

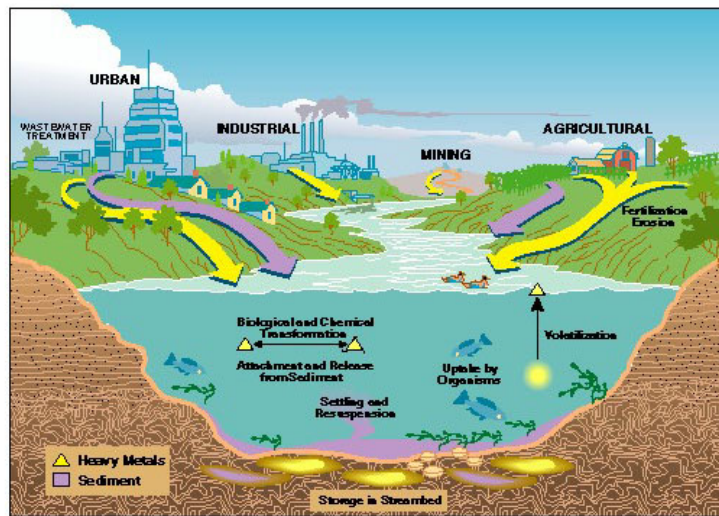


Diffusive Gradients in Thin Films for in situ Monitoring of Free Metals in Water

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Background



U.S. Geological Survey Circular 1133, 1995



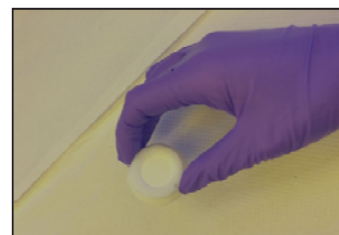
- Many trace metals are micronutrients and represent dietary components of aquatic organisms, such “nutrient” metals can include: Fe, Cu, Zn, Mn, Co, Cd, Mo, Se, Sn, and V
- In natural marine environments and freshwaters, most metals are typically present in trace quantities (<10 nM) and are passively and/or actively assimilated by organisms to satisfy physiological requirements
- However, in metal contaminated systems, metals can accumulate within cells and tissue, causing impaired metabolism or death

Background

- Measurements of metal concentration in soils and water typically involves grab sampling techniques, which provide:
 - “Total metal” concentration
 - “Dissolved metal” concentration (filtered through a 0.45 μm membrane)
- The dissolved portion is representative of the biologically available (and hence toxic) fraction
- However, the dissolved concentration may be an overestimation of bioavailable metal, as it includes:
 - Colloidal metal species
 - Complexed metals
- These are potentially capable of remaining inaccessible to aquatic species

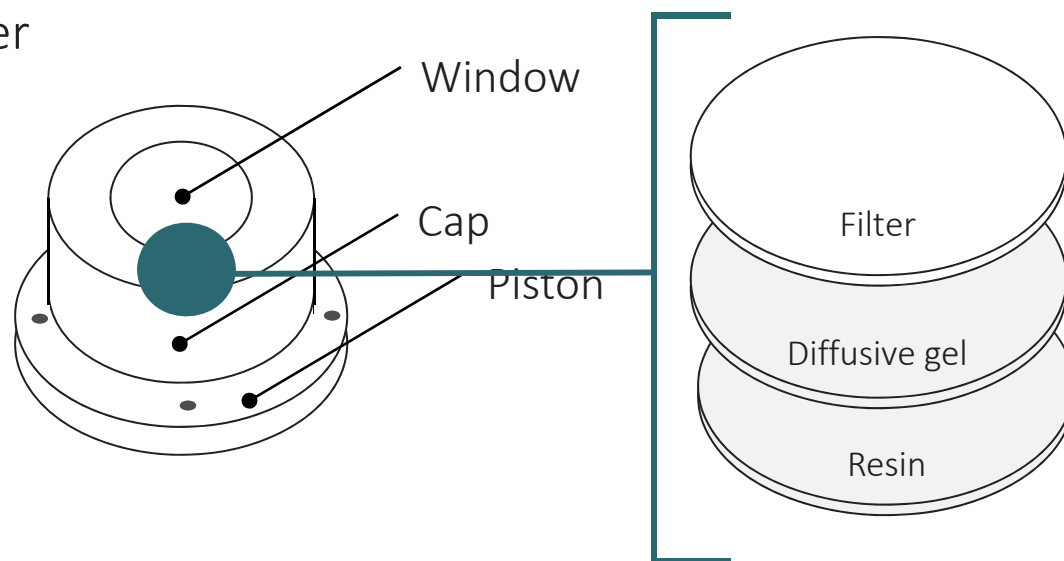
Diffusive Gradients in Thin Films

- An *in situ* technique developed by Davison and Zhang (1994), which employs a diffusion gradient in a thin (DGT) film polyacrylamide gel to measure kinetically-labile metal species concentrations
- Passive samplers with a fixed uptake/sampling rate
- Provides a better measure of biologically-available metals than dissolved or total metal concentrations
- The resin is selective for free and/or weakly complexed metal species
- Since its development, hundreds of scientific articles have been published focusing on DGT development and application
 - Sediment and soil
 - Water and porewater



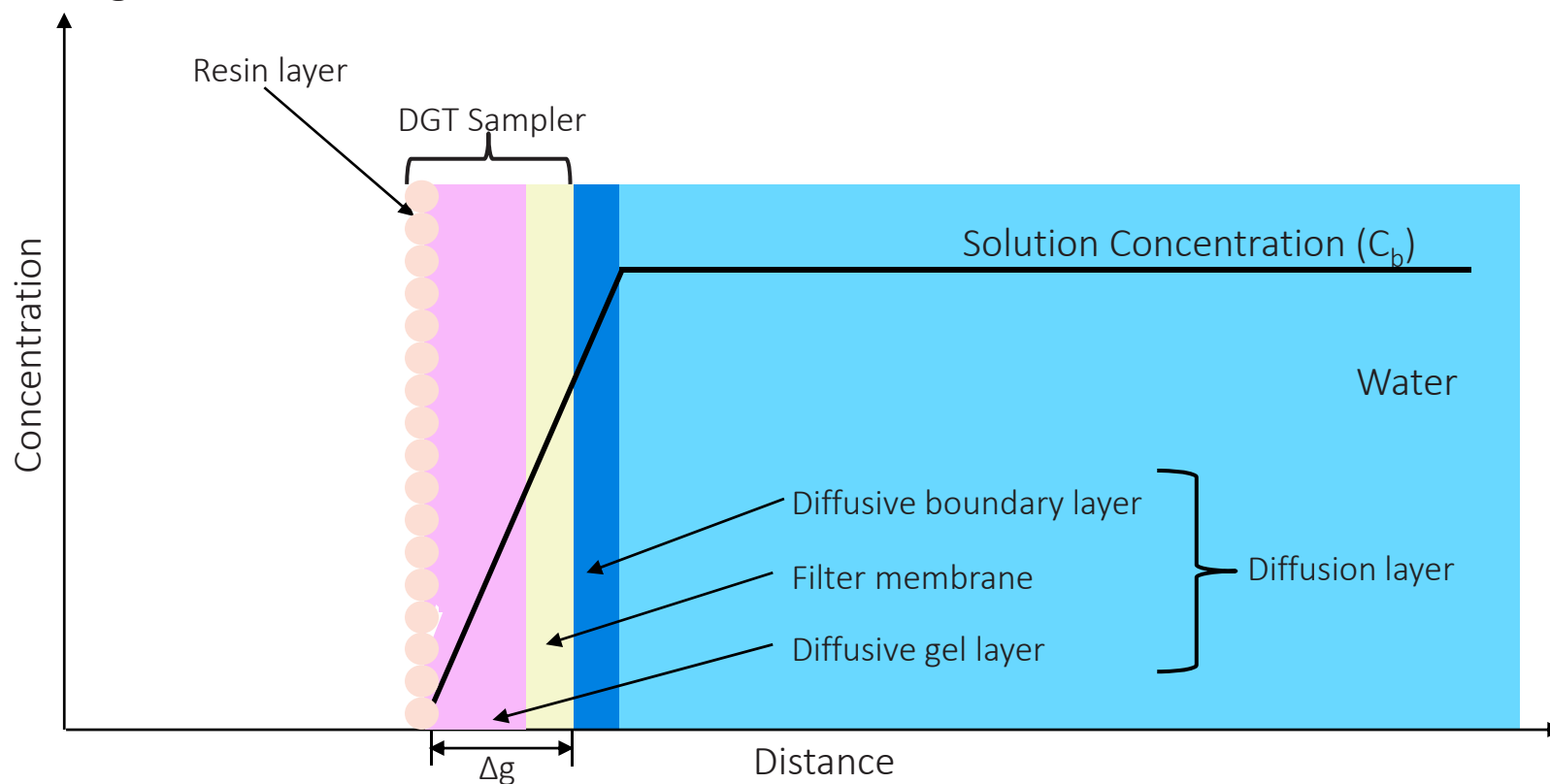
How do they work?

- DGT passive samplers use the laws of diffusion to control the flux of metals to the resin (binding layer)
- They utilize a three layer system:
 1. resin-impregnated hydrogel layer (binding layer or resin gel)
 2. hydrogel diffusion layer
 3. protective membrane filter
- These three layers are enclosed in a small plastic device, so that only the filter is exposed to the bulk solution being analyzed
- The entire plastic unit is then deployed *in situ*



How do they work?

- Once deployed, a diffusive gradient is created across the bulk solution and the resin gel
- Metal ions pass through a gel diffusion layer and bind to a chelating or ion-exchange resin



What do they measure?

- Several resin (adsorptive) gels exist, which are selective towards certain metal species
- DGTs can be used for any analyte with a suitable adsorbent available

<i>Resin Type</i>	<i>Resin Specifications</i>	<i>Metal Selectivity</i>
Chelex-100	Cation-exchange resin -Styrene divinylbenzene co-polymer containing paired iminodiacetate ions, which act as the chelating groups	Di- and tri-valent cations (Al, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni)
Metsorb	Titanium-dioxide based adsorbent	Oxyanionic species (As, Sb, Mo, V, W)
Ferrihydrite	Iron-oxide based adsorbent	Oxyanionic species (As, Sb, P, Se, V)
Chelex-Metsorb	Cation-exchange resin + Titanium-dioxide based adsorbent	Di- and tri-valent cations + Oxyanionic species (As, Sb, Cd, Co, Cu, Pb, Mn, Y, P, W, V)
Spheron-Thiol	Chelating resin with thiol groups bound to hydroxyethyl methacrylate gel	Mercury

Deployment and Retrieval



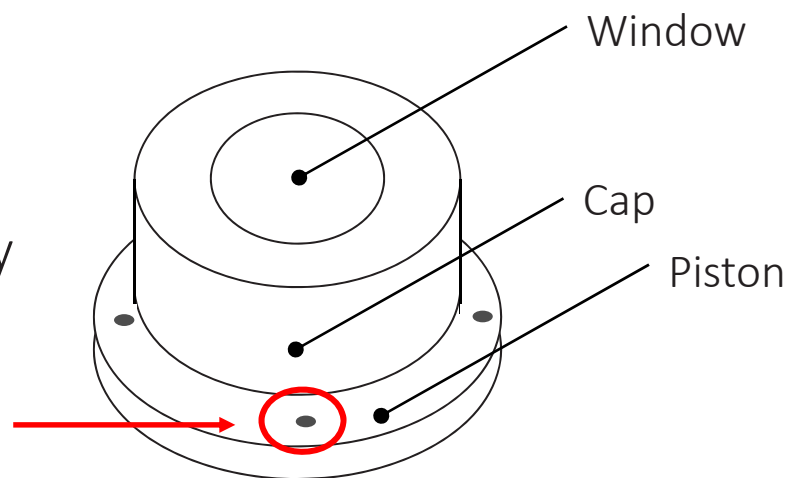
Deployment

- Stored refrigerated prior to deployment and brought to the field in sealed plastic containers
- Handlers must wear metal-free gloves
- Small holes in the DGT unit make for easy deployment



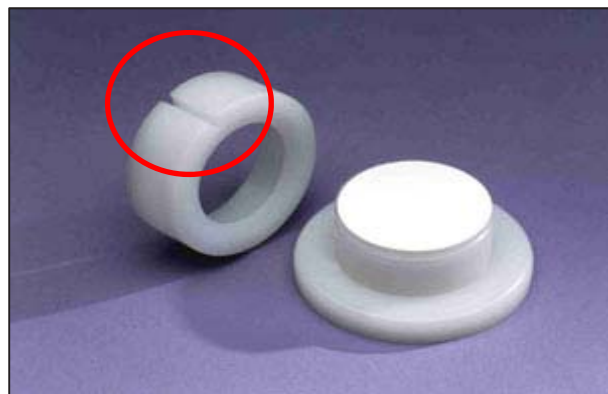
Retrieval

- Samplers collected and delivered to lab in individually sealed plastic containers
- Samplers should be shipped on ice to the lab for analysis



Lab Processing

- Upon arrival to lab, the plastic casing (cap) is removed using a flathead screwdriver



- The resin is digested in an appropriate digest solution
 - Solution and concentration depends on resin type used
 - Digestion typically occurs for 24-48 hours at room temp
- Samples are diluted, filtered and analyzed by ICPMS (or equivalent instrumentation)

DGT Calculations

- Concentrations of metals are determined by standard instrumental methods (often ICPMS)
- There are two results that you can obtain from analysis of DGTs:
 1. Mass accumulated by the DGT resin, M
 2. Time-weighted estimated water concentration, C_w

$$C_w = \frac{M \cdot \Delta g}{D_g \cdot t \cdot A}$$

Where:

M	=	mass accumulated on the resin
Δg	=	thickness of the diffusive layer (gel + filter membrane)
D_g	=	diffusion coefficient of metal species in the diffusive gel
t	=	total time of deployment
A	=	area exposed to the bulk solution

Diffusion Coefficients

- Representative of the diffusion through the diffusive gel layer (they are metal specific and temperature dependant)
- To use in DGT calculations, they must be corrected to the deployment temperature, T

$$\log_D = \frac{1.37(T - 25) + 8.36 \cdot 10^{-4} (T - 25)^2}{109 + T} + \log \frac{D_{25} (273 + T)}{298}$$

Where:

D = diffusion coefficient at the deployed temperature

D_{25} = diffusion coefficient at 25°C

Example:

Cadmium's reported DC in the diffusive gel at 25°C: $D_{25} = 6.09$

At a deployment temperature of 10°C: $D_{10} = 3.90$

Considerations for Deployment

Once deployed, there are several factors that can affect DGT performance, which can include:

1. Factors affecting precision and accuracy
 - diffusive boundary layer
 - biofouling
2. pH
3. Ionic strength
4. Accumulation capacity



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Factors affecting precision and accuracy

Diffusive Boundary Layer (DBL)

- A diffusive boundary layer is formed at the interface between the protective filter and the bulk solution
- It works as an extension of the diffusion layer and is larger in low flow and stagnant waters or sediments
 - In flowing waters, the DBL can essentially be ignored
 - Deployments in stagnant waters and sediment must consider the effect of the DBL in calculations
 - Ignoring will lead to underestimation of the results
 - Equations are available to correct for the effect of the diffusive boundary layer

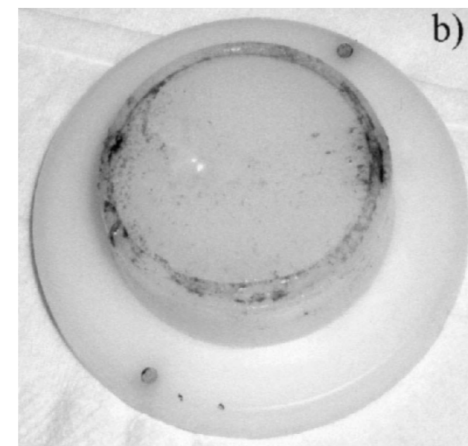
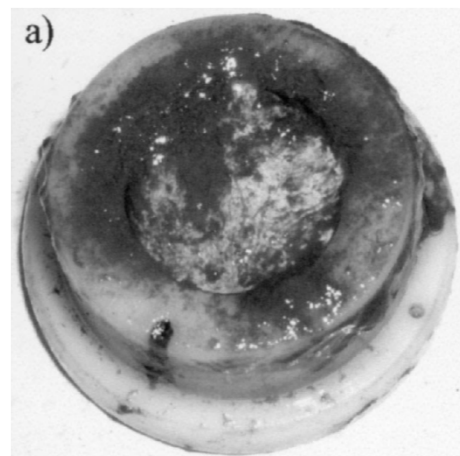
Factors affecting precision and accuracy

Biofouling

- Deployment in natural waters can cause biofilm to develop on the device
- Biofilm can adsorb analytes, prevent metal uptake by plugging pores or work as an extension of the diffusive layer
- Can result in an underestimation of metal analyte concentration
- Field staff need to make note of any samplers that appear to have significant biofouling



Uher et al., 2012



Dragun et al., 2008

pH and Ionic Strength

pH

- Most resins effectively adsorb analytes between pH 2-8
 - At low pH, the Chelex-100 resin can become protonated and the chelating efficiency is impaired
 - At pH <1 and pH >11, the polyacrylamide gel can swell

Ionic
Strength

- Several adsorptive resins (including Chelex and Metsorb) have deteriorated accumulation at low ionic strengths (< 0.001 mol/L)
- Can result in an underestimation of the metal concentration
- However, ionic strengths < 0.001 mol/L are uncommon and the majority of deployments should not be affected

Accumulation Capacity

- Maximum analyte accumulation in the DGT is limited by the capacity of the adsorbent incorporated in the binding layer
- Max capacity of the Chelex-100 DGT is 0.65 mg Cd (Zhang and Davison, 1995)
 - In ocean water this has been estimated to correspond to a 2.5 year deployment to collect metals
 - In freshwaters, metal concentrations are estimated to be 10x higher, and therefore the max deployment will be 10x lower, i.e. 3 months
 - The high accumulation capacity assures that the deployment time is rarely the limiting factor

Summary



- *In situ* technique developed by Davison and Zhang that is used for the determination of labile metal species concentrations
- Provides a better measure of biologically-available metals than dissolved or total metal concentrations
- Resin (adsorptive) gels are selective towards certain metal species
- DGTs can be used for any analyte which has a suitable adsorbent available
 - Common resins include: Chelex-100, Metsorb, Ferrihydrite, Chelex-Metsorb, Chelex-Ferrihydrite

Summary



- Measurements from deployed samplers include:
 - The mass of metal analytes accumulated on the adsorptive resin
 - Time-weighted estimated water concentrations
- Quick and easy deployment and retrieval procedures
 - Need to consider the duration of the deployment and water conditions
- Straightforward sample preparation and commonly used instrumentation

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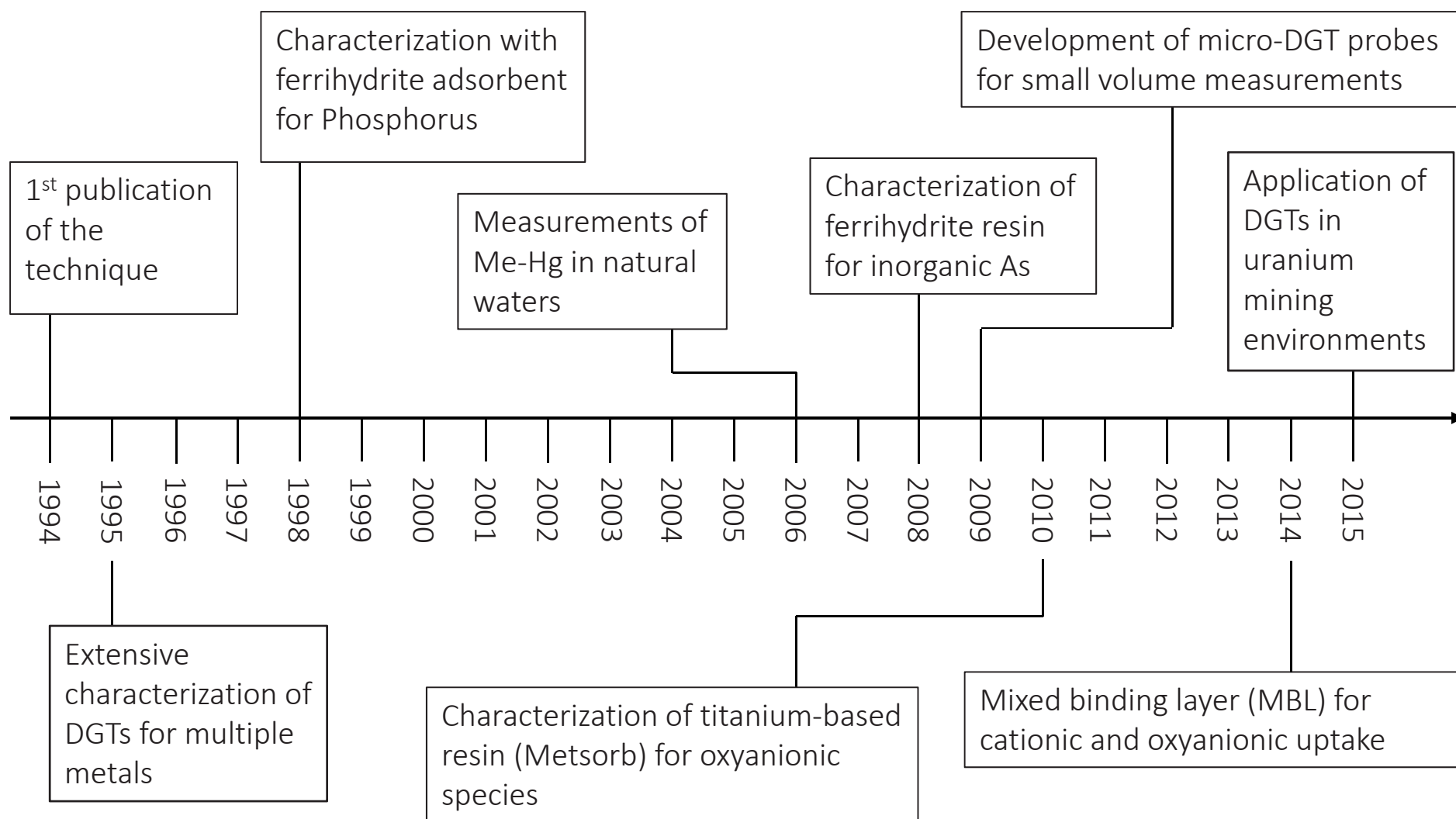
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History of DGT Development



Background

- Trace metals exist in natural waters in a variety of chemical phases, mostly as cations complexed by inorganic and organic ligands (Florence, 1982)
- The chemical speciation of metals has significant influence on cellular uptake, and hence bioavailability and toxicity
- Only a fraction of metal contamination in the environment is biologically available, the emphasis lies with dissolved (0.45µm filterable) rather than total metal concentrations
 - “Dissolved concentration” may be an overestimation of bioavailable metal as it also includes colloidal metals and metal bound to organics, which are potentially capable of remaining inaccessible to aquatic species
- There was a need for a device that was capable of measuring *truly bioavailable metal*