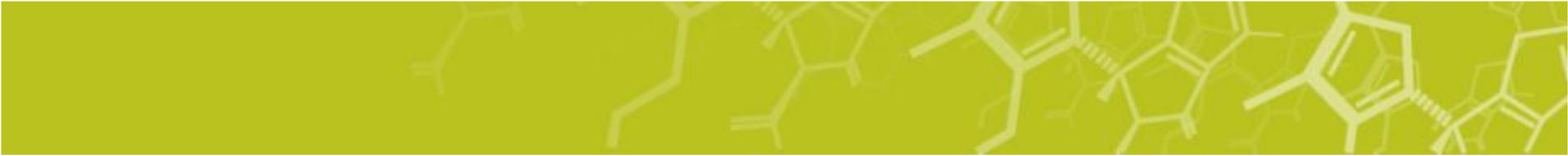




Overview of Diffusive and Accumulation Passive Sampling Options for Marine and Freshwater Environments

Maxxam
A Bureau Veritas Group Company

Dr. Heather L. Lord



Outline

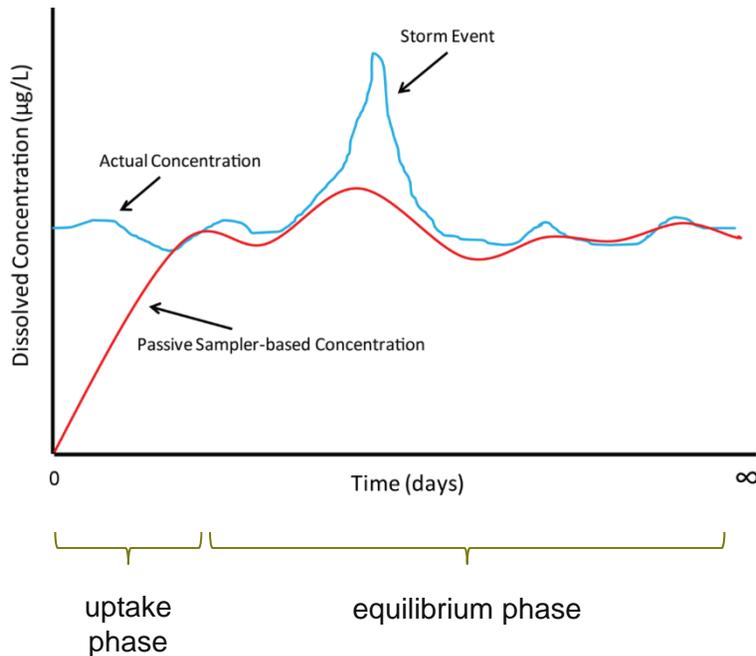
- Introduction to passive sampling for water analysis
- Overview of passive sampling devices for:
 - Volatiles
 - Metals
 - Semi-volatiles
 - Polars
- Case Studies



Introduction to Passive Sampling

How a water passive sampler works:

Red line is the passive sampler concentration



Reference: EPA - Office of Research and Development, and Office of Superfund Remediation & Technology Innovation, OSWER Directive 9200.1-110 FS

Water concentration is estimated from the passive sampler concentration based on the compound specific partition coefficient K_{SW}

$$C_W = \frac{C_{PS}}{K_{SW}}$$

- Only valid once equilibrium is reached!
- Before equilibrium, sampling rate must also be measured and included
- After equilibrium, changes in C_{PS} reflect moving average of past water concentrations

Goal: A representative picture of water quality

Passive sampling addresses the following:

- 1. Where concentrations vary over a timeframe of days to weeks, a discrete grab sample may not accurately represent water quality**
 - Performing multiple grab samples over a given time is costly and will not necessarily capture episodic events
- 2. Reports the freely dissolved concentration**
 - Presence of sediment in the water can skew grab sample results
- 3. Detection limits for estimated water concentrations typically lower than what is achievable with grab samples.**
- 4. For aquatic monitoring at trace levels, a very large volume of water may need to be taken/shipped for grab samples**
 - Passive sampler shipment is typically easier and extracted compounds are (usually) stabilized

Available Guidance Documents

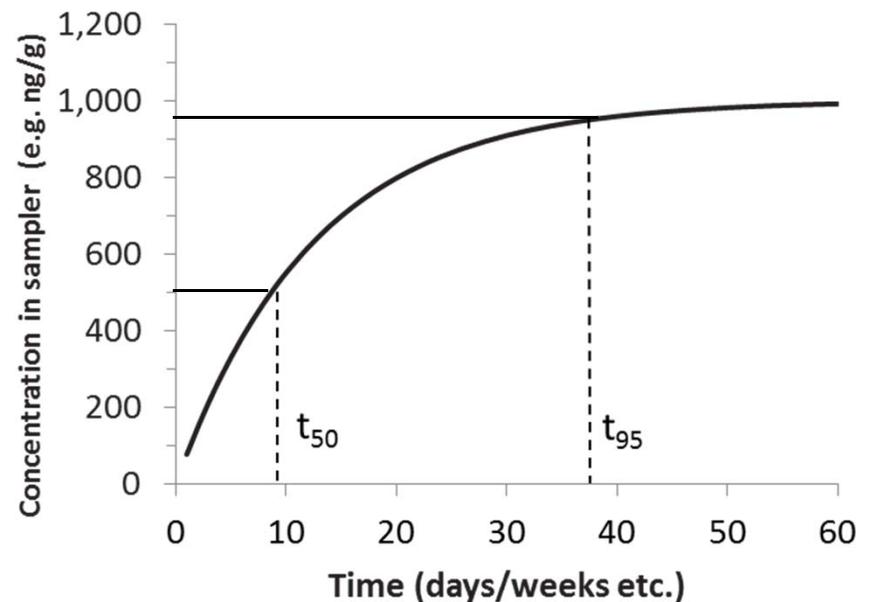
- **ISO 5667-12: Water quality Sampling Part 23: Guidance on passive sampling in surface waters**
- Focus is exclusively on passive sampling devices that use a diffusion gradient to collect pollutants over a period of days to weeks. This process is followed by extraction and analysis of the pollutants in a laboratory.

