM, remedy performance, etc.)**
  - **Project/program Data Quality Objectives (DQOs)**
  - **Chemical analytical requirements**

Transition to Passive Sampling – Comparative Evaluation

- **Side-by-side performance evaluation of passive sampling vs. existing (traditional) methods**

Photo courtesy U.S. Navy

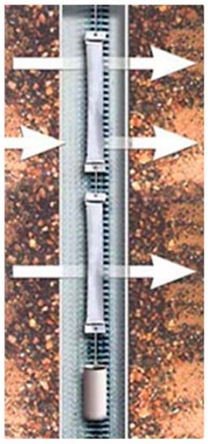

Photo courtesy ITRC

21 Transition to Passive Sampling – Step 2 RITS 2013: Passive Sampling Techniques

Passive sampling may not work at a site due to inherent site conditions such as those mentioned in the “advantages and limitations” slide notes. Must understand the site CSM and the limitations of passive samplers prior to deploying.

Potential Issue: results may be higher/hard to correlate - targeting a zone vs. getting an average over a well screen after purging

Transition to Passive Sampling – Comparative Evaluation (cont.)

- Develop sampling design
  - Understand DQOs
  - Develop acceptance criteria for the data sets (*i.e.*, equal to or better in quality and representativeness than current method)
  - Use CSM to consider screen length, lithology, COCs, etc… to decide method (grab vs. passive diffusion) and applicability
  - Understand percentage of wells needed for concurrent evaluation
  - Understand number of data sets needed for concurrent evaluation

22 Transition to Passive Sampling – Step 2 RITS 2013: Passive Sampling Techniques

When performing a comparative study, passive sampling should be performed prior to purge sampling. This concurrent sampling approach minimizes disturbance of the well column so that passive grab sampling can be performed according to the intent for which the sampler was designed. Conventional sampling should be performed immediately following passive sampling, as the purging approach should ensure that a representative sample will be collected. Collection of a low-flow (or three purge volume) sample immediately following the passive sample minimizes the potential for results to be skewed due to the variability with time. Groundwater concentrations can fluctuate considerably over relatively short time periods, especially during periods of extensive precipitation.

Regarding data quality and acceptance, you need to consider the sampling variability and decision criteria should be conservative, ie. concentrations higher using passive samplers.

Regarding the percentage of wells needed for a comprehensive evaluation, typically sampling of 100% of the wells is over-conservative, but for a heterogeneous site or one with few wells, it may be appropriate. For a homogeneous site or many wells, the site team will select a percentage of the wells that represent the range of conditions at a site, including groundwater flow rates, concentrations of contamination, lithology, etc.

Regarding the number of data sets necessary, if traditional and passive samples are taken concurrently only 1 data set is likely necessary.

Multiple data sets over time may be necessary if no concurrent sampling occurred in order to understand temporal effects.

Transition to Passive Sampling – Comparative Evaluation (cont.)

- **Establish decision process, factoring in cost and sustainability**
  - **Establish inherent sampling variability**
    - Estimate general sampling variability (*i.e.*, ±10%)
    - Use laboratory duplicates/spikes/blanks to calculate sampling/laboratory variability (%)
    - Use duplicate samples to calculate chemical-specific variability (%) or Relative Percent Difference (RPD)
      - Original = 100 mg/L and duplicate = 114 mg/L; chemical specific variability = 14 %
  - **Establish data evaluation method**
    - 1:1 comparison; consider sampling variability
    - Statistical evaluation *(e.g.,* linear regression, two one-sided testing [TOST]

Transition to Passive Sampling

Case Study #1 – NAWC Warminster

- Fractured bedrock site; '3 volume purge' conventional sampling
- COCs include PCE, TCE, CCl_4
- 100% of monitoring wells sampled
- One LDPE sampler per 5-ft of screen; 3 max per well
- Fractures targeted in open borehole wells
- Passive sampler with highest concentration used for comparison (conservative)

Case studies were selected based on different PS techniques and based on different site conditions.

Transition to Passive Sampling

Case Study #1 – NAWC Warminster (cont.)

- Passive sampling accepted if concentrations ≥ conventional sampling
- Estimated sampling/laboratory variability from duplicate samples
- Passive sampling accepted at 2 of 3 sites
- Not acceptable at site with very low concentrations that made correlation difficult
- Estimated 30-year cost savings of >$500K

The Warminster comparative study, completed in 2002, cost about $50k.

Transition to Passive Sampling

Case Study #2 – Allegheny Ballistics Laboratory (ABL)

- Alluvium and fractured bedrock site
- Low-flow traditional groundwater sampling
- COCs include TCE, *cis*-1,2-DCE, and VC
- One LDPE passive sampler collected at low-flow traditional sampling depth in 27% of monitoring wells
- Concurrent results compared graphically to evaluate variation
  - Linear regression analysis performed
- Strong linear correlation indicated passive sampling is acceptable

Passive samplers were used in open borehole wells at the ABL site

Transition to Passive Sampling

Case Study #3 – Hill AFB

- Heterogeneous alluvium site with TCE as primary COC
- Sampled using '3 volume purge' method; transition to HydraSleeve™
- Paired samples collected in 60 wells; 6 groups of 10 wells selected based on 3 variables: groundwater velocity, TCE concentrations, and water depth
- Concurrent results evaluated for statistical significance and to see if variables affect results

27 Transition to Passive Sampling – Case Study #3 RITS 2013: Passive Sampling Techniques

Passive samplers were used in open borehole wells at the ABL site

Transition to Passive Sampling

Case Study #3 – Hill AFB (cont.)

- HydraSleeve™ method produces lower TCE concentrations
- Methods are predictably statistically different – likely based on inherent sampling differences and not on selected variables
- Difference was tolerable; not substantial enough to influence site management strategies
- Cost analysis
  - $9M 20-year cost savings (1,500 samples per year)
- Carbon footprint analysis
  - 58% reduction in CO_2, >99% reduction in water

Passive samplers were used in open borehole wells at the ABL site

Transition to Passive Sampling – Lessons Learned

- Must consider project/program DQOs
  - Thoroughly understand sampler Standard Operating Procedures (SOPs) to avoid improper sample collection
- Elevated total metals and/or Total Dissolved Solids (TDS) can result from improper sampling methods
  - Lower samplers slowly into well and avoid disturbing fines at base of well; equilibration time may be warranted
- Improper application – understand what information will be collected using the selected passive sampling method
- Understand inherent variability between passive and traditional sampling
- Consider site-specific variables such as lithology and groundwater velocity
  - May not be appropriate at highly stratified sites
  - Low groundwater velocity may result in stagnant water in the screened interval

GW Passive Sampler Selection Tool

- Excel-based passive sampler selection tool for GW
- Recommends passive samplers to consider at your site based on analytes, well construction, site specifics
- Cost/footprint savings estimate
- Due out Summer 2013
- ARTT will present this to RPMs at brown bag presentations this summer

30 Transition to Passive Sampling RITS 2013: Passive Sampling Techniques

This tool is designed to help RPMs select passive samplers that may work well for their site. It is similar to the Excel based SiteWise™ tool *i.e.*, easy to use

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- Summary
  - Conceptual Site Model
  - Traditional Sampling Methods and Their Limitations
  - Passive Sampling: Technical Overview
  - Case Studies
    - Hunters Point Naval Shipyard, San Francisco, CA
    - Palos Verdes Shelf, Los Angeles, CA

Contaminated Sediments and the Navy

- The Navy has more than 200 contaminated sediment sites (as of Fall 2010)
- Projected remediation cost of $1.3 billion
  - Munitions Response Program (MRP) sites add another $1 billion
- 35% of Environmental Restoration, Navy (ER,N) budget is sediment sites
- RITS Sediment Survey (Fall, 2009)
  - 67% of sites in investigation, 33% in remediation phase
  - 44% ocean/marine/brackish; 56% freshwater
  - Contaminated sediments include a wide variety of contaminant classes

32 Sediment Porewater/Surface Water Samplers RITS 2013: Passive Sampling Techniques

Since most of us engineer and science folks like to hear stats, here's some quick statistics on the world of contaminated sediments that the Navy has to deal with. 200 sites is a large number. The number of Superfund sites (largely non-federal, though some Navy and other government sites are included on this list) with a significant amount of contaminated sediments is about 120 and remedy decisions are yet to be made at about 50 of those sites. Of the Navy sediment sites, 2/3rds are in the pre-decision phase. Like groundwater passive samplers, porewater and surface water passive samplers are useful in the long-term monitoring phase, but, unlike groundwater passive samplers, there are a variety of applications in the RI/FS stage where passive samplers may improve the understanding of contaminate fate and transport. Such information is always critical to making well informed remedy decisions at Superfund sediment sites.

Why use passive samplers to measure contaminant concentrations in surface water or sediment porewater?

1. They more accurately measure:
   - Freely-dissolved concentrations, bioavailability, relative chemical activity
2. Results are more relevant
   - To toxicity, to risk, to decision making
3. They are cheaper

33 Sediment Porewater/Surface Water Samplers RITS 2013: Passive Sampling Techniques

You use these samplers if you are interested in having an accurate understanding of the freely dissolved concentrations of contaminants. I think that passive samplers for HOCs in surface water and porewater have more advantages than the fact that they don't require electricity or a constant operator. 1) They are more accurate. These samplers concentrate HOCs from the surrounding water to high enough concentrations that detection limits are typically reduced 10 – 100 fold. They only absorb contaminants from the "truly dissolved phase," which means that the samples accurately reflect the dissolved concentration without needing to be corrected for the effects of dissolved organic carbon (DOC). The presence of DOC in a traditional surface water or porewater sample will bias the measurements toward higher concentrations and will greatly increase the uncertainty in the measurements. 2) They are more relevant because these samplers measure "truly dissolved phase" of the contaminant, which correlates strongly with the bioavailability of the contaminant. Because of this, passive sampler measurements are better able to explain the results of toxicity tests. Passive samplers are also "time integrated" samplers and are more representative of exposures to the contaminants. Both of these characteristics are useful in designing effective remedies. 3) They are cheaper than both traditional water sampling methods and the early type of surface water passive sampling known as semi-permeable membrane device (SPMD). Note- transitioning issues related to groundwater PS are less of an issue with sediment samplers, in part because we're just starting to address sediment issues at many sites. In some cases, it might be necessary to compare results from traditional and PS measurements of the same samples, but bear in mind that PS is not directly comparable to traditional methods because the presence of DOC skews traditional methods towards much higher values, particularly for very hydrophobic compounds. It is also necessary to compare results from bioassays to passive samplers, depending on how you decide to use the passive sampler data.

