



EMA of BC – Species at Risk Speaker Session

Analytical Methods used with Non-lethal Sample Collection

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RIGHT SOLUTIONS | RIGHT PARTNER

- Sample Preservation Uses Strong Acid/Base
 - PPE and no contact lenses
 - MSDS available online at www.alsglobal.com
 - Eye Wash / Rinse Station



Non-lethal Sampling for Metals



- Tissue plug or dermal punch procedure was developed by Baker et al. in support of Hg testing requirements for EEM for MMER
- BC Ambient Water Quality Guidelines
- Health Canada consumption guidelines for acceptable levels of metals in food/fish.

How to take a Tissue Plug or Biopsy Sample

- Practice first on your dinner if possible
- Prepare 2 holding tanks, one oxygenated, the other with anaesthetic, such as Clove oil or MS-222
- Capture and Anaesthetize the fish
- Take your sample

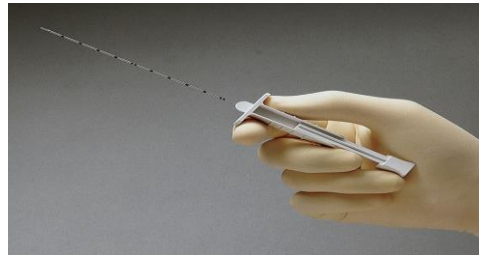


How to take a Tissue Plug or Biopsy Sample



- A Biopsy Needle harvests 10-25 mg of tissue.

- Tru-Cut TM



- A 4mm Dermal Punch harvests 50-75 mg of tissue, used on fish 200mm in size.

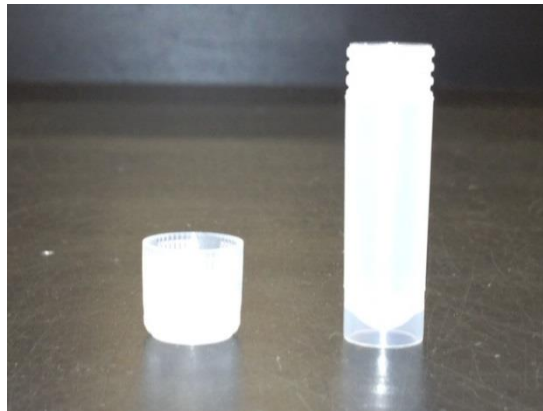
- Miltex



How to take a Tissue Plug or Biopsy Sample



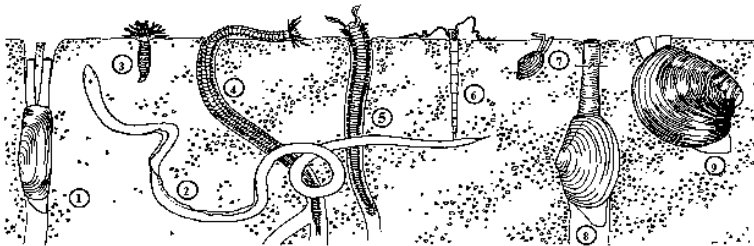
- Typically an experienced surgeon can remove the sample in less than 10 seconds to reduce stress on animal.
- Samples should be preserved by freezing with liquid nitrogen or dry ice if possible in 2 mL vials and transported to the laboratory as soon as possible.



How to take a Tissue Plug or Biopsy Sample






- Tissue plugs often leave open wounds, which need to be sealed to prevent infection.
- Sterile crazy glue, such as Nexaband™, which acts like a waterproof bandage, should be used to close the wounds to decrease the chance of infection.
- Return fish to the oxygenated holding tank and release once recovered and swimming normally.

- 50-100 mg sample size is ideal
- Full metal scan by ICP-MS or HR-ICP-MS and CVAF/AS
- Samples types can include



Passive Samplers

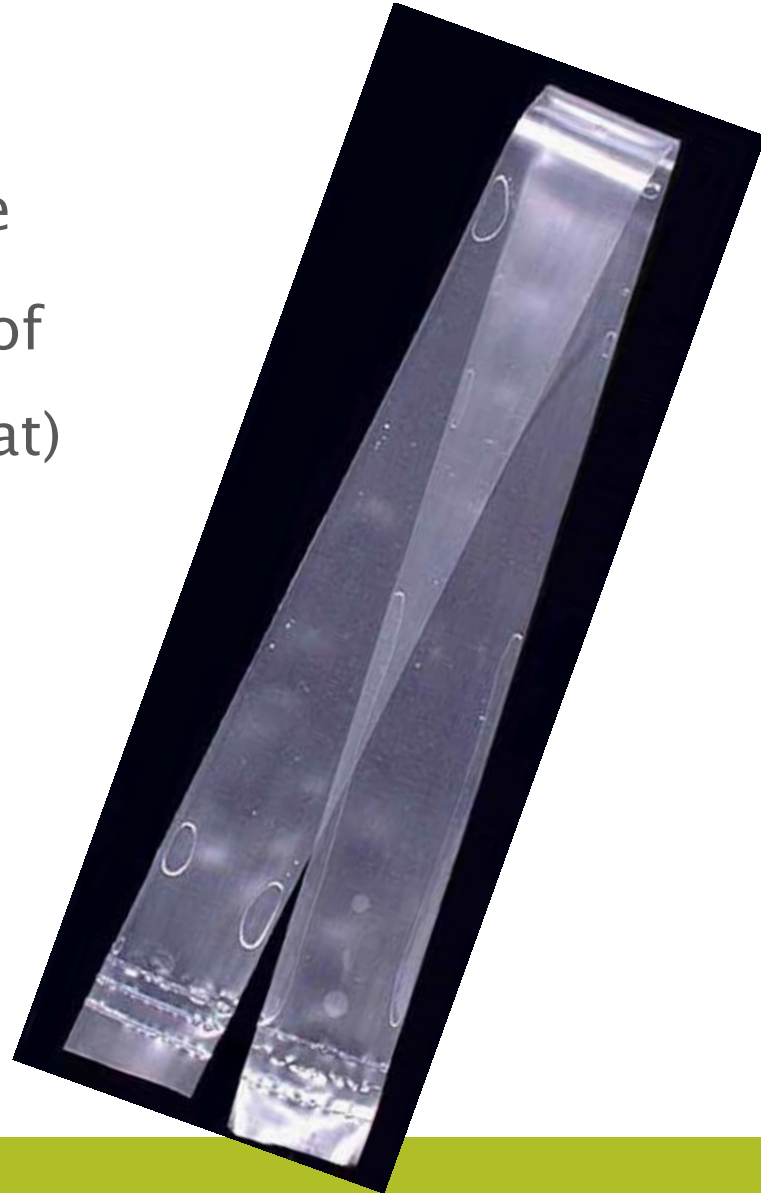


Sampler	Construction	Compounds
SPMD 	Semipermeable membrane device: flat tube of LDPE filled with lipid	Hydrophobic semivolatiles organics with $\log K_{OW} > 3$
POCIS  <small>PS Polar</small>	Sampler consists of solid sorbent enclosed between two membrane layers that are mounted on a pair of stainless steel washers	Polar pesticides and pharmaceuticals with $\log K_{OW} < 3$
RPP 	Rigid Porous Polyethylene (RPP) Samplers are made of thin porous polyethylene filled with water	Polar pesticides and pharmaceuticals with a $\log K_{OW} < 3$ and inorganic constituents
PDB 	Polyethylene bag filled with ASTM Type II deionized water	Volatile organics compounds with $\log K_{OW} < 3$
DGT 	Plastic sampler with filter, hydrogel and an ion exchange resin	Dissolved metals and organometallic complexes