ASTM D7929-14: Standard guide for selection of passive techniques for sampling groundwater monitoring wells

- Describes three passive sampling strategies for use in groundwater
 - Diffusion samplers
 - Accumulation samplers
 - Passive-grab samplers ← Not covered in this talk

Typical Passive Sampler Uptake Profile

- Initially uptake is considered linear
 - To about 50% of sampler capacity
- At about 95% of sampler capacity equilibrium has been reached between the water and the device
- **Some devices work in only the linear or equilibrium regimes**
- If an equilibration device is removed prior to equilibration, you need to know fractional uptake (f) to calculate water concentrations
- Pre-loaded **PRCs** assist in calculating f

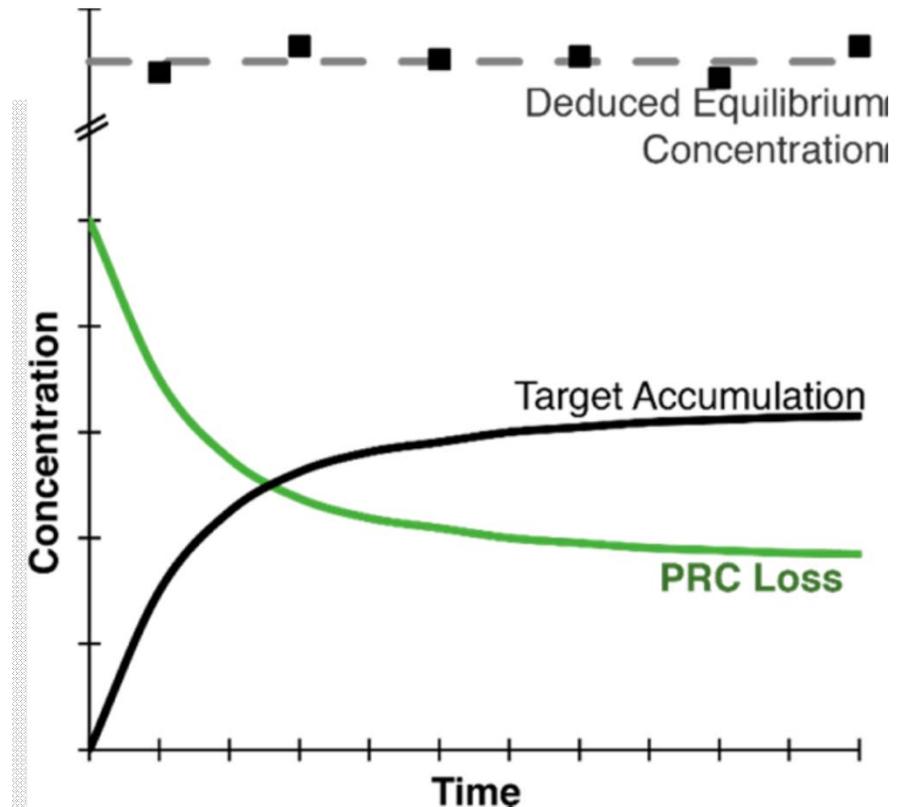


< Linear | Transition (curvilinear) | Equilibrium >

PRC = Performance Reference Compound (labeled analog of target compound)

Typical Passive Sampler Uptake Profile

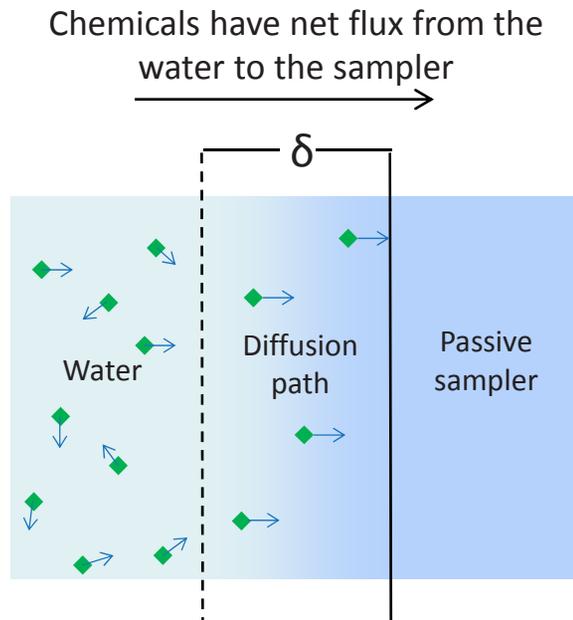
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Appel & Gschwend, 2014, ES&T, 48, 10301

PRC = Performance Reference Compound (labeled analog of target compound)

Equilibrium vs. Linear Uptake



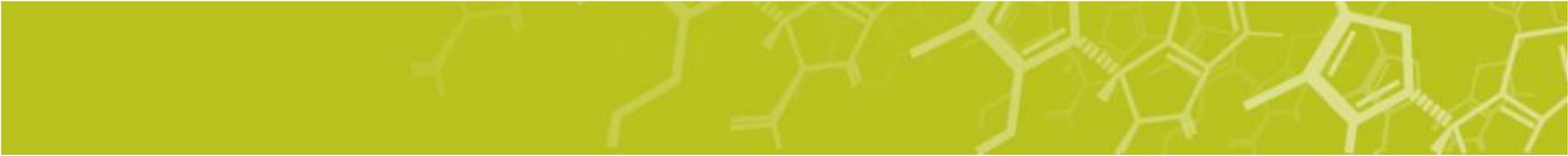
- Flux is controlled (in part) by the width of the diffusion path (δ)
- Diffusion path may be either fixed physically or determined by the water boundary layer