Types of Surface Water/Sediment Porewater Samplers

- For Metals
  - Peepers
  - Diffusion Gel Thin Film Device (DGT)
  - Gellyfish
- For Polar and Semi-polar Organic Contaminants
  - Polar Organic Chemical Integrative Sampler (POCIS)
- For Hydrophobic Organic Contaminants (HOCs)
  - Solid-phase microextraction (SPME)
  - Polyethylene (PE)
  - Polyoxymethylene (POM)

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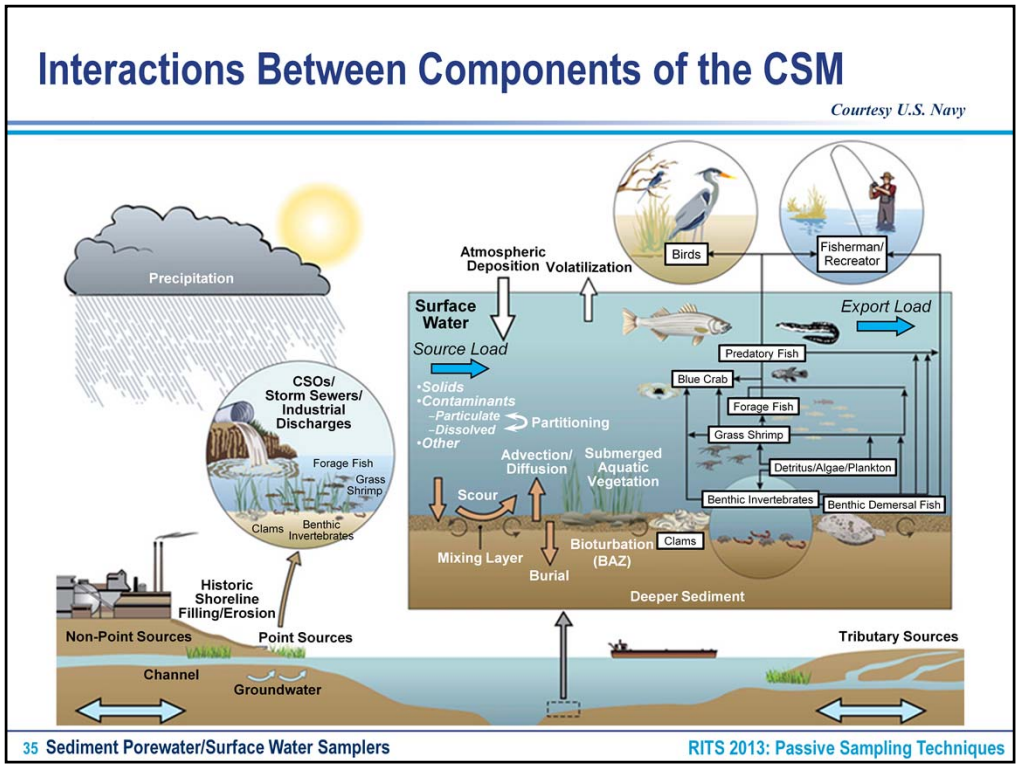
A large portion of today's discussion will focus on PS for hydrophobic organics for 3 reasons: they have well developed methods for surface water AND sediment porewater (but Superfund sites have been slow to adopt their use), 50% of Tier 1 (i.e., large) Superfund sediment sites are due to PCB contamination (PCBs plus PAHs account for 70%), and they're my area of expertise.

For metals, Peepers are an established passive sampling technology that can be used in surface and porewater, as well as in groundwater, but it is a diffusion sampler rather than a diffusion/sorption or equilibrium sampler (ie. peepers don't accumulate contaminants). Two new diffusion/sorption passive sampling methods are being investigated for metals- DGT and the Gellyfish. These are comparable to the passive samplers for HOCs in that they are time-integrative and have the potential to reduce detection limits, but the chemical process is different. Although the DGT and Gellyfish samplers show potential, their performance in the field is not as well documented as those for HOCs and many people in this field don't think they're ready for wide spread use.

For polar and semi-polar organic contaminants in surface water, POCIS is a well documented passive sampler, but typically it is not used to measure porewater concentrations and it is proprietary. At Navy sites, this is a useful way to measure dissolved munitions concentrations. The samplers for HOCs may have some ability to measure semi-polar compounds as well, but there has been little research to support that use.



This is a familiar image to anyone who has worked on a contaminated sediment site. One of the many reasons that sediment sites are more complicated than other contaminated sites is that the primary risk tends to come from the bioaccumulation of contaminants through the food chain- hydrophobic contaminants sorbed to the sediment make their way into benthic organisms and then accumulate up the food chain. We know that not all of the contaminants sorbed to the sediment are “bioavailable” or able to interact with an organism, which means that the total sediment concentration does not necessarily explain the toxicity or bioaccumulation that is observed. Freely dissolved concentrations are much more closely correlated to the observed toxicity or bioaccumulation. This is NOT because the freely dissolved concentration is the only exposure route, it is because the freely dissolved concentration and the bioavailability of the contaminants are sensitive to the same chemical mechanisms in the sediment.

In the risk assessment or remedial investigation phase of a Superfund site, developing a more accurate understanding of the causes of observed affects in bioassays is critical to developing an accurate and useful CSM. During feasibility studies or remedial design, freely dissolved data will be important for planning some types of remedies and less useful for other types. For example, dredging alternatives are based on mass removal; cleanup levels and action levels will likely be developed based on total sediment concentrations. *In situ* remedies, such as the placement of activated carbon, monitored natural recovery, or capping, require greater accuracy in understanding the bioavailability and exposures at a site. Any clean up metrics at a site will need to be able to measure the bioavailability of the COCs.

Traditional Sampling Methods and Their Limitations

Traditional Surface Water Sampling

"Grab sampling"

1. Collect a volume of water
2. Flocculate colloidal Organic Carbon (OC) and centrifuge to separate
3. Extract the water with solvents
4. Analyze
   – GC-MS, LC-MS, GC-FID, etc.
5. Correct for dissolved OC (DOC)

Key Point Method has logistical challenges, high detection limits, and large uncertainty

Photo courtesy Matt Lambert, U.S. EPA

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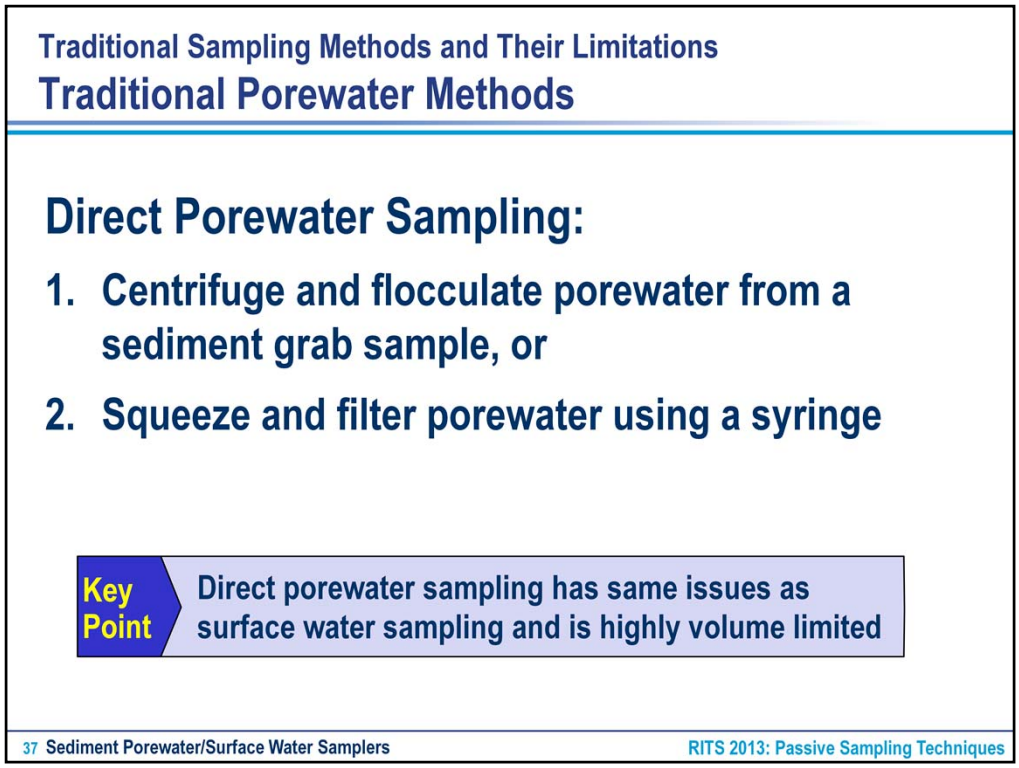
The size of the sample collected strongly influences the detection limits of the analysis, but samples that are larger than a few liters can be difficult to handle properly in many field situations. Colloidal OC must be removed and the water sample extracted with solvents. Often, this requires handling large volumes of water and sample cleanup to remove the water from the solvent and remove any interfering compounds. The analysis can be performed using a variety of standard methods. (These will generally be the same for both traditional sampling and passive sampling.) Finally, the data must be adjusted to account for the effect of dissolved OC (DOC). The correction factors in the literature vary by 100-fold for HOCs, depending on the contaminant and the type of DOC, which adds a large degree of uncertainty to the data.



Direct sampling of sediment porewater involves collecting a sample of sediment and the associated porewater. Once this sample is in the laboratory there are 2 methods to separate the porewater from the sediment. The first is centrifuge the sample, decant the porewater off the compressed sediment, and flocculate the dissolved and colloidal OC. The second is to insert a syringe, fitted with a filter, into the sediment and pull the porewater out of the sediment. Both methods leave some amount of DOC in the water sample. Also, both methods are limited to the amount of porewater in the sediment sample, often only a few milliliters. This means that these 2 methods have the same uncertainties and detection limit issues as surface water sampling, but they have no ability to increase the amount of porewater sampled in order to reduce the detection limits.