SPMD Construction



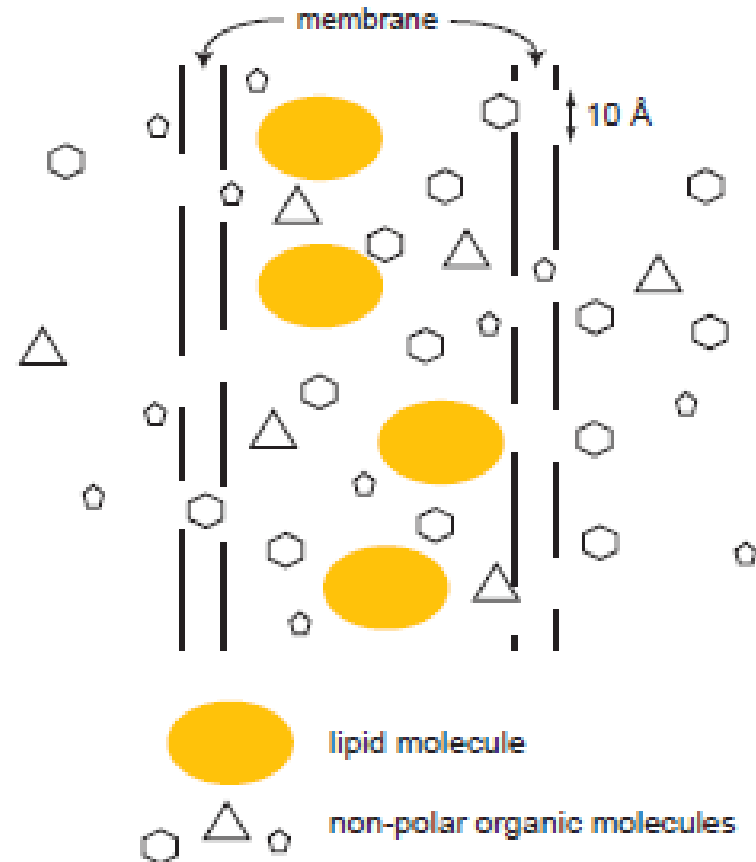
- 2.5 cm wide (layflat) and 1m long LDPE membrane
- Contains 1 mL (0.915g) of triolein (lipid or animal fat) as a thin film



- Oil and water don't mix
- Many organic chemicals dissolve in oils better than water
- Organics are fat loving (lipophilic) not hydrophobic (water hating)
- Organic contaminants may be present in low concentrations in the water but bioconcentrate in the lipid or fat of animals.
- SPMDs can detect these low concentrations in the water as they mimic the bioconcentration in animal fats.

How SPMDs work

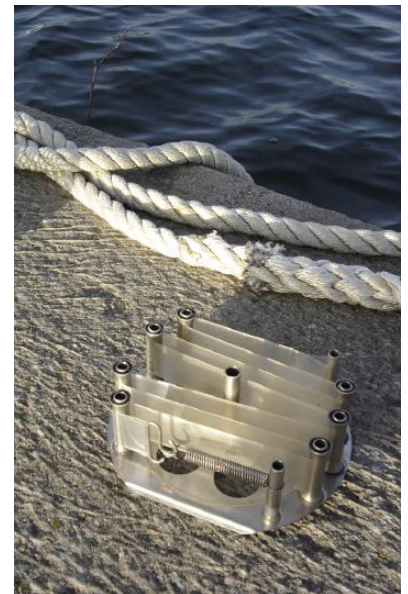
- Contaminant molecules smaller than 1 nm can pass through the pores and dissolve in the lipid (triolein)
- The lipid molecules are too large to pass through the membrane and so the contaminants are retained (bioconcentrated)



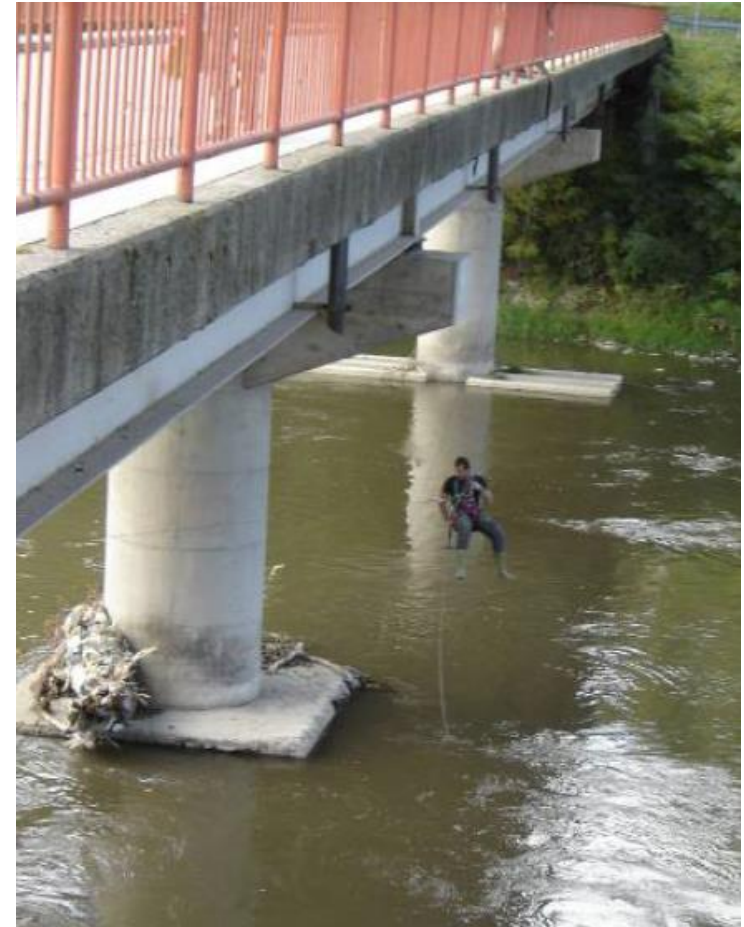
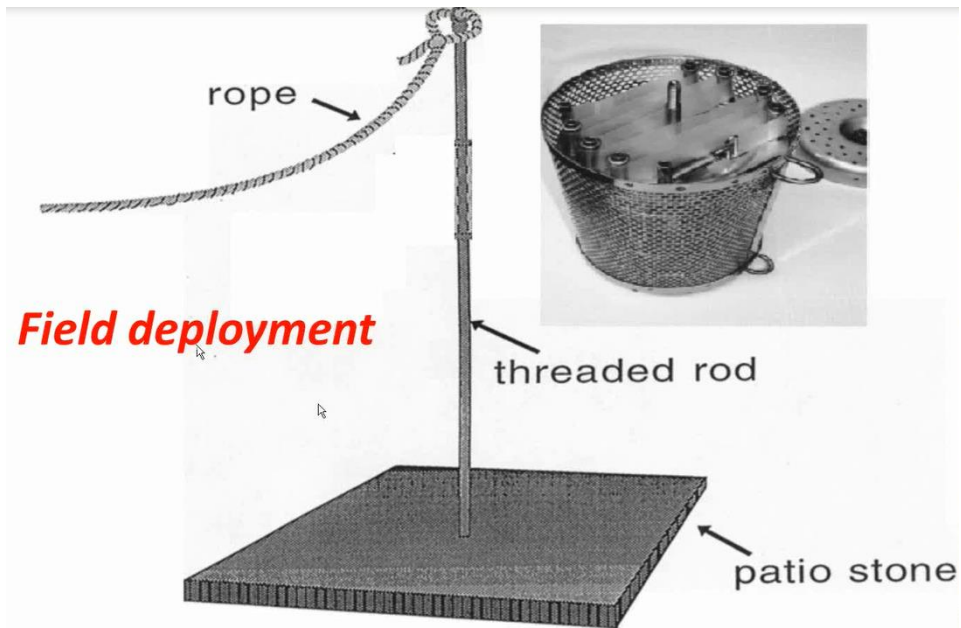
How SPMDs are Deployed