Linear

- Large sorbent capacity
- Long (fixed) diffusion path
- Short deployment time

Equilibrium

- Small sorbent capacity
- Short diffusion path
- Long deployment time



Overview of passive sampling devices for:

Volatiles

Metals

Semi-volatiles

Polars

Volatiles: Passive Diffusion Bags (PDB)

“Polyethylene Diffusion Sampler”

Example targets: BTEX, naphthalenes, chlorinated hydrocarbons

Equilibration sampling in Groundwater

- Low Density Polyethylene (LDPE) tube filled with distilled water, 10 Å pores
- Deploy in monitoring well
- Equilibrates within 7 days
- No pre-concentration:
 - $K_{SW} = 1$
 - water concentration in PDB = well
- Typically exchanged at standard sampling intervals (2 weeks – 1 month)

Protective Mesh Sock

Weight Hanger

Weight



Diffusion Bag (inside mesh sock)

Filling and Sampling Port

<http://www.itrcweb.org/Documents/PDBFAQs2.pdf>

Regenerated Cellulose Diffusion Samplers

Example targets: metals, ions, DOC, VOCs incl. polar VOCs

Equilibration sampling in Groundwater

- Based on diffusion through dialysis membrane
- Regenerated cellulose tubing containing distilled water, ~20 Å & larger pores
- Deploy in monitoring well
- Usually equilibrates within 7-14 days
- No pre-concentration:
 - $K_{SW} = 1$
 - water concentration in sampler = well



NAVFAC Technical Report 2007 ER-0313

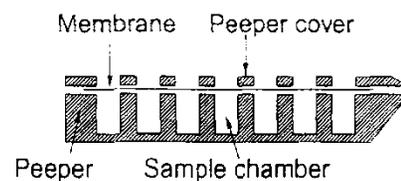
Disadvantages

- Regenerated cellulose is susceptible to microbial attack
- Strict handling/cleaning/storage requirements
- Short shelf-life
- Possible sampling bias due to surface charge
- Poor performance for Hg, Ag, Sn

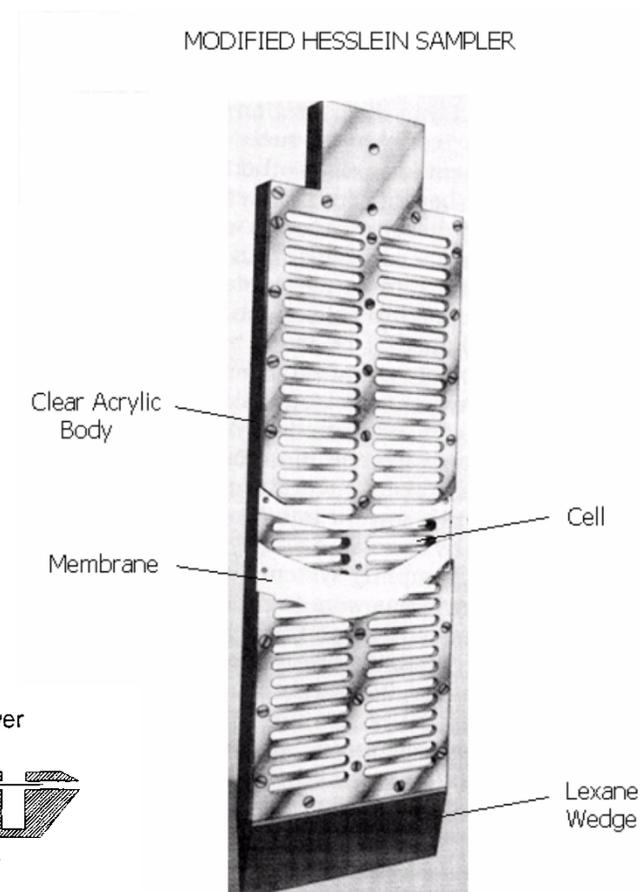
Peepers: Diffusion Sampler for Sediment Profiling

Example targets: metals, ions, DOC, VOCs incl. polar VOCs
(same as regen. cellulose samplers)

- Useful for depth profiling of sediment porewater chemistry and sediment/water column interface
- Acrylic body contains a series of wells filled with distilled water
- Face plate holds diffusion membrane at sample well opening
- Deploy into sediment/water interface (hop waders or divers)
- Usually equilibrates within 7-14 days
- No pre-concentration:
 - $K_{SW} = 1$



Teasdale 1995



Rickly Hydrological

DGT: Accumulation Samplers for Metals/Ions

Example targets: heavy metals (unbound), trace elements, radionuclides

Diffusion gradient thin-film (DGT)

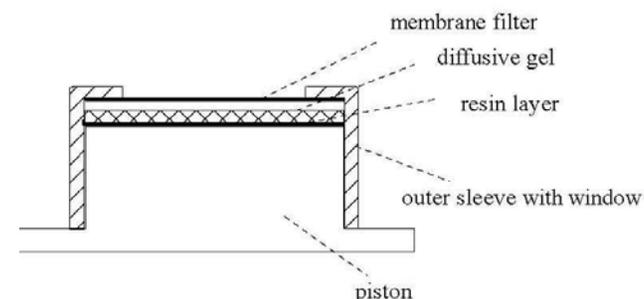
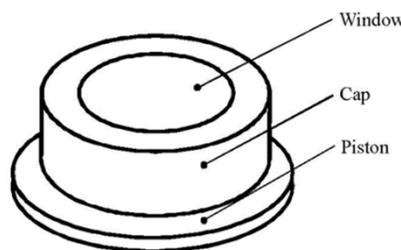
- Sampling by ion exchange with chelating resins
 - Chelex for cations
 - Metsorb for anions
 - Combination sorbent may also be possible
- Linear uptake sampling due to a fixed diffusion barrier
- Must remain hydrated
- DGT capacity is $\sim 500 \mu\text{g}$ total metal ions
 - Linearity lost @ 50% capacity



DGT water probe



DGT sediment probe



DGT Lab Processes

DGT Research Ltd., Lancaster, UK <http://www.dgtresearch.com/>

DGT Processing:

- Resin gel removed from device
- Digested in nitric acid
- Submitted for ICP-MS analysis, total mass of metal in sampler determined

Water Concentration Calculation:

- m : mass of metal in sampler
- Δg : thickness of diffusion path
- D : diffusion coefficient of metal in diffusion path
- A : area of sampler face
- t : deployment time

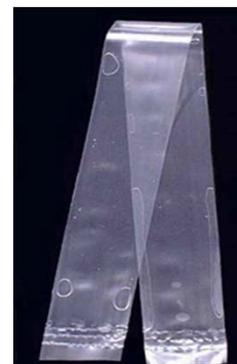
$$C_{DGT} = \frac{m\Delta g}{DA t}$$

Devices for Semi-Volatiles Analysis

Uptake kinetics determined using pre-loaded standards: PRC

Targets: PAHs, PCBs, PHCs, $K_{ow} > 1$ ($K_{ow} > 3$ in practice)

- **Semi-permeable membrane devices**
 - LDPE tube filled with triolein oil
 - Linear uptake sampling
 - Surface water or groundwater
- **Low density polyethylene (LDPE, PE, PED)**
 - Flat sheets of LDPE in various thicknesses
 - Linear through equilibrium sampling
 - Surface water or groundwater
- **Solid Phase Microextraction (SPME)**
 - Polydimethylsiloxane (silicone rubber) coated fibers
 - Linear through equilibrium sampling
 - Surface water to date



EST-Lab.com



Maxxam.ca



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SPMD Details

EST Lab (Environmental Sampling Technologies)
<http://www.est-lab.com/>

- Tubing: lay flat low density polyethylene, additive free
- Length: 91.4 cm; Width: 2.5cm; Thickness: 70-95 μm
- Triolein: 99% purity (1.0 mL used for standard 91.4 cm length)
- Store in freezer in original shipping container
- Ship on ice in original shipping container
- For deployment SPMD needs to be mounted on 'spider carrier'
- Large sorbent capacity provides linear uptake for full deployment time

SPMD on Spider Carrier



EST-Lab.com

Spider Carriers loaded in Deployment Cannister

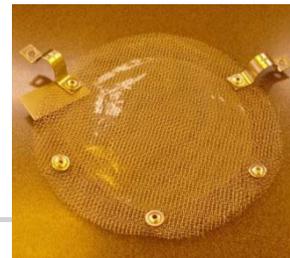


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LDPE Details

No Commercial PE Device Suppliers Most users fabricate their own devices

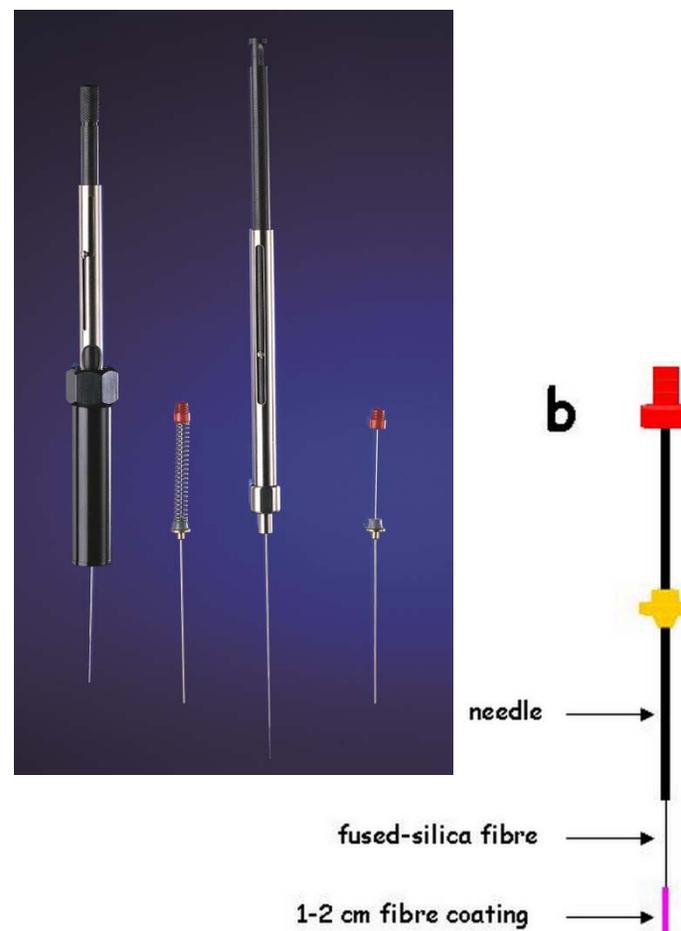
- Many users purchase paint drop sheets or heavy gauge vapour barrier films from a local hardware store – very inexpensive
 - Requires extensive cleaning before use and has higher variability
- Films available from Maxxam:
 - High quality flat sheet films normally used in food and pharmaceutical packaging
 - Thicknesses from 1.4 mil to 8 mil (30 to 200 μm)
 - Contains UV blockers
- Modeling can be used to estimate needed film size and thickness
 - High flexibility to tailor film size/thickness to deployment needs
- Pre-loading with PRC highly recommended
- Works throughout uptake isotherm
 - Linear, curvilinear, equilibration



SPME Details

Supelco (Sigma-Aldrich): www.sial.com

- Optical fiber coated with sorbent, mounted in a GC injection needle
 - Numerous sorbent and configuration options are available
 - For passive sampling of semi-volatiles, choose the PDMS coated fibers, usually 100 μm thickness is appropriate
 - For field deployment, select the fiber without spring, spring may be needed for injection
- Sorbent volume low but advantage is everything that is extracted gets injected
- PDMS partition coefficients are different than PE diffusion coefficients, otherwise functioning is similar
- Works throughout uptake isotherm
 - Linear, curvilinear, equilibration



Field Processes

General Recommendations, all devices

Deployment:

Ahead of time:

- Determine appropriate deployment support/containment & anchoring

In the field:

- Remove from shipping container and deploy well-submerged
 - Avoid directly touching film surfaces
 - Provide sufficient anchoring/locating
 - Minimize air exposure time
- Record deployment time and estimate/measure water temperature during deployment
- Expose field control to the air similarly to deployed devices

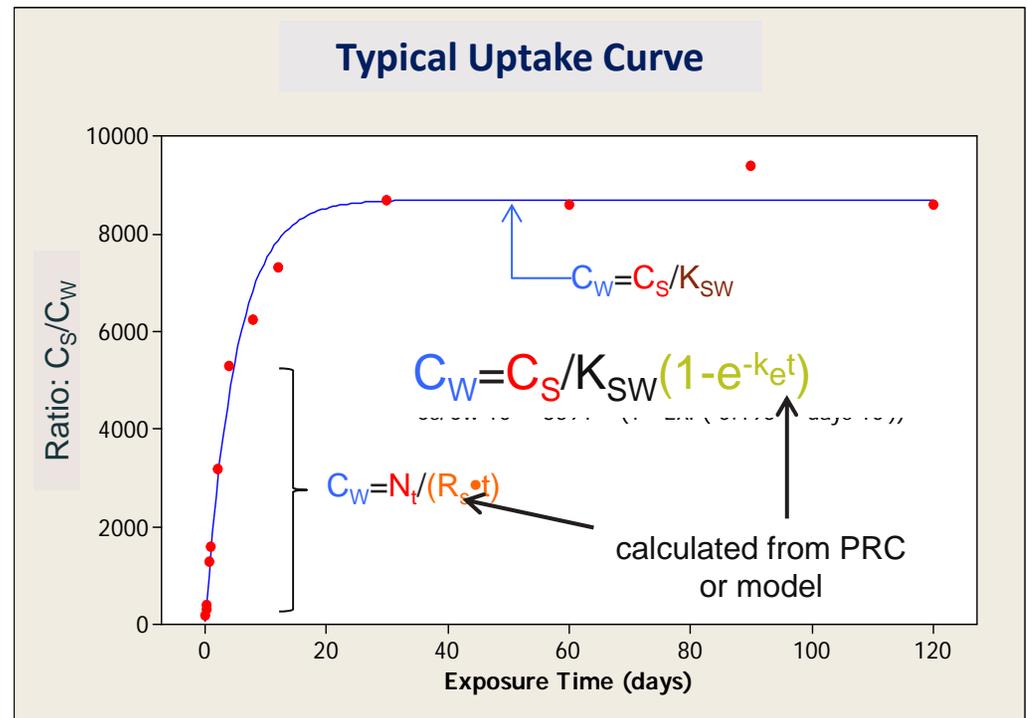
Retrieval:

- Remove from water and return to shipping container
 - Avoid directly touching film surfaces
 - Minimize air exposure time
- Record retrieval time
- Expose field control to the air similarly to deployed devices



Lab Processes

- Samplers removed from holders and surface fouling physically removed
- SPME injected directly in GC/MS
- LDPE/SPMD extracted in hexane
 - Extract submitted for GC/MS analysis
- total mass of (each) chemical in sampler determined
- Water concentration determined from:
 - m : mass of chemical in sampler
 - t : deployment time
 - R_s : sampling rate (L/d)
 - Established uptake equation



Passive Samplers for Polars – e.g. PPCP

POCIS and Chemcatcher

Chemcatcher



U. Portsmouth



POCIS



EST Lab



Features: POCIS vs. Chemcatcher

POCIS

- Loose Oasis® HLB sorbent sandwiched between two membranes
- Extract sorbent, report mass per sampler
- Estimate water concentration if uptake rate available
- Linear uptake range only
- PRCs cannot be used
- R_s determined experimentally or estimated
- Qualitative or Semi-quantitative
- **Single use**
- **More expensive**
- **Commercially available**
- www.est-lab.com/

$$C_w = \frac{M_s}{R_s t}$$

used for both

Chemcatcher

- Any commercial 47 mm sorbent-impregnated SPE disk (3M or Horizon recommended)
- Extract sorbent, report mass per sampler
- Estimate water concentration if uptake rate available
- Linear uptake range only
- PRCs cannot be used
- R_s determined experimentally or estimated
- Qualitative or Semi-quantitative
- **Re-usable**
- **Less expensive**
- **Research tool**
- www.port.ac.uk/research/chemcatcher/



Case Studies

- Case Study #1 - Regenerated Cellulose Diffusion Sampler Evaluation
- Case Study #2 – PCBs and DDX in an off-shore marine contaminated site (LDPE and SPME)

Case Study #1 - Regenerated Cellulose Diffusion Sampler Evaluation

Demonstration and validation of a regenerated cellulose dialysis membrane diffusion sampler for monitoring ground water quality and remediation progress at DoD sites (ER-0313)

Study Objectives:

- Determine the usefulness of dialysis samplers in collecting a range of organic and inorganic water quality constituents from ground water,
- Determine the optimum equilibration times for these constituents to diffuse into the dialysis sampler,
- Compare water quality results and sampling costs from samples collected with dialysis samplers to samples collected with a low-flow purging technique and polyethylene diffusion bag (PDB) samplers, and
- Transfer the technology while gaining regulatory acceptance.

Case Study #1 - Regenerated Cellulose Diffusion Sampler Evaluation

Approach

Range of target compounds with favourable performance in lab studies:

- VOCs
- Cations & trace elements
- Anions
- Other: DOC, silica, methane, sulfide

Field comparisons were conducted at three Department of Defense (DoD) sites:

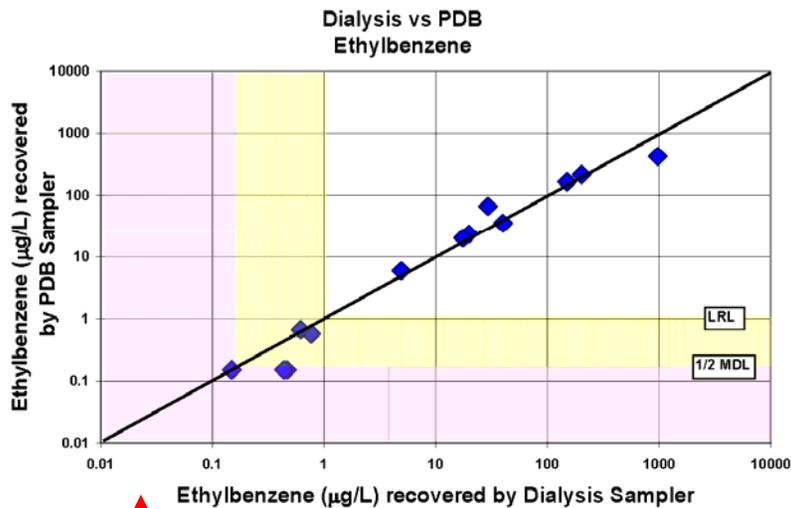
1. Naval Air Engineering Station (NAES) Lakehurst, NJ,
2. Naval Base Ventura County (NBVC), Port Hueneme and Pt. Mugu, CA, and
3. Naval Air Warfare Center (NAWC) West Trenton, NJ.

Compare three sampling approaches:

- Low flow purge
- PDB (LDPE passive diffusion sampler)
- Regenerated Cellulose passive diffusion sampler

Case Study #3 - Regenerated Cellulose Diffusion Sampler Evaluation

Results - volatiles

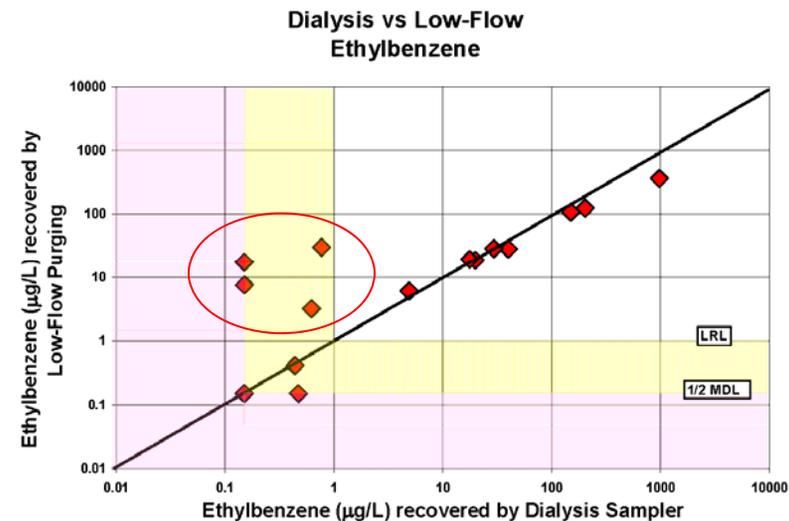


Dialysis sampler vs. PDB

Dialysis sampler vs. low flow

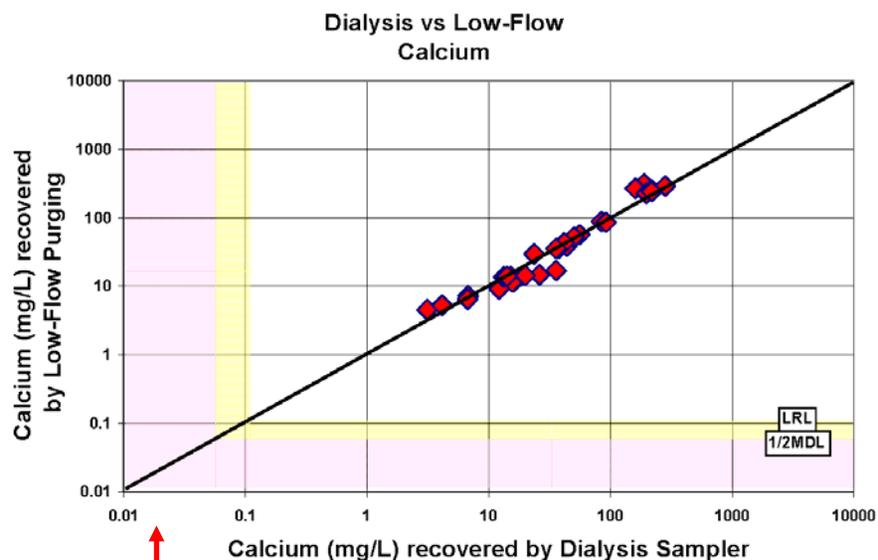
Ethylbenzene:

- PDB results agree for DL over 3-4 orders of magnitude
- Low flow results agreed well for concentrations above the reporting limit.
 - Between DL and RL, several instances where ethylbenzene was found in the low flow samples but not the dialysis samples.
 - Suspicion is that ethylbenzene is being drawn in vertically or laterally during pumping



Case Study #3 - Regenerated Cellulose Diffusion Sampler Evaluation

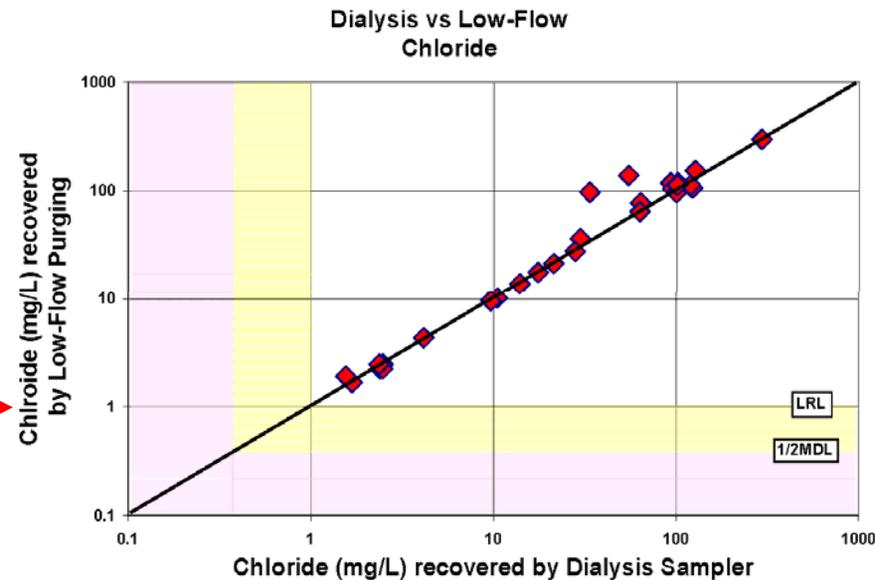
Results – metals/ions



Ca: Dialysis sampler vs. low flow

Cl: Dialysis sampler vs. low flow

- For metals, comparison was only to low flow as metal ions cannot cross the LDPE membrane of PDB.
- Ca and Cl cations results showed very good agreement between dialysis and low flow over 1 – 1000 mg/L.
- Above RL similar results were found for magnesium, sodium, potassium, alkalinity, fluoride, nitrate, bromide, silica, and total dissolved solids



Case Study #1 - Regenerated Cellulose Diffusion Sampler Evaluation

Findings

- Good correlation with PDB (volatiles) and low flow purge (semi-volatiles)
- Dialysis samplers were found to cost significantly less than samples collected with a low-flow purging procedure.
- Field sampling time was reduced by a factor of more than six times, compared to low-flow purging.
- The total sampling costs per sample was estimated to be three times less, compared to low-flow purging.
- Mercury, silver, tin: >28 d equilibration

Favorable Bench-Scale Equilibration Testing Results		
<i>VOCs (1-3 day equilibration times at 10°C and 21°C)</i>		
1,1,1-Trichloroethane	cis-1,2-Dichloroethene	1,2-Dibromo-3-chloropropane
1,1,2,2-Tetrachloroethane	Dibromomethane	1,3,5-Trimethylbenzene
1,1,2-Trichloroethane	Dichlorodifluoromethane	1,3-Dichloropropane
1,1-Dichloroethene	Ethylbenzene	2,2-Dichloropropane
1,2,3-Trichloropropane	m-Xylene	2-Chlorotoluene
1,2,4-Trimethylbenzene	Naphthalene	4-Chlorotoluene
1,2-Dibromoethane	o-Xylene	Bromobenzene
1,2-Dichlorobenzene	p-Xylene	Bromochloromethane
1,2-Dichloroethane	Tetrachloroethene	Bromomethane
1,2-Dichloropropane	Toluene	Hexachlorobutadiene
1,3-Dichlorobenzene	trans-1,2-Dichloroethene	Isopropylbenzene
1,4-Dichlorobenzene	Trichloroethene	Methyl tert-butyl ether
Benzene	Trichlorofluoromethane	Methylene chloride
Bromodichloromethane	Vinyl chloride	n-Butylbenzene
Bromoform	1,1,1,2-Tetrachloroethane	n-Propylbenzene
Carbon tetrachloride	1,1-Dichloroethane	p-Isopropyltoluene
Chlorobenzene	Dibromochloromethane	sec-Butylbenzene
Chloroethane	1,1-Dichloropropene	Styrene
Chloroform	1,2,3-Trichlorobenzene	tert-Butylbenzene
Chloromethane	1,2,4-Trichlorobenzene	
<i>Cations and Trace Elements (1-7 day equilibration times at 10°C and 21°C)</i>		
Calcium	Barium	Molybdenum
Magnesium	Cadmium	Nickel
Potassium	Chromium	Selenium
Sodium	Copper	Vanadium
Aluminum	Iron	Zinc
Arsenic	Lead	
Antimony	Manganese	
<i>Anions (1-3 day equilibration times at 21°C)</i>		
Bicarbonate/Alkalinity	Chloride	Nitrate
Bromide	Fluoride	Sulfate
<i>Other Constituents (1-3 day equilibration times at 10°C and 21°C)</i>		
Dissolved organic carbon	Silica	Methane
Sulfide		

Case Study #2 – PCBs and DDX in an off-shore marine contaminated site

Passive sampling to measure baseline dissolved persistent organic pollutant concentrations in the water column of the palos verdes shelf superfund site

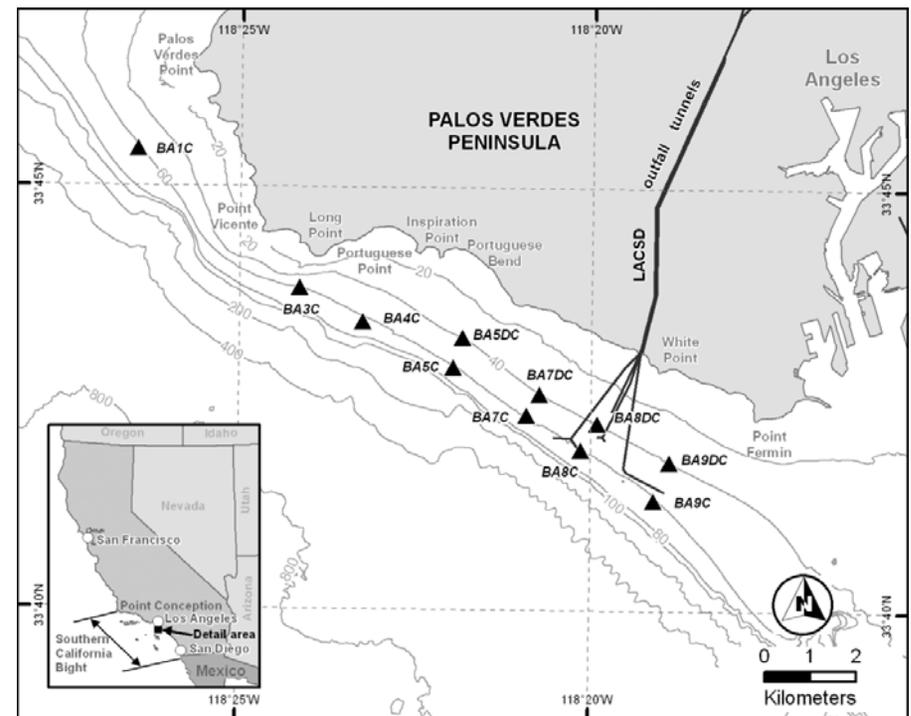
Study Objectives:

- Monitor stratification of contaminants in a water column in the vicinity of known contaminated sediments
 - PCB congeners and sum, DDT and degradation products
 - Water column data compared to previous EPA sediment data
- Compare performance of LDPE sheets with SPME fibers
- Compare two uptake models for calibrating fractional uptake in LDPE films
 - *wbl diffusion only vs. exponential approach to equilibrium*

Case Study #2 – PCBs and DDX in an off-shore marine contaminated site

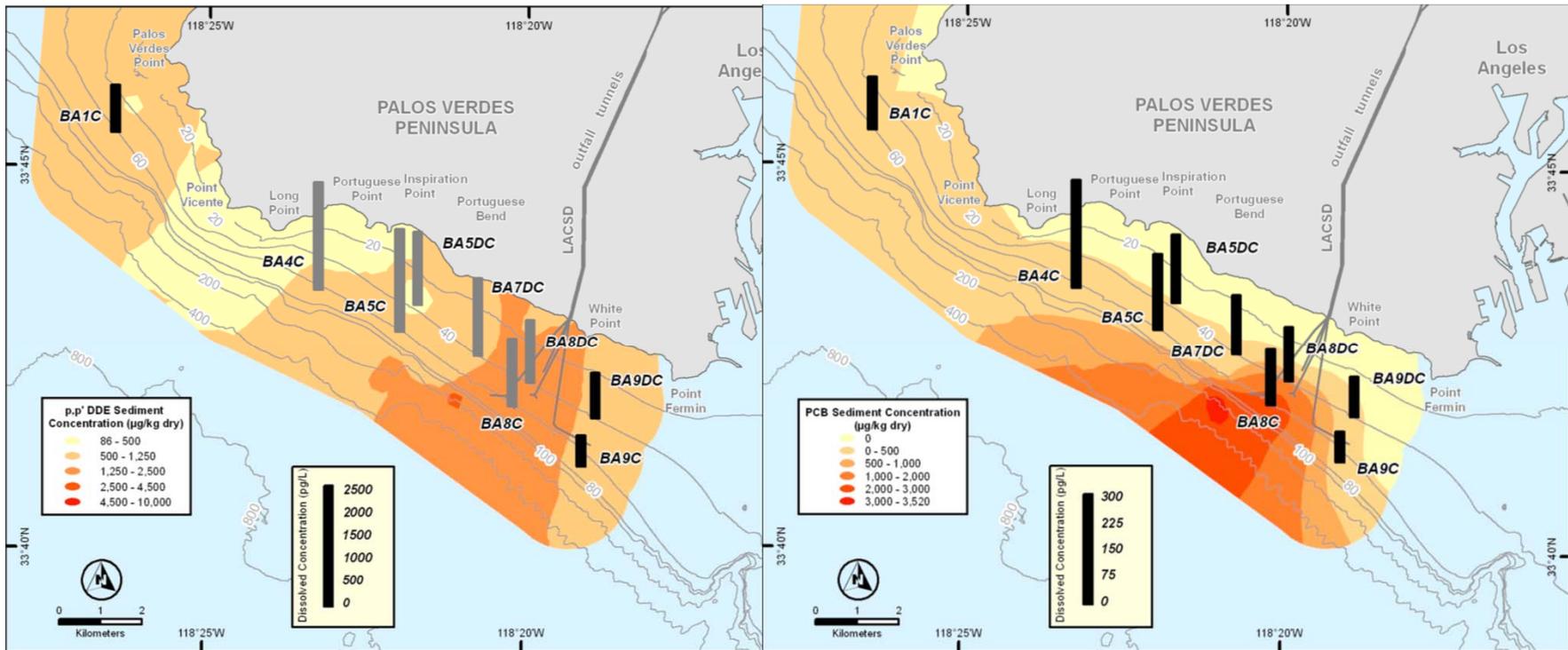
Approach

- LDPE films (PRC loaded) and SPME fibers
 - PRC used with LDPE only
- Marine location ~2 km offshore of L.A. (45-46 m isobaths)
- In an area of contaminated sediment in the vicinity of a sewage outfall along the 45-46 m isobaths
- 2 km upcurrent (south) and 10 km downcurrent (north)
- Films and fibers co-deployed at three depths: 5 m above sediment; 5 m below surface; mid-depth (30 – 35 m below surface)



Case Study #2 – PCBs and DDX in an off-shore marine contaminated site

Results



(b) p,p'-DDE from PE

(c) Σ PCB from PE

Black columns: concentration exceeded human health ambient water quality criteria (AWQC)
Gray columns: concentration exceeded both human health and aquatic life AWQC.

Case Study #2 – PCBs and DDX in an off-shore marine contaminated site

Findings

- SPME data trended lower than PE, likely because equilibration was assumed
 - If fractional uptake is estimated and incorporated, data comparability was improved
- No significant difference in the two uptake models used for LDPE
- PCBs could not be detected with SPME, due to very low water concentrations and low sorbent mass in SPME
- Other than the apparent systematic error, SPME and PE data correlated well
- Concentrations near sediment are higher than those above in the water column, across compound classes
- Highest concentrations are found down-current of most highly contaminated sediments



Thank You!

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