Traditional Sampling Methods and Their Limitations

Traditional Porewater Methods

Equilibrium Partitioning (EqP) Modeling:

- Measure the sediment sorbed concentration
- Apply a model:

$$\text{Freely Dissolved Concentration } (C_{iw}) = \frac{\text{Organic Carbon Sorbed Concentration } (C_{iOC})}{\text{Organic Carbon Partitioning Coefficient } (K_{iOC})}$$

Key Point: K_{iOC} values introduce 1-2 orders of magnitude uncertainty

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This is an official EPA method and is widely used at Superfund sediment sites and elsewhere. Measuring the sediment sorbed concentration or the organic carbon (OC) sorbed concentration is a common and cheap laboratory procedure. However, there are many types of organic carbon, such as humic, fulvic, black carbon, etc., that have very different K_{iOC} values. Because this particular model treats all OC types as equal, it introduces about 2 orders of magnitude of uncertainty into the predicted C_{iW} values. More robust models have been proposed to account for these other types of carbon, but difficulties in accurately characterizing the carbon types present in sediment make these other models impractical. An example K_{iOC} value for PCB 77 (3,3',4,4'-PCB) is ~90,000 (log K_{iOC} = 4.96). In other words, at equilibrium, there will be approximately 90,000 PCB77 molecules sorbed to OC for every 1 PCB77 molecule that is freely dissolved. An example for Benzo(a)pyrene is ~490,000 (log K_{iOC} =5.69). These numbers were measured using organic matter standards; sorption to black carbon for both compounds can be ~100 times higher.

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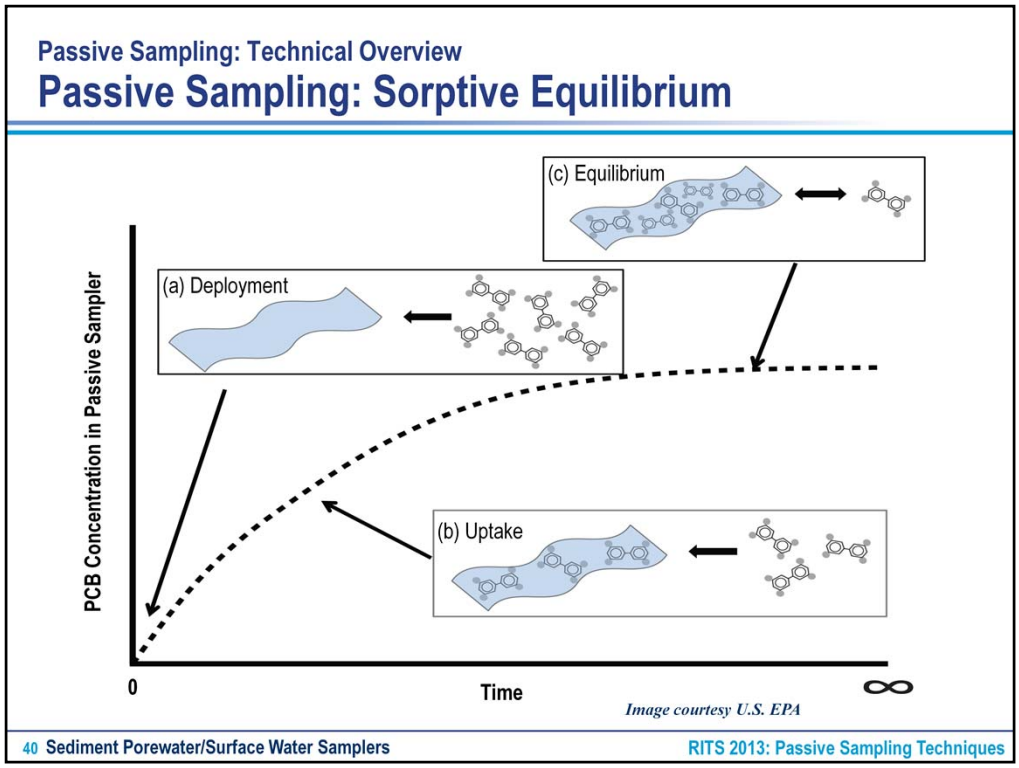
  - Passive Sampling: Technical Overview
  - Case Studies
    - Hunters Point Naval Shipyard, San Francisco, CA
    - Palos Verdes Shelf, Los Angeles, CA



These passive samplers work by absorbing hydrophobic organic contaminants, through the process of diffusion, until the chemical activity of the HOC is the same in the passive sampler and the surrounding environment. Chemical activity is a function of 1) the HOC concentration and 2) how much the HOC "likes" to be dissolved in that particular media (ie., the plastic polymer of the sampler, the water, the sediment OC, etc.). You can think of it as the amount of energy required to dissolve the HOC. It takes a great deal more energy to dissolve PCB 77 in water than it does in polyethylene (PE). In this figure, PCB 77 would be at equilibrium when there is about 6,000,000 PCB 77 molecules in the passive sampler for every 1 PCB 77 molecule in the water. The passive sampler starts with no HOCs in it because it has been cleaned in the laboratory. When first placed in contact with the environmental media, in this case water, it steadily absorbs HOCs until equilibrium is reached. At equilibrium there is some exchange of HOC molecules between the sampler and the environment, but the concentrations remain constant over time. A good rule of thumb is that it takes ~4 weeks for most HOCs to equilibrate with the passive sampler. In reality, lighter compounds, such as phenanthrene, may equilibrate as quickly as 2 weeks, while heavier molecules, such as octachlorinated dibenzo-*p*-dioxin, could take 12 weeks or more. This process is different than that in the diffusion based samplers for groundwater, because the groundwater diffusion bags have distilled water on the inside. At equilibrium, the chemical concentration of the contaminant will be the same in the groundwater and in the diffusion bag.

Passive Sampling: Technical Overview

Non-Depletive Sampling: "The Observer Disturbs the System"

- To be an "equilibrium-based" passive sampler, the measurement cannot shift the balance of equilibrium
- In surface water, the system is the body of water that flows by the sampler and the associated dissolved and colloidal OC and Black Carbon (BC)
- In sediment porewater, the system is the porewater, OC, BC, and minerals close enough to the sampler that the COCs may diffuse through the water and into the sampler

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The general rule of thumb is that passive samplers should not remove more than 5% of the total COC mass in a system in order to be non-depletive. 5% is generally too small of a variability to be detected by our analytical technology. Passive samplers placed in surface water meet this criteria easily. Passive samplers placed directly into the surface sediment to measure porewater concentrations require long time periods to meet this criteria (generally 4-8 weeks, sometimes longer). When used to measure porewater concentrations from sediment grabs or sediment cores, this criteria is easily met provided enough sediment is used relative to the volume of the passive sampler used. We will discuss these two different porewater methods shortly.

Passive Sampling: Technical Overview

What information do you get from passive samplers?

1. The Freely Dissolved Concentration of the HOC
   - It involves the following calculation (the partitioning coefficient (K_{iPS}) must be known):

$$\text{Freely Dissolved Concentration } (C_{iw}) = \frac{\text{Passive Sampler Sorbed Concentration } (C_{iPS})}{\text{Passive Sampler – Water Partitioning Coefficient } (K_{iPS})}$$

Key Point

Passive sampler = factor of 2 estimate of freely dissolved concentrations

Traditional methods = factor of 10-100 estimate of freely dissolved concentrations

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This is the primary reason for using passive samplers- they provide a much more accurate estimate of the freely dissolved concentrations. It's a simple measurement to make, but arriving at a dissolved concentration requires the use of this equation. The PS sorbed concentration is measured. This is easy and accurate to do, and it uses well established methods. The PS-w partitioning coefficient must be known. These are widely available in the academic literature for common HOCs and a list of some of these is included in the EPA fact sheet on passive sampling. A link to this document is available at the end of this powerpoint. These KiPS values are much more accurate than those for OC because plastic polymers have very regular chemical structures and the partitioning of contaminants to these polymers is consistent. The "typical" variability of passive sampling measurements is ~ a factor of 2; the "typical" variability of traditional methods range from a factor of 10 to a factor of 100.

Passive Sampling: Technical Overview

What information do you get from passive samplers? (cont.)

2. Chemical Activity in Lipids, also know as "Biomimicry"
   - Passive samplers accumulate HOCs in a similar manner as simple aquatic and marine organisms, particularly benthic organisms
   - For many test species, a concentration in a passive sampler can be directly related to a tissue concentration

Key Point Passive Samplers = potential surrogate for bioassays

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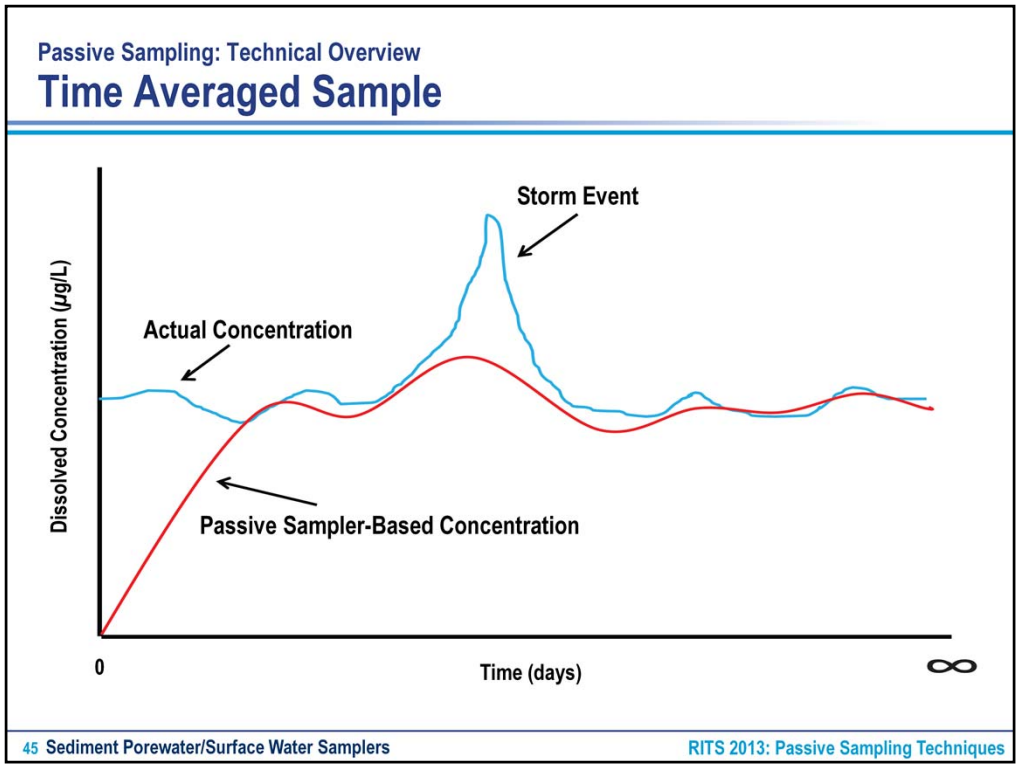
This is a secondary use of passive samplers. They accumulate contaminants in a similar manner as simple organisms. Often, passive sampler measurements correlate strongly to the lipid concentrations measured in test species, particularly benthic organisms. This allows passive samplers to be used as a proxy for some bioassays. However, in order to do this, a comparison study between passive sampling measurements and bioassay tests needs to be performed and this will add a significant cost to using passive samplers. In cases where the contaminants are being metabolized by the test organisms, the bioassay and passive sampler measurements are unlikely to be correlated. The benefit of using passive samplers as a proxy for sediment bioassays is that passive samplers will not die if oxygen concentrations drop too low or if ammonia concentrations get too high. They can be used in a wide range salinity concentrations. Also, they are easier for laboratories to analyze, which may decrease the cost of laboratory analyses.

What information do you get from passive samplers? (cont.)

- Concentration of total PCBs in the polychaete worm *Nereis virens* versus the total PCBs in PE samplers after 28 days of concurrent exposure to New Bedford Harbor sediments



This is a hypothetical concentration curve. The x-axis is time and the y-axis is the dissolved concentration in μg/L. The actual concentration is blue and the concentration that would be measured by a passive sampling device is in red. Once the sampler has reached equilibrium, it adjusts slowly to any changes in the actual dissolved concentration in the adjacent water. Thus, when the storm event increases the concentration of the contaminant due to run-off, the passive sampler absorbs more contaminant, but it is also still influenced by the pre-storm concentration.

Passive Sampling: Technical Overview

Cost Estimate for Different Types of Sampling

- Cost estimates provided courtesy of an independent laboratory in dollars per sample

Type of Sample	Materials	Chemical Analysis	Total
Water (5 L by conventional method)	< $5	$525	$530
Semi-permeable Membrane Device (SPMD)	$505	$400	$905
Polyethylene (PE)	~ $5	$375	$380
Polyoxymethylene (POM)	~ $50	$375	$425
Solid Phase Micro-extraction (SPME)	~ $35	$275	$310

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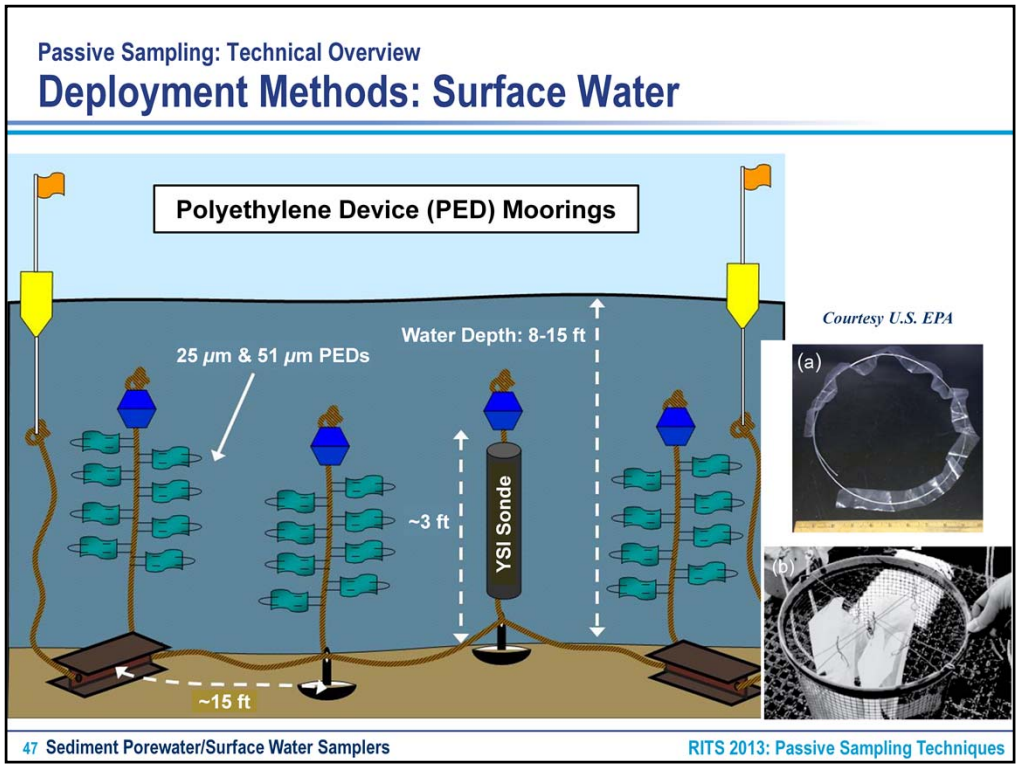
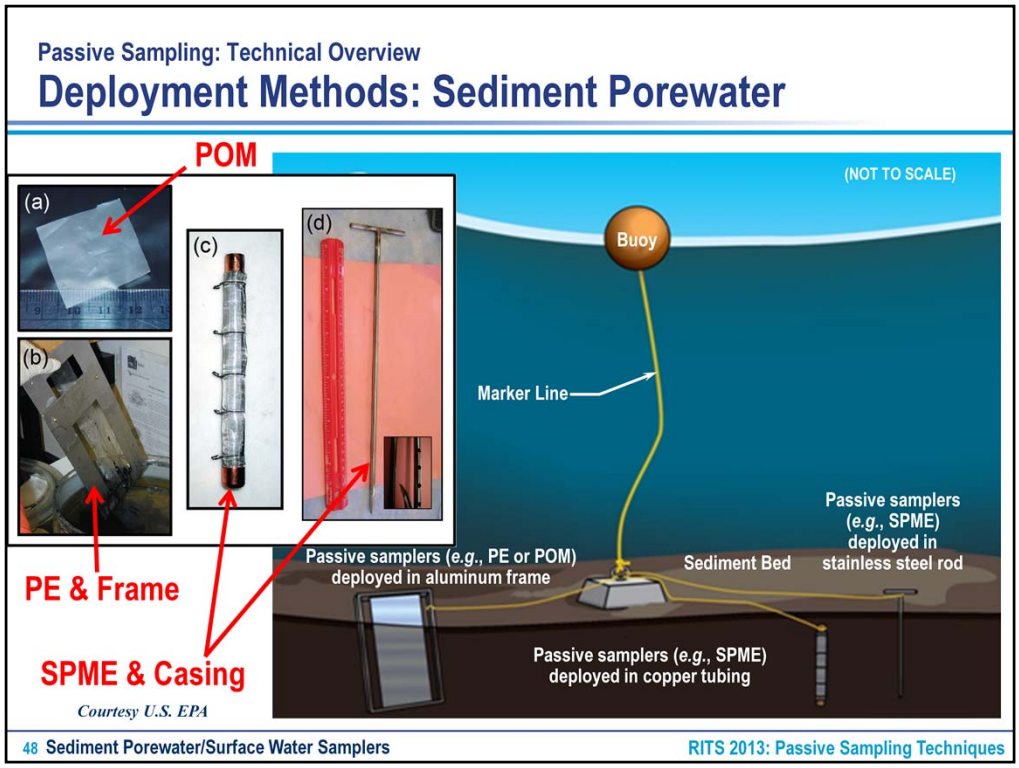
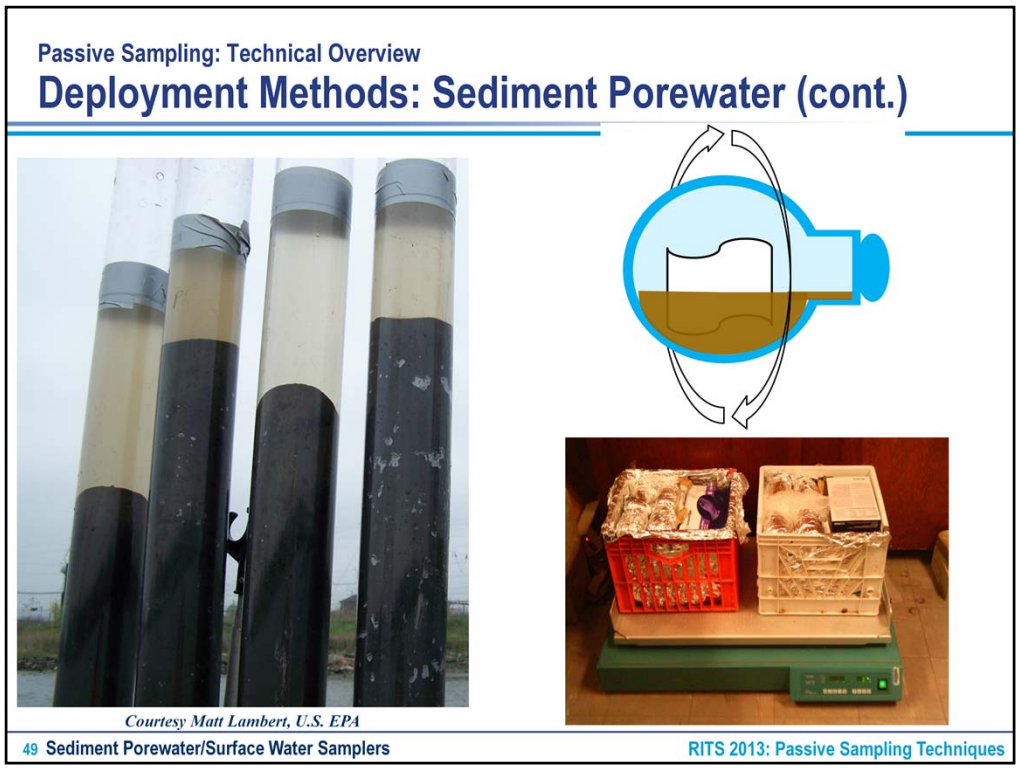
These costs are associated with the preparation and analysis of the passive samplers. Passive samplers require at least 2 days of field work to deploy and retrieve the samplers. However, it is typically possible to deploy and retrieve many more sample stations when using passive samplers than traditional sampling methods. Whether there are cost savings associated with the field work for passive sampling, relative to the traditional methods, depends on the site, the number of stations, distance between stations, etc. Despite the decreased cost in analytics, there are some ways in which passive sampling could incur higher costs. One example is that contract laboratories are not equally skilled in passive sampling and most studies using passive sampling have either relied on research experts to analyze the samples or hired experts to help plan the study and oversee the contract laboratory. Also, if a comparison study is deemed necessary, there will be a high up-front cost associated with the comparison study.



There are a variety of methods of deployment for surface water passive samplers. The set up in the cartoon shows a high sampling resolution setup. Alternatively, the passive samplers could be deployed on one line with its own anchor and its own buoy. Water column samplers could also be deployed concurrently on the same anchor as porewater samplers, as shown in the next slide. The pictures on the right indicate 2 methods of attaching the polyethylene (PE) or polyoxymethylene (POM) samplers to the deployment line. In image (a) the sampler is strung on a wire. In image (b) the sampler is contained in a fish exposure cage. SPMEs, not pictured here, are generally protected in a copper or steel envelop or tube.



This cartoon illustrates the deployment of porewater passive samplers. This method would generally be deployed by a diver or by wading. The images on the left show different methods for supporting the samplers and inserting them into the sediment. A few simple modifications of these holders also allow porewater passive samplers to be deployed in deep water from a vessel. I will show some images of this type of deployment in the Palos Verdes Shelf case study.



I mentioned earlier in the talk that if you were taking sediment cores or grabs for other types of analyses, you could still use passive samplers to generate much more accurate measures of porewater concentrations. The method works by taking a known mass of sediment, typically 1-5 grams, and adding it to a small, clean container. This amount of sediment generally leaves plenty of sample to run other analyses and it is generally enough sediment to be "non-depletive," as we discussed earlier. A small volume of passive sampler and a enough distilled water to remove all air from the container are added to the sediment sample. The addition of the sampler AND of the distilled water together, must remove less than 5% of the mass of sediment contaminants in order to be non-depletive and produce an accurate measure of the porewater concentration. The sample container is then placed on a shaker table and agitated for several weeks until equilibrium is reached. This method of measuring of dissolved concentration tends to have much lower sampler variability than any other type of porewater measurement. However, it is not influenced by natural forces such as tidal fluctuations and groundwater flow. Also, sediment coring can disturb the sediment characteristics such as the redox potential. This is not generally an issue for HOCs, but it may be if you are looking at metals or SVOCs.

Passive Sampling: Technical Overview

Deployment Time

aka Has the sampler reached equilibrium?

The time to equilibrium is affected by

1. the polymer thickness,
2. the temperature and salinity of the water,
3. advection of water adjacent to the polymer, and
4. algal growth (biofouling) on the sampler.

The sampler must be at equilibrium in order to make accurate measurements

– Unless you know how "close" to equilibrium the sampler is

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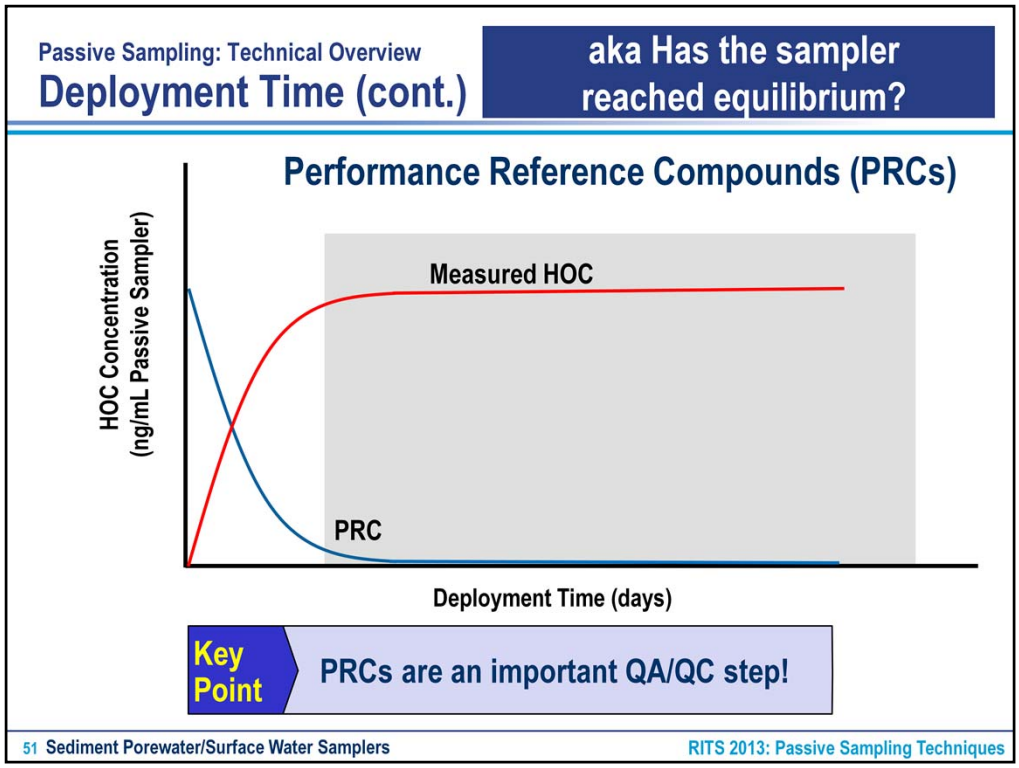
Throughout this talk, I have emphasized that these samplers are equilibrium based samplers. It is therefore critical to obtaining an accurate measurement that these samplers be in equilibrium with the porewater or surface water that they are measuring and it takes time for them to reach equilibrium. The amount of time it takes to reach equilibrium is influenced by the polymer thickness; thicker polymers have smaller surface area to volume ratios and therefore take longer to reach equilibrium. Lower temperatures slow down the transfer of contaminants into the sampler and cause longer equilibrium times. Higher salinities can decrease equilibrium times. The movement of water adjacent to the sampler can greatly decrease equilibrium times. The slow rates of water movement in porewater is one of the biggest reasons that porewater measurements take much longer to achieve equilibrium. Biofouling is also a big question when using passive samplers. The growth of organisms on a sampler will increase the length of time to equilibrium.

It is possible to adjust the measurement to equilibrium, if you know how far out of equilibrium the sampler is. See the next slide.



Performance Reference Compounds (PRCs) are the most common and most applicable method for determining if the sampler has reached equilibrium. PRCs are compounds that are similar in structure to the contaminants that are being measured, but do not exist in the environment being investigated. Because these PRCs are not found in the environment, the vast majority will diffuse out of the passive sampler. PRCs are loaded into the passive sampler in the laboratory prior to deployment. When the passive sampler is deployed, the PRCs diffuse out of the sampler at the same rate that the HOCs diffuse in. When the sampler is retrieved, it is analyzed for both the contaminants of concern and the PRCs. If the PRCs are not detected, then equilibrium was reached. If the PRCs are detected, you can use the concentration of the PRC to calculate what the equilibrium concentration of your contaminants is. The gray box above indicates the point at which the sampler would typically be considered in equilibrium. This is a critical step for ensuring the accuracy of your data.

PRCs may be congeners that are similar in size, but not found at the site. For example, a non-aroclor PCB congener could be used at a site where there is Aroclor contamination. In other cases, the PRCs used are isotopically labeled versions of the same contaminants that are being measured. You do not need to have a PRC for every compound that you wish to measure, but you should have several compounds that cover all of the contaminant classes and the range of solubilities of the contaminants that you wish to measure.

Passive Sampling: Technical Overview

Sample Extraction and Analysis

- HOCs are typically extracted from passive samplers using solvents at room temperature for 24 – 48 hrs
  - Soxhlet Extractors or Accelerated Solvent Extractors are not necessary
  - SPMEs can be inserted directly into a GC without any extraction or cleanup
  - Fewer cleanup steps are necessary relative to sediment, water, or tissue extractions
- Sample analysis uses the same methods as traditional samples

Key Point: Passive samplers generally use fewer chemicals and are easier to prepare for analysis, making them a sustainable, green remediation technology

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Sample extraction and analysis is the last step in the passive sampling process and it is nearly identical to the analytical process for water or sediment analyses, once they have been extracted. Some important differences are the methods used to extract passive samplers. Passive samplers are efficiently extracted by room temperature organic solvents over 24-48 hours. SPME's may be extracted this way, but may also be inserted directly into a Gas Chromatograph/Mass Spectrometer and "thermally" extracted. Also, passive sampler extracts require very little clean up because they only absorb HOCs. Because these extraction methods are simple and do not require significant clean up, they use less organic solvents and are typically more green and sustainable.

Passive Sampling: Technical Overview

Passive Sampling Method Limitations

- There is no standardized method to use, which creates two primary hurdles:
  1. Regulatory acceptance – to date, the use of passive samplers has been negotiated between the parties involved at each site and typically a pilot study to demonstrate the acceptability of the technology has been required
  2. There is a small pool of experienced commercial laboratories
- Long deployment times
  - Plenty of opportunity for mother nature and pranksters to steal your samplers; anchor them well

53 Sediment Porewater/Surface Water Samplers RITS 2013: Passive Sampling Techniques

The lack of a standard method is the biggest hurdle to using these samplers at a Superfund site. This does not mean that the methods for using passive samplers are not well established or accepted, but there is no official standard method that has been validated by a multi-laboratory study and is endorsed by the EPA, the American Society for Testing and Materials, or other federal agency. To date, the Superfund sites that have used these samplers have done so on a case-by-case basis; regulatory acceptance varies by region, state, program office, and decision maker. Also the lack of a standard method puts greater onus on the RPMs during the development of the sampling program and in over-seeing the sampling and analysis. Often a research expert is engaged who can help the RPM with the planning and oversight.

Another limitation is the long deployment times that are necessary. This generally does not affect the amount of work required to complete the sampling, but it does not allow for “real time” analysis. Also, long deployment times increase the likelihood that the samplers might be damaged in storms or cut free by pranksters.

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Hunters Point Shipyard - Site History & Background

- Large, active Superfund site, currently undergoing cleanup
- Intertidal zone at South Basin
- PCB hot spot, 1-10 ppm
- Cohesive sediment with low erosion rate, net depositional (1 cm/year)

55 Case Studies – Hunters Point, San Francisco, CA RITS 2013: Passive Sampling Techniques

This site is located on the south side of San Francisco, in San Francisco Bay. The site was selected as a SERDP/ESTCP study site for using Activated Carbon (AC) to reduce the bioavailability of the PCBs in sediment. The application of AC occurred in an intertidal mudflat on the south side of the Hunters Point Naval Shipyard.