- SPMD is wrapped around a stainless steel spider and shipped and stored in a one gallon paint can
- Up to 5 SPMDs can then be mounted into a stainless steel cage for deployment



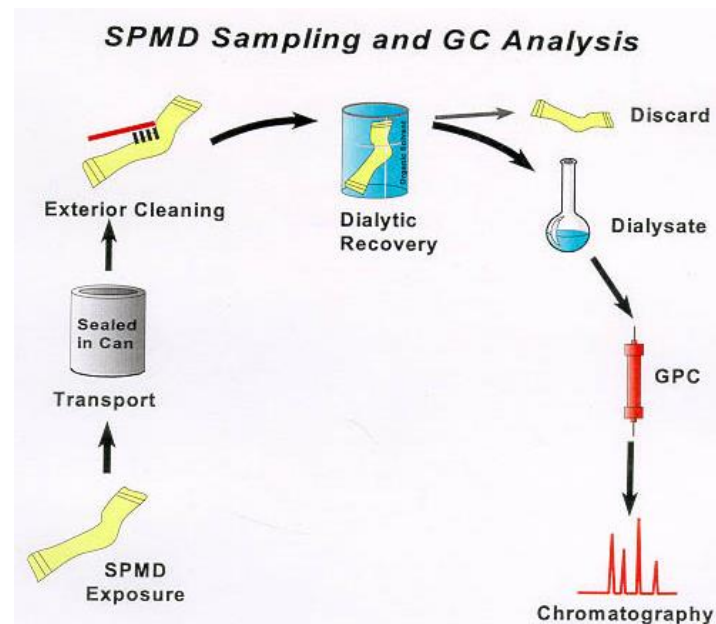
How SPMDs are Deployed



How SPMDs are Analyzed at ALS



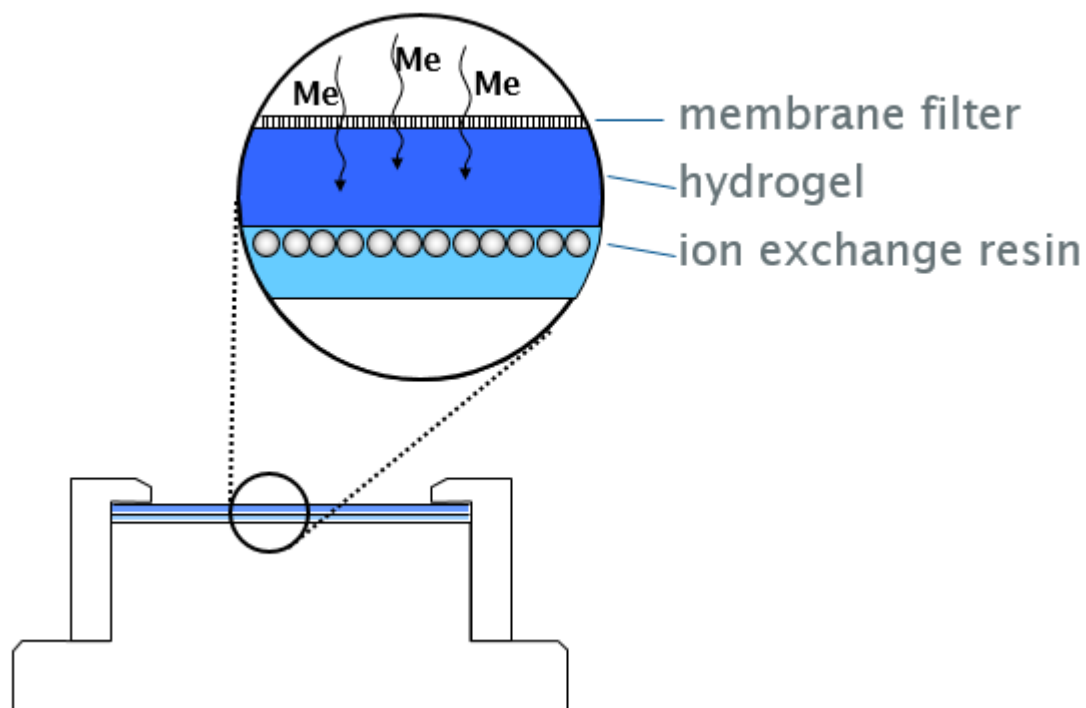
- SPMDs are recovered from environment and sealed in original can and placed on ice or frozen
- Membrane is cleaned with soft brush to remove barnacles, periphyton, mineral precipitates
- Integrity of sampler is checked
- Dialysis
- GPC Clean-up
- Analysis by GC-MS or GC-HRMS



Organic Compounds that can be Measured

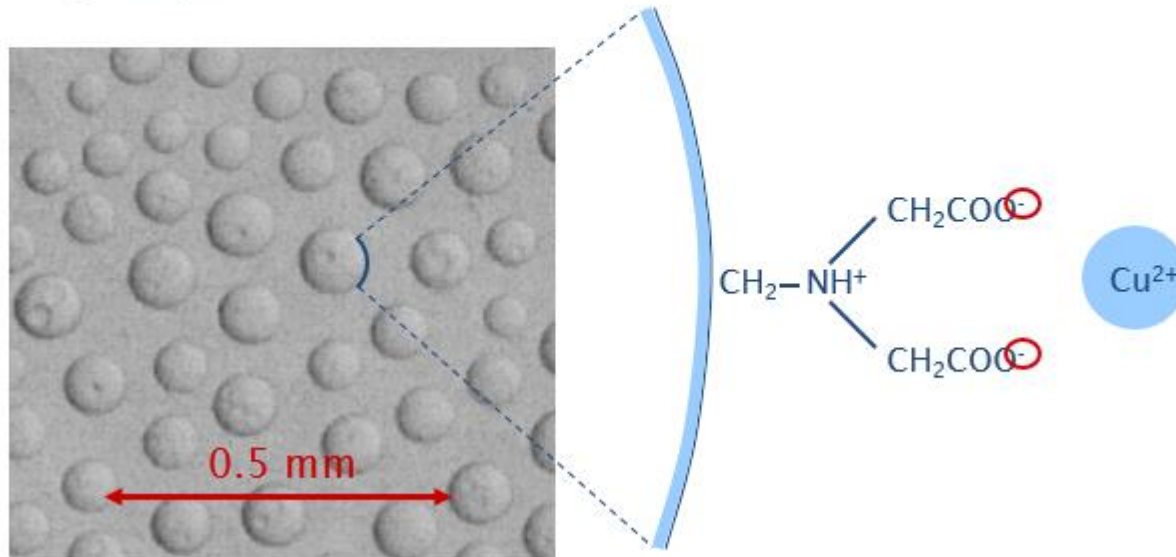
- Priority Pollutant PAHs + alkylated PAHs
- Organochlorine pesticides, OPPs
- PCBs, PBDEs, Dioxins/Furans
- TBT
- Alkyl phenols
- Essentially any compound with $\log K_{ow} > 3$

DGT – Diffusive Gradients in Thin Films

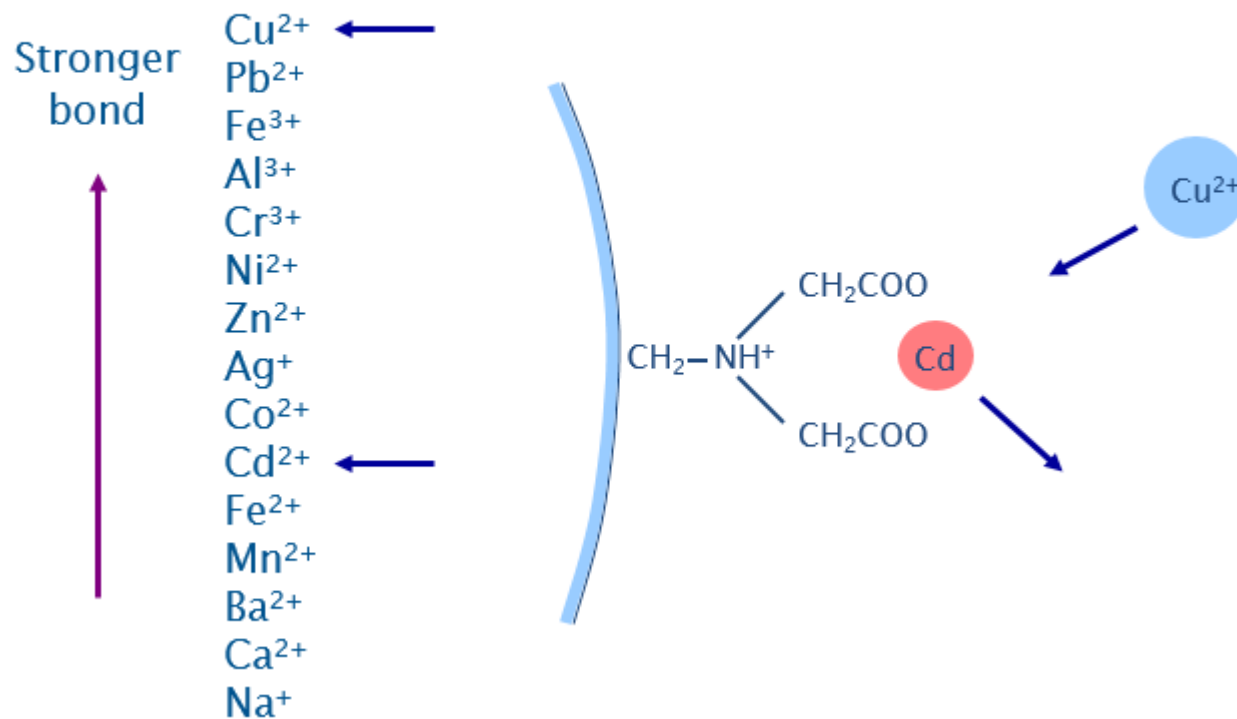


DGT – Diffusive Gradients in Thin Films

- Chelex® 100 ion exchange resin (Bio-Rad, USA)
- Styrene divinylbenzene polymer with iminodiacetate groups

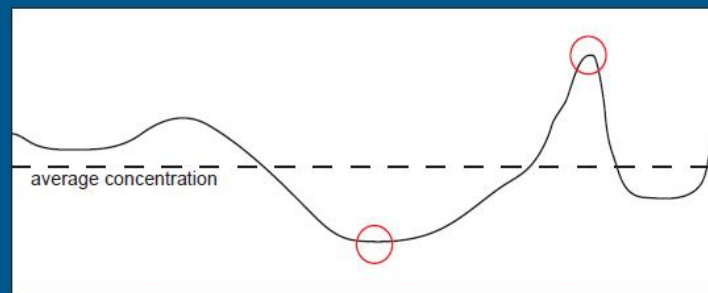


- Binds stronger to some ions



Summary of the Advantages of SPMDs/DGTs

- Can be used to estimate bioconcentration factors for fish uptake of contaminants.
- Easier to use than fish
- Can be deployed over long periods of time, so TWA concentrations can be determined
- Can be fixed and therefore do not have the associated problems when sampling biota



Time integration

A common property of all three passive sampling methods is that they give time-averaged concentrations. In this way, the risk of underestimation or overestimation of total mass flows as a result of accidental sampling at times of minimum or maximum concentration is reduced. In addition, these sampler types exclusively sample the bioavailable fraction, i.e., the part that can be assimilated by organisms.

