On-site Mercury Speciation, Does Passive Sampling Provide An Answer?

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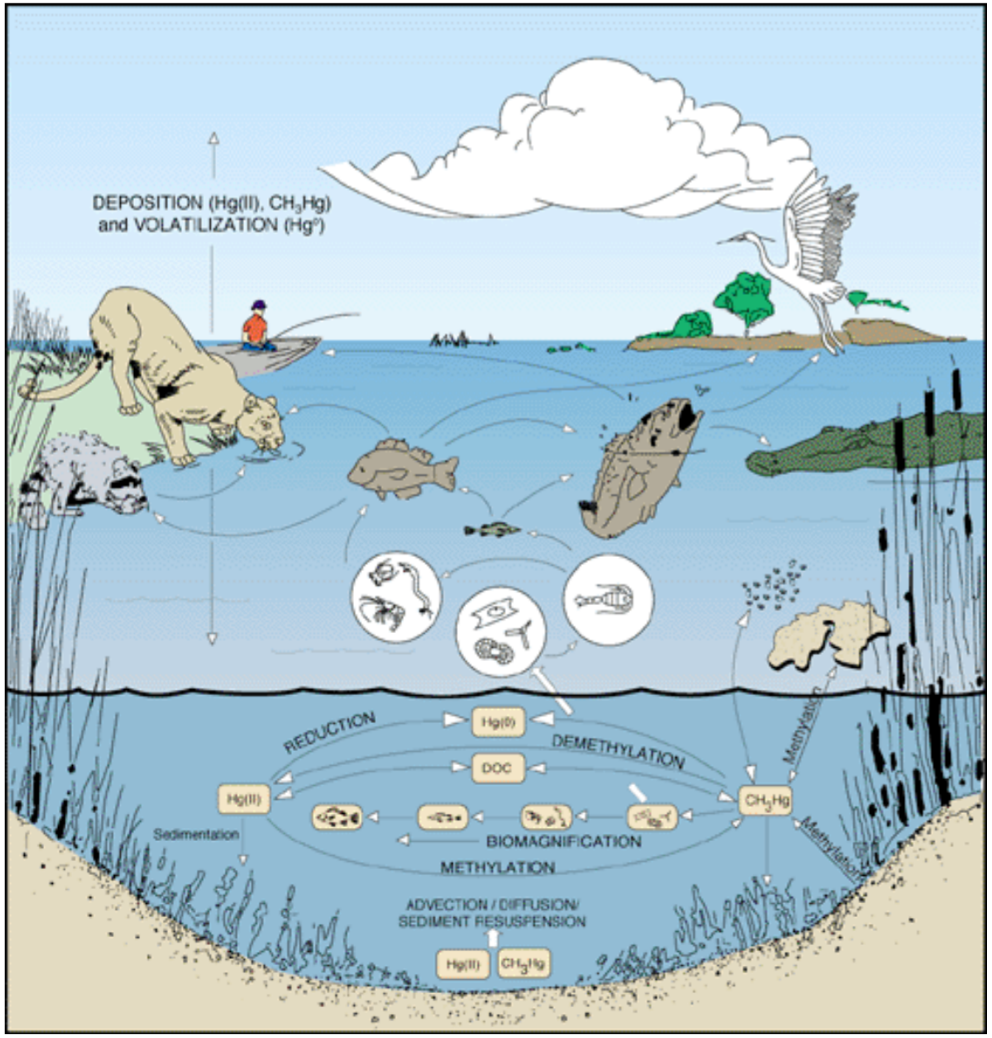
Maxxam
A Bureau Veritas Group Company

Why is Mercury Speciation of Interest?