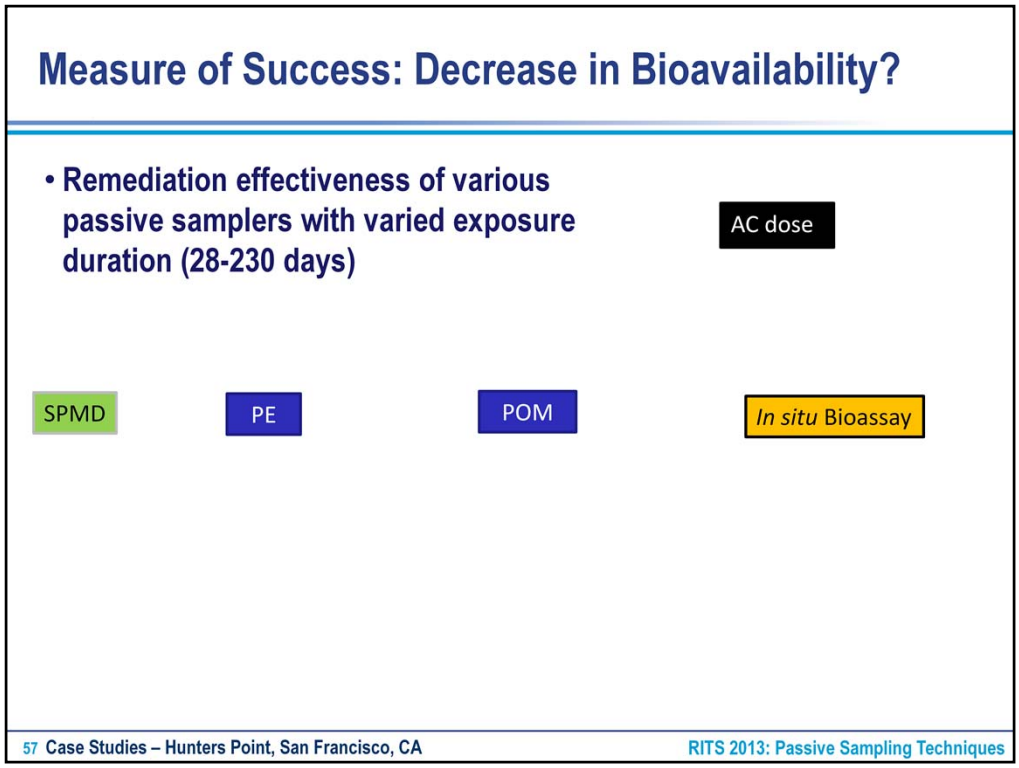
Pilot Study

- **Plot area: 34 m^2**
- **PCB level: 1-2 ppm**

Plot	
A and **D**	Activated Carbon(AC) mixing with rotovator
B and C	Control
F	AC mixing with injector
E	Reference for benthic community survey

56 Case Studies – Hunters Point, San Francisco, CA RITS 2013: Passive Sampling Techniques

The pilot study involved 6 small plots of sediment, three of which were amended with carbon, two of which were disturbed using the AC application mechanisms (the rotovator and the injector), but no AC was added, and one plot was left undisturbed as a reference for benthic community surveys.



Traditional sampling methods were not sufficient to measure the efficacy of the AC treatment. This study used SPMDs (also known as "fat bags," these are the early prototype passive samplers discussed earlier), PE, POM, and an *in situ* bioassay to assess the bioavailability of the PCBs before, shortly after, and 5 years after the application of AC. This allowed them to compare the passive sampling methods to the bioassay and the SPMD method. They also used small push cores to recover sediments and analyze for the amount of AC present.

One important limitation of this study is that all of these samplers or assays were not used during every sampling event.

Lessons Learned

- Similar performances and good correlations among passive samplers (SPMD, PE, and POM)
  - Passive samplers responded proportionally to AC applications
  - PE somewhat easier to handle and more versatile
- Local sediment heterogeneity affected measured concentrations
  - Need adequate spatial controls to assess sorbent amendment performance
- Sorbent amendment effectiveness improves with time, thus temporal assessments needed as well

58 Case Studies – Hunters Point, San Francisco, CA RITS 2013: Passive Sampling Techniques

This study set out to investigate the efficacy of AC amendments in reducing bioavailability and the utility of passive samplers in quantifying these effects. The uptake measured by all three of the passive samplers varied proportionally to the uptake in bioassays, but a quantitative comparison of these measurements is not currently available. The passive samplers were sensitive to changes in the bioavailability caused by the addition of AC.

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Site Background for Palos Verdes Shelf Case Study

- Deep water marine site (~60m)
- COCs – PCBs, DDT & breakdown products
- Montrose Chemical Corporation discharged to local sewers from 1947 to 1983
- Two passive sampler studies have been done at this site:
  - Water column and in situ porewater monitoring
  - Ex situ sediment core analysis

60 Case Studies – Palos Verdes Shelf, Los Angeles, CA RITS 2013: Passive Sampling Techniques

The risks at this case study site are driven by consumption of fish contaminated with PCBs, DDT, and DDT breakdown products. We'll look at 2 different passive sampling efforts that are on-going at this site. Both studies are a collaboration between the Superfund program and a federal research program, but the site does intend to use the data generated by these studies to inform their remedy decision. They are not pilot studies or passive sampling transitioning studies.

Water Column and *In Situ* Porewater Monitoring

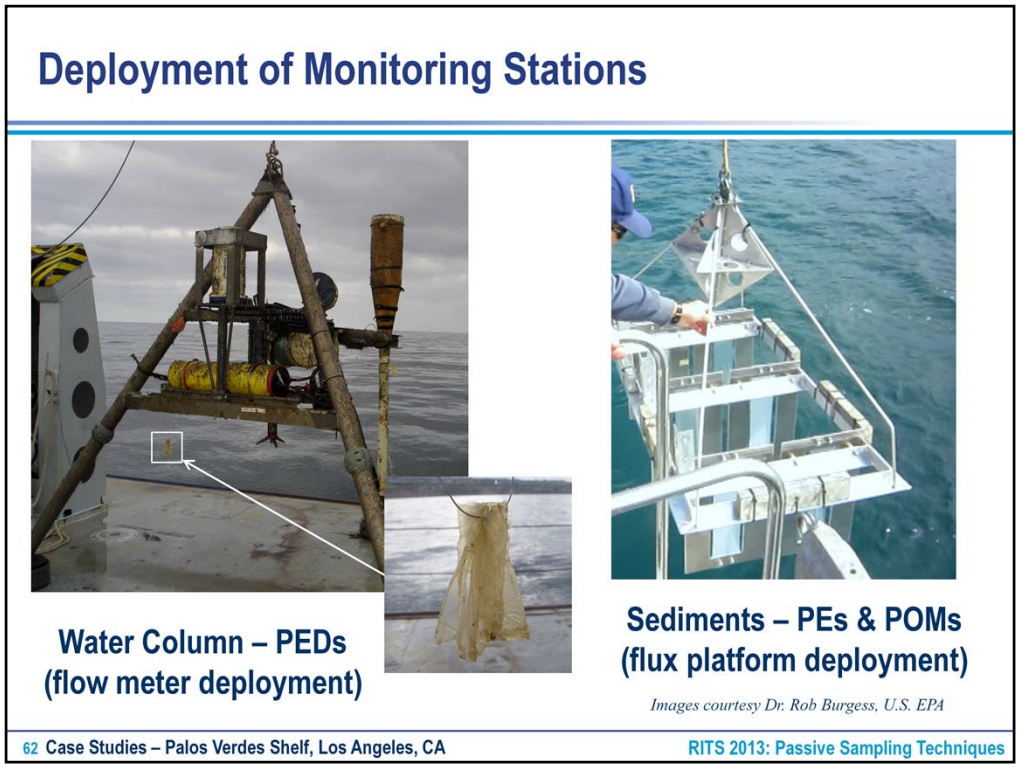
- 7 water column stations and 5 sediment stations

Objectives:

- Monitor water column concentrations before, during, and after remediation
- Determine direction and magnitude of COC flux
- Compare applicability of SPME, PE, and POM at this site

61 Case Studies – Palos Verdes Shelf, Los Angeles, CA RITS 2013: Passive Sampling Techniques

The first study is using *in situ* sampling to measure surface water and porewater concentrations with the goals of monitoring, calculating a flux, and comparing the usefulness of SPME, PE, and POM.



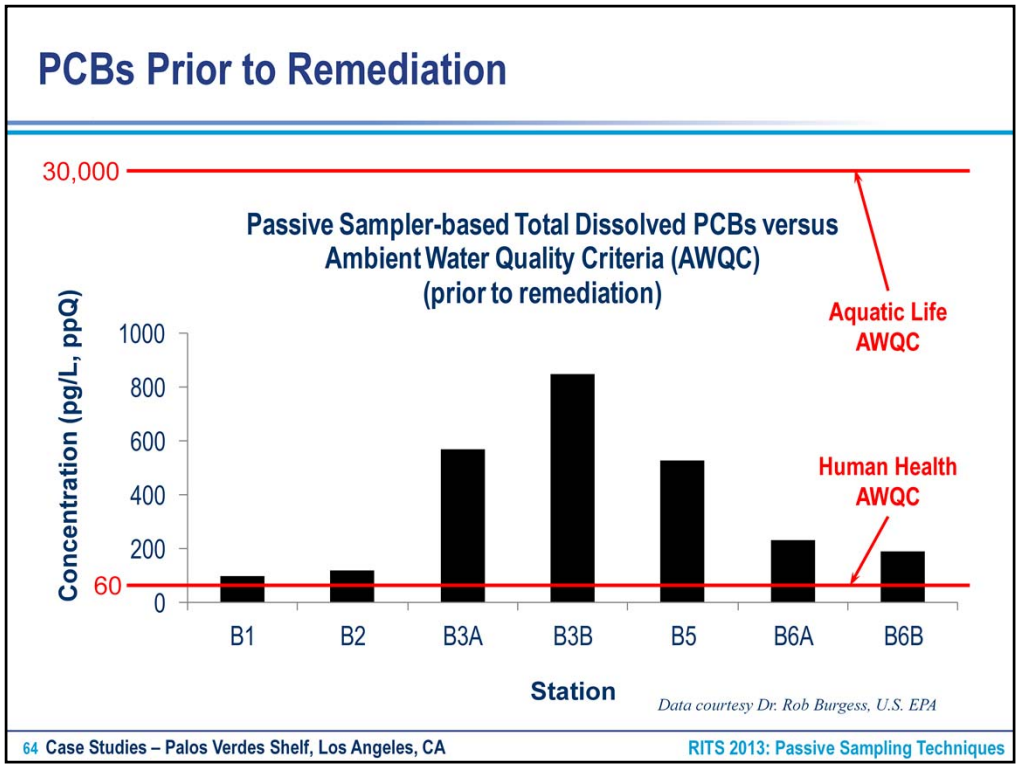
On the left, and in the inset, is an image of the deepest water column sampler. These samplers were attached to an array of other oceanographic instruments and were about 0.5 m off the bottom when deployed. The image on the right shows the porewater deployment of PE and POM from a vessel.

Sediment Monitoring Platform in Place

Image courtesy Dr. Rob Burgess, U.S. EPA

63 Case Studies – Palos Verdes Shelf, Los Angeles, CA RITS 2013: Passive Sampling Techniques

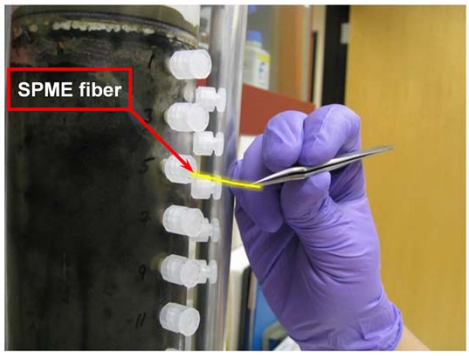
Here is an image of the porewater deployment. Images were taken from a remotely operated vehicle to ensure that the samplers were properly exposed to the sediment. The depth of passive sampler penetration can be adjusted by changing the weight on the frame and by adjusting the position of the sampler relative to the frame.



Here are the results from the water column samplers. The results from the sediment samplers are not yet available. On the x-axis is the sampling station name and on the y-axis is the freely dissolved concentration of PCBs in pg/L or parts per **quadrillion** (ppQ). That is not a typo. The limits of quantitation for this study were less than 60 ppQ AWQC for total PCBs. These measurements showed that the bottom water concentrations are above the Human Health AWQC, but are well below the aquatic life AWQC. Once the porewater concentrations are available, the study will be able to calculate the flux of PCBs and DDT into or out of the sediments.

AWQC = Ambient Water Quality Criteria

In Situ Sediment Core Analysis: SPME



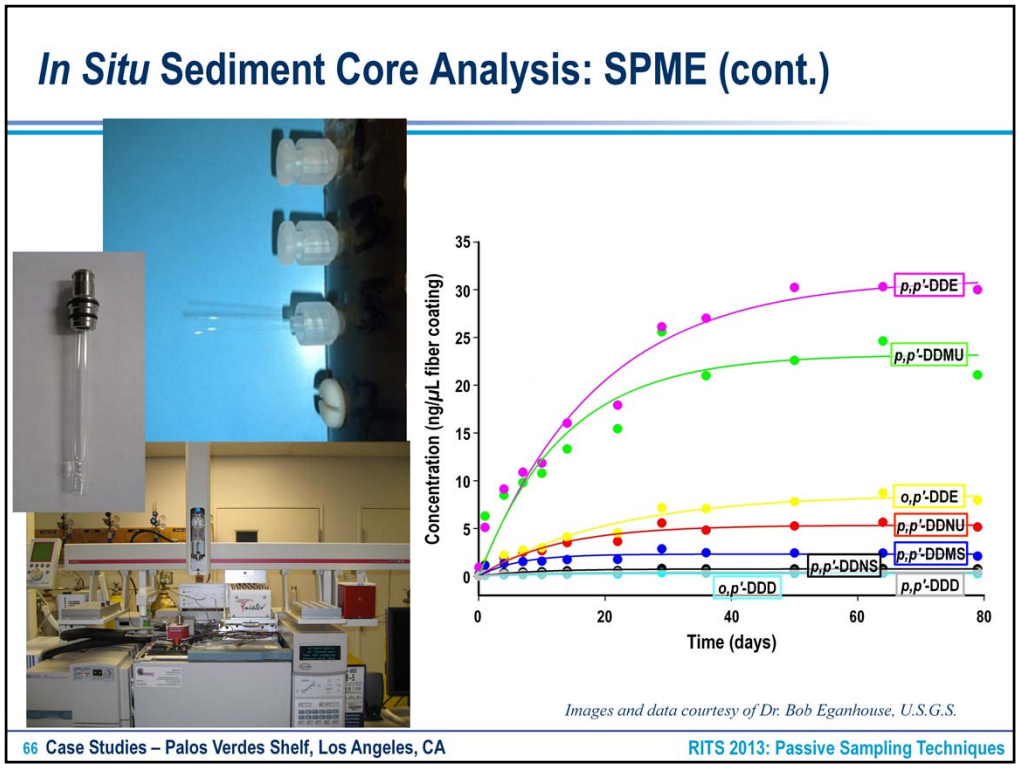
Objective

- **Investigate the factors controlling reductive dechlorination rates of *p,p'*-DDE (microbiological, chemical, physical) and assess bioavailability of DDT compounds to indigenous fauna**

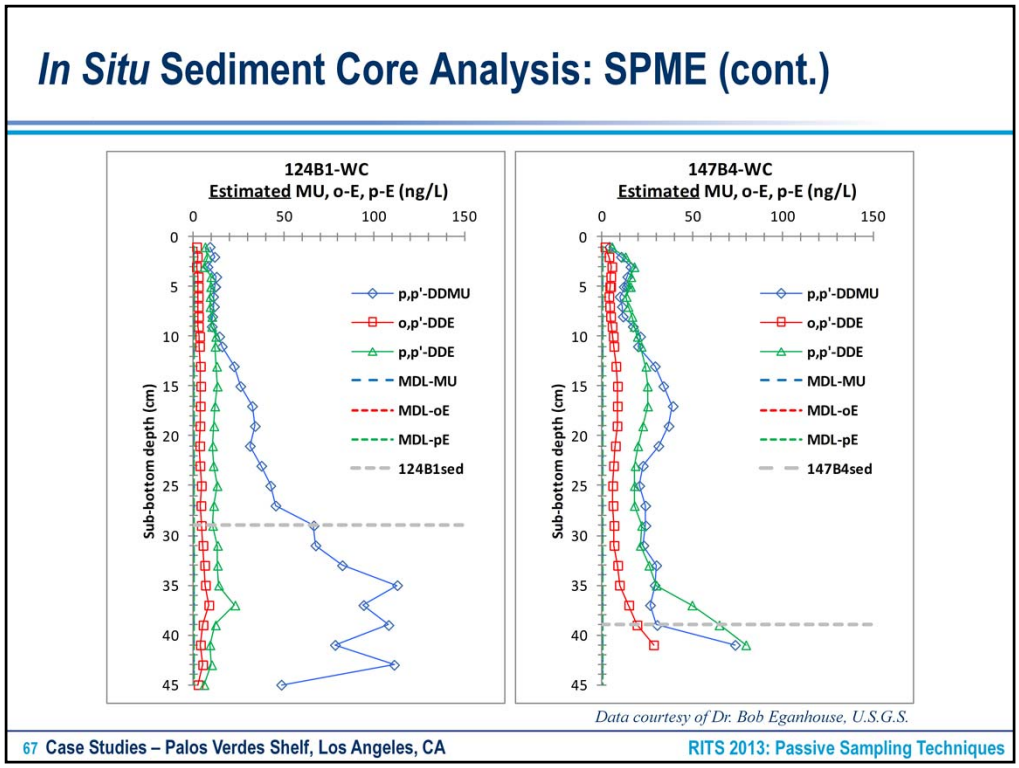
Images courtesy of Dr. Bob Eganhouse, U.S.G.S.

65 Case Studies – Palos Verdes Shelf, Los Angeles, CA RITS 2013: Passive Sampling Techniques

In this second Palos Verdes Shelf study, 3 sediment box cores were taken and were subdivided into six smaller cores. Porewater measurements were taken from one of these cores using SPME fibers in order to assess the bioavailability of DDT compounds to benthic organisms and to assess the factors driving the chemical breakdown of these compounds.



The SPME fibers were inserted into the sediment core through plastic "ports." The cores were then left to come to equilibrium. They were not shaken in the manner that we discussed earlier because the study was interested in measuring a high resolution, downcore profile of DDT compound concentrations. An equilibrium experiment was also performed using another sediment core from this site in order to determine the length of time necessary to achieve equilibrium. This figure shows time in days on the x-axis and the concentration of DDT compounds in ng/μL of SPME coating on the y-axis. It shows that all compounds have achieved equilibrium between 37 and 50 days.



Here are the results for two of the sediment cores. The right hand core is closer to the source of the PCBs and DDT. The y-axis is depth in the sediment core and the x-axis is the concentration of DDT compounds in ng/L or parts per trillion. These results indicate that the dechlorination of DDT at the left hand site is 2-3 times greater than at the right hand site. At both sites, it is clear that the highly contaminated sediment is being buried by cleaner sediment. This data will be used to calculate fluxes from deeper sediments and to assess the process of natural attenuation.

Advantages

RPM perspective

- Passive sampling data has the potential to explain the link between the sediment concentrations and the fish tissue concentrations
- Having passive sampler data in the RI phase may have allowed the RAOs to be better tailored to this site

Principle Investigator perspective

- PE, POM, & SPME are extremely sensitive
- *In situ* equilibration of PE & POM is feasible in deep water, when using PRCs
- Direct exposure of SPME to sediment is not problematic
- High spatial resolution in cores is possible because sampler is small

Limitations

- Relatively long equilibration times are required for HOCs; PRCs are necessary!
- K_{fiber}, the water-SPME partition coefficient, must be determined for each fiber/analyte combination
  - Known for common COCs, but unknown for DDT breakdown products
- SPME fiber coatings are limited
  - Detection limits of ~ parts per trillion versus detection limits of parts per quadrillion for PE and POM

69 Case Studies – Palos Verdes Shelf, Los Angeles, CA RITS 2013: Passive Sampling Techniques

In situ equilibration of SPMEs is not presently feasible in deep water

Presentation Overview

- Introduction
- Groundwater Samplers
- Transition to Passive Samplers
- Sediment Porewater/Surface Water Samplers
- ► Summary

Take-Home Points – Groundwater

- Passive sampling should be considered at GW monitoring sites
  - Typically saves money and more sustainable
  - Reduces field sampling variability
  - Enables sampling from discrete intervals
  - Requires transition study
  - Is not a good fit for every site or analyte
  - Passive
  - One line of evidence in addition to traditional sampling

Take-Home Points – Sediment Porewater/Surface Water

- Passive sampling is a significant improvement over traditional methods, though not a perfect method
  - Better detection limits, less uncertainty
  - Better able to explain toxicity results
  - Concentrations measured are more similar to those that organisms are exposed to
  - Cost less than traditional methods
  - Long deployment times
  - One line of evidence in addition to traditional sampling

References – Groundwater

- EPA. 2000. Environmental Technology Verification Report, Groundwater Sampling Technologies. EPA/600/R-00/091.
- ITRC. 2006. Technology Overview of Passive Sampler Technologies. DSP-4.
- ITRC. 2007. Protocol for Use of Five Passive Samplers to Sample for a Variety of Contaminants in Groundwater. DSP-5.
- EPA Clu-In Site on Passive Samplers
- USACE and AFCEE. 2005. Results Report for the Demonstration of No-Purge Groundwater Sampling Devices at Former McClellan Air Force Base, California.
- DON Guidance for Planning and Optimizing Monitoring Strategies (Aug 2008)

References – Sediment Porewater/Surface Water

- EPA. 2012. Sediment Assessment and Monitoring Sheet- Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites. OSWER Directive 9200.1-110 FS
  - This document contains a useful list of references for more detailed information. The Appendix contains a list of partitioning coefficients for measuring common HOCs with SPME, PE, and POM.
- Navy Interactive Sediment Remedy Assessment Portal (ISRAP)
- ESTCP. 2012. Passive PE Sampling in Support of *In Situ* Remediation of Contaminated Sediments: Standard Operating Procedure for PE Analysis. ESTCP Project ER-200915.
- ITRC. 2011. Incorporating Bioavailability Considerations into the Evaluation of Contaminated Sediment Sites. CS-1. Section 4 & Appendix C.

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Note that the ITRC document describes SPMDs, an older version of passive samplers for HOCs in surface water that is still used at Superfund sites and elsewhere. These are more expensive than the passive samplers discussed here and typically are not used to measure porewater concentrations, but they provide similar quality data as those discussed here.

Passive GW Samplers Reference Info

For your reference:

- ARTT workgroup will present their Passive Sampler Selection Tech Transfer Tool this summer
- RITS Fall 2000: Low-Cost Diffusion Samplers for VOCs in Groundwater
- RITS Fall 2007: Long Term Site Management
- ARTT / EXWC brownbag presentation in 2008 Innovations in Contaminant Monitoring in Groundwater
- CECOS Optimizing Remedy Selection and Site Closeout
- Interstate Technology & Regulatory Council (ITRC) Diffusion and Passive Sampling Webpage

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The next 3 slides are for reference

In addition to your ARTT workgroup member, Josh.Fortenberry@navy.mil at EXWC is a good POC if you have questions about using passive samplers.

To find the RITS and ITRC page, just use your favorite internet search tool.

Technology Transfer (T2) Tools

- **T2 Products:**
  - **Passive Sampler Selection ER T2 Tool Coming**
    - Excel based, just GW initially
    - ARTT Workgroup will provide brown bag presentation
  - **Contaminated Sediments Web Page**
    - Coastal Contamination Migration Tool
    - ISRAP Tool
    - SPME Tool
    - Benthic Flux Sampling Device
  - **Passive Diffusion Sampler Tool**
    - Update pending in 2013, legacy PDB focused tool available upon request

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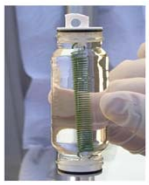
Contact Josh Fortenberry (NAVFAC EXWC) to get access to the Passive Diffusion Sampler Tool on the private side of the ERB website. Contractors are allowed to access it.

Reference: Grab Sampling Technologies

- **HydraSleeve™**
  - Lay flat LDPE tube, weight attached at the lower end, lowered to desired depth; tube fills when sampler is pulled up in the well
  - 2" and 4" diameter (30" length) and custom sizes available
  - Must consider screen length and depth of borehole when determining HydraSleeve™ size to ensure appropriate screened interval is sampled
  - HydraSleeve™ sampler should be lowered into the well slowly to minimize disturbance

- **Snap Sampler™**
  - Deployed open in a well; snap mechanism seals the sampler in the well with trigger line
  - High quality sample – not exposed to air
  - No purge waste to dispose
  - Plastic dedicated Snap Samplers™ house commercially available sample bottles (40, 125, and 350 mL)

Images courtesy ITRC



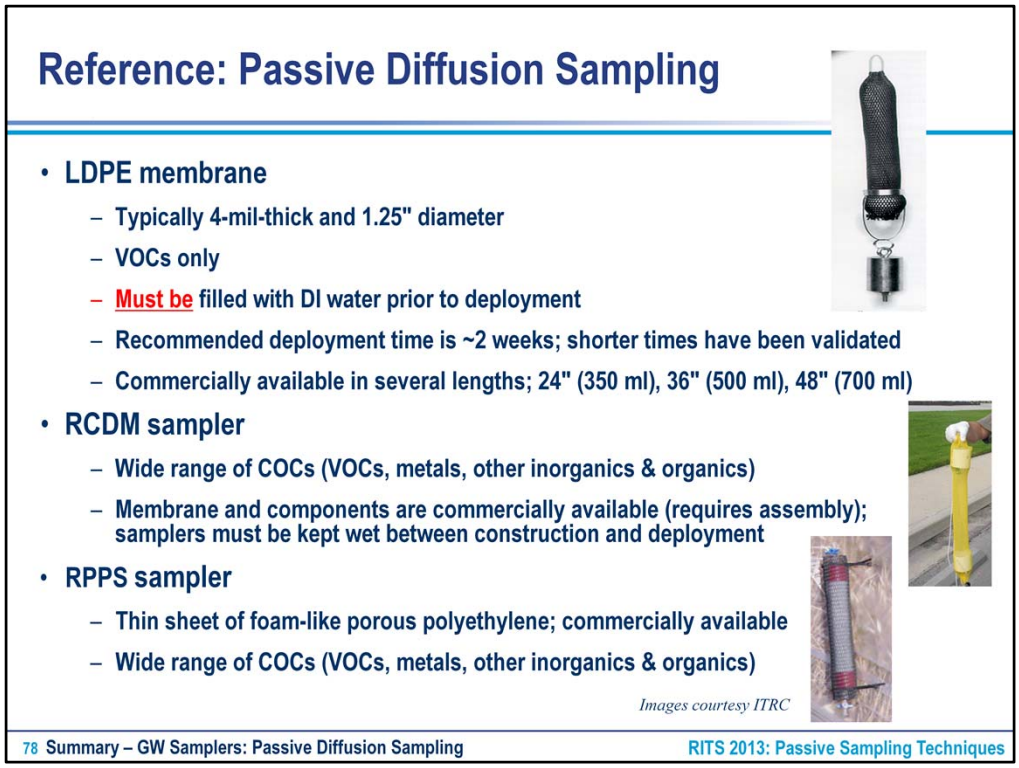
77 Summary – GW Samplers: Grab Sampling RITS 2013: Passive Sampling Techniques

A few notes and lessons learned on the HydraSleeve that were documented in the HydraSleeve evaluation report we put together for EPA.

The HydraSleeve SOP should be consulted prior to use – they are not as easy to successfully deploy as you would think. An improperly filled HydraSleeve is a commonly reported problem.

Multiple HydraSleeve samplers can be attached concurrently to the same tether in the same well. These samplers may either be placed at the same interval (*i.e.* "clustered") to accommodate larger sample volumes or at different discrete intervals (*i.e.* "sequentially") in order to sample a larger number of discrete points within the site. Clustered samplers should all be tied to a single tether, which has the weight suspended from it. Care must be taken to assure that a cluster's diameter is less than the inner diameter of the monitoring well.

Higher total metals concentrations may be observed in the HydraSleeve samples due to the sampling technique. The HydraSleeve is commonly deployed so that the weight at the base of the sampler rests on the bottom of the well. If any fines have settled in the base of the well, they could be disturbed and forced into suspension within the water column during deployment, resulting in elevated sample turbidity if not allowed to re-settle prior to sample collection. To minimize this potential issue in future sampling events, the weight at the base of the HydraSleeve sampler should be suspended just above the base of the well to eliminate or minimize agitation of any fines that may have settled out. In addition, the HydraSleeve sampler should be lowered into the well slowly to minimize disturbance to the water column.



These are commonly called passive diffusion bag (PDB) samplers. They have to be used in a screened interval or open bore. The water passing by is what matters. Results are skewed if there is vertical flow within the borehole.

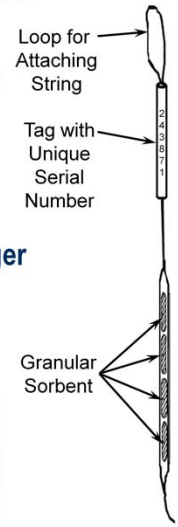
Can attach multiple PDBs in series (see inset figure) to evaluate multiple zones and perform vertical profiling within a well screen. The results from vertical profiling can be used to target future monitoring or identify remediation zones. Also useful in fractured bedrock monitoring to identify fracture zones with high dissolved chemical concentrations.

Does require multiple site visits for sampling – one to deploy and one to recover.

Samplers are brought to surface where contents are decanted into appropriate sample containers.

Reference: Passive Diffusion/Sorption Sampling

- Typically constructed of a permeable hydrophobic membrane that houses engineered sorbents
  - Compounds partition across membrane and are captured by the sorbents
- Screening tool – focused on characterization rather than LTM
- Can detect VOCs, SVOCs, explosives, PCBs
- Narrow diameter enables deployment in wells 0.5" dia. and larger
- Typical period of 15 minutes to 4 hours
- Sample results give total mass desorbed; requires calibration with measured concentration in wells
- Example – GORE® module



Images courtesy ITRC

79 Summary – GW Samplers: Passive Diffusion/Sorption Sampling RITS 2013: Passive Sampling Techniques

This can be used as a screening tool designed to focus subsequent sampling efforts.

Also, the Gore Module fits into a thermal desorption apparatus for analysis by GC/MS