Source: USGS Fact Sheet 146-00 (October 2000)

2 primary forms of mercury in natural aquatic systems:

- Hg(II) – inorganic
- MeHg – organic

- Other anthropogenic species
- Complexes with sediment, colloids and dissolved organics also form
- 'Bioavailable' mercury is the most relevant for toxicity
  - MeHg is most relevant
- Total mercury overestimates toxic potential

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Comparison: Grab sampling vs. Passive sampling

Grab sampling:

- Water removed from the field and shipped to the lab
- *Set volume* of the water sample is extracted; *all chemicals removed* for analysis
- **Data is a concentration at a single point in time**

Passive sampling:

- Device that attracts chemicals from water is placed in the water body, typically for a few weeks
- Chemical is collected gradually at a rate determined by the local water concentration and environmental conditions
- Device is shipped to the lab, mass of chemical in device is measured
- **Estimated average water concentration over the deployment is calculated**

Why Passive Samplers?

- **Generally accepted to only report the bioavailable fraction**
  - Do not respond to species bound strongly to sediment or other ligands
- **Data representative of average water concentrations during deployment**
  - Episodic peaks or sags in concentration don't significantly skew results
  - Toxicity is better correlated with average exposure concentration
- **Once sequestered in passive sampler media, species are stabilized**
  - Limited degradation or interconversion of different forms of a species

DGT* Passive Samplers for metals sampling

Why only the Bioavailable Fraction?

- Defined as species that can pass through a 0.45 µm membrane and bind to an embedded resin
  - Freely dissolved and 'kinetically labile' species
  - Once in the resin they are immobilized
  - Species distribution is preserved
  - Isolated from biological processes

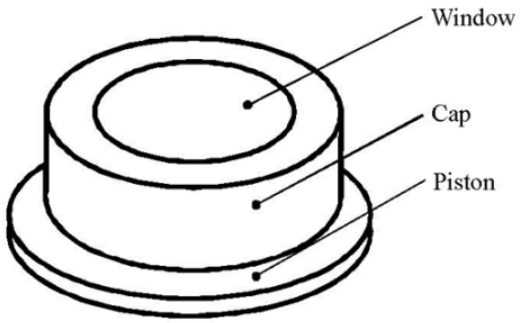
* DGT: **D**iffusive **G**radient **T**hin-film

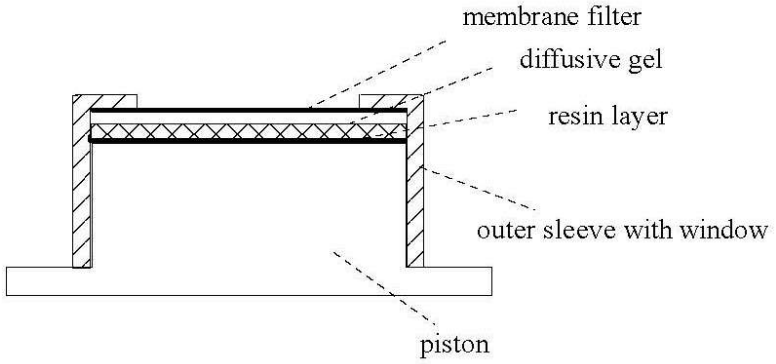
DGT Research – Lancaster UK

DGT Sampler Details

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

- Sampling by ion exchange or chelating resins
  - Chelex for cations
  - Metsorb for anions
  - Various chelating resins for general metals sampling
- Metals diffuse slowly from surrounding water into the sampler, typically over 2-6 weeks
- Linear uptake sampling due to a fixed diffusion barrier
- Must remain hydrated before and during deployment





Zhang, H., Davison, W. 1995, Anal. Chem., 67, 3391-3400

Lab Details

DGT Research Ltd., Lancaster, UK www.dgtresearch.com
-in North America - Sofa Logic, N.Y. www.sofalogic.com

DGT Processing:

- Resin gel removed from device
- Acid-digested
- Lab analysis of digest
  - ICP/MS, total mass of metal in sampler
  - LC-ICP/MS, separated species analysis

Water Concentration Calculation:

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

$$C_{DGT} = \frac{m\Delta g}{DAt}$$

Types of DGT Resins

commercially available

Ion Exchange Resins	
Chelex	$Hg^{+2}>Cu^{+2}>>Pb^{+2}>Fe^{+3}>Al^{+3}>Cr^{+3}>Ni^{+2}>Zn^{+2}>Ag^{+}$ $>Co^{+2}>Cd^{+2}>Fe^{+2}>Mn^{+2}>Ba^{+2}>Ca^{+2}>>>Na^{+}$
Metsorb	PO_4^{3-} ≈ As(V) > V(V) ≈ As(III) > Se(IV) ≫ Se(VI).
Chelex-Metsorb	combination of above
Chelex-Ferrihydrite	PO_4^{3-} ≈ As(V) > V(V) ≈ As(III) > Se(IV) ≫ Se(VI).

Production discontinued

Chelating plus Ion Exchange Resins – thiol functionalized	
Spheron Thiol	Hg, Sb, Bi, As > Ag, Cu, Pt > Pd, Cd, Pb
3-mercaptopropyl functionalized silica gel (Aldrich)	Hg, Pd, Pt, Cu, Cd, Ag, Ni, Co, Cu and Pb
thiol functionalized divinylbenzene: Duolite GT73 (Sigma) Ambersep GT74 (Rohm&Haas)	Hg > Ag > Cu > Pb > Cd > Ni > Co > Fe > Ca > Na

Field processes

General Recommendations

Ahead of time:

- Determine appropriate deployment location support/containment & anchoring
- Determine appropriate deployment time

Deployment:

- 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 average water temperature
- Expose field control device 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
- Ship to lab on ice

Overview: Hg Speciation with DGTs

Several papers and much development activity in the past ~6 years

1. Resin development
2. Diffusion gel developments,
   - types and associated uptake rates
3. Digestion/elution/analysis protocol development
   - Efficient removal of ALL Hg species from resin
   - Verify preservation of speciation
   - Developments in instrumental measurement techniques
4. Verification of results with comparison to conventional analysis
5. Studies on the impacts of DOC with the bioavailable fraction

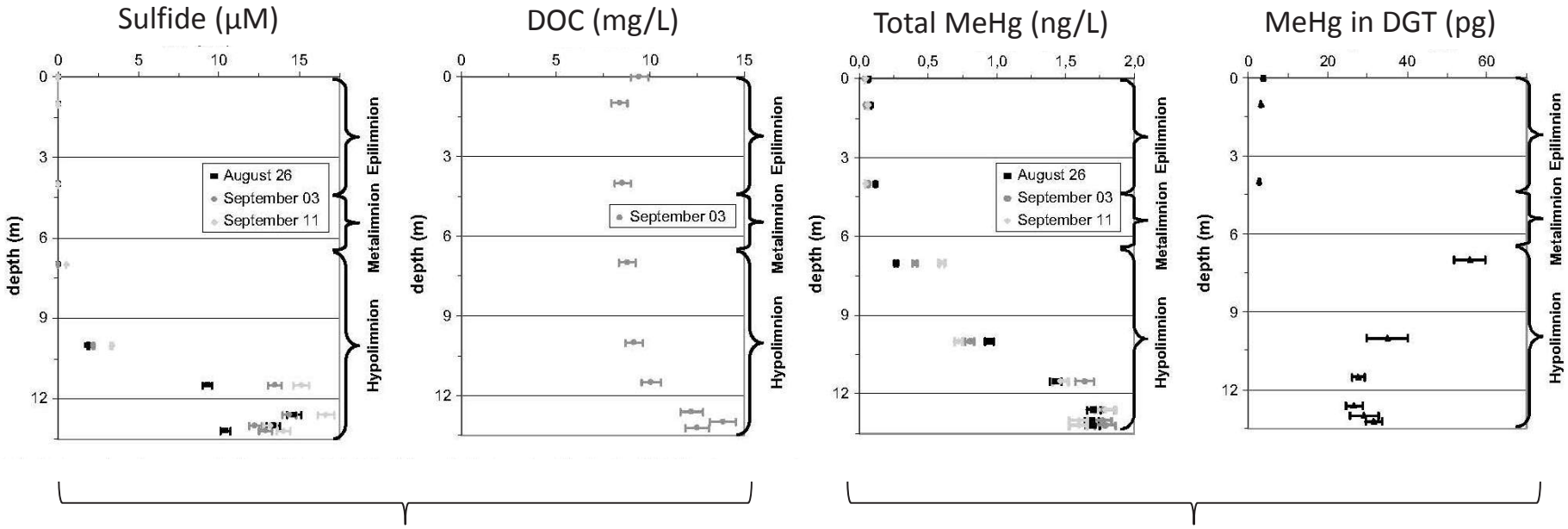
Methyl Mercury Determination

Clarisse, O. et al. 2009, Environmental Pollution 157: 987–993.
-Trent University

- **Objective**: Monitor methyl mercury in a stratified lake water column
- **Approach**: DGTs deployed in Lake 658 of the Experimental Lakes Area (ELA) in Ontario, Canada
  - MeHg measured both conventionally and by DGT
  - DOM, Temp., pH, sulfides also measured
- **Diffusion gel**: polyacrylamide
- **Resin**: 3-mercaptopropyl functionalized silica gel (Aldrich).
- **Elution & Analysis**: thiourea/HCl, derivatization, GC-ICP/MS

Methyl Mercury Determination

Results



Sulfide and DOC are strong ligands for MeHg, expected to drive overall speciation at depth.

The increase in total MeHg and drop in free MeHg at depth correlate with close to 100% of MeHg bound to ligands at depth.

Methyl Mercury Determination

Study Conclusions

- Observed that complexes with particles, DOC and sulfide were all affecting the proportion of bioavailable mercury
- Overall effect differed with depth in the water column
  - Bioavailable mercury species concentrations peaked in the middle of the water column
  - Total mercury species concentrations peaked near the sediment

Methyl Mercury Determination

Technology Conclusions

- Only MeHg was reported
- Complications observed due to variable diffusion coefficients in the gel
  - Uncertainties observed with water concentration estimates
- Other authors suggested the polyacrylamide itself bound Hg-species
  - Issue has not been fully proven, however…
  - Agarose subsequently became the preferred diffusion gel for Hg-analysis
- Commercial availability of Spheron-Thiol resin problematic

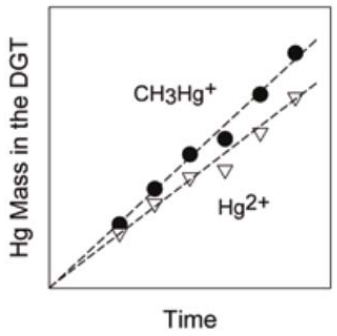
Mercury Speciation – Hg^{2+} vs. MeHg

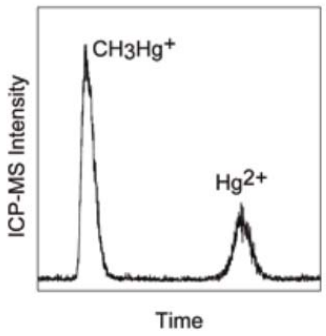
Hong et al. 2011, Envir. Sci. & Technol, 45: 6429-6436.
-Johns Hopkins University

- **Objective**: Demonstrate simultaneous measurement of free MeHg & Hg(II); Show the sum ≈ total free Hg in oxic water
- **Approach**: DGTs deployed at three surface water sites in the US: a) freshwater river; b) estuarine bay, c) marine bay
  - Significant technology development
  - Studied diffusion coefficients and ligand complexes (Cl^-, OH^-, DOM)
  - Comparison of DGT performance vs direct measure
- **Diffusion gel**: agarose
- **Resin**: 3-mercaptopropyl functionalized silica gel (Aldrich).
- **Elution & Analysis**: thiourea/HCl, IC-ICP/MS

Mercury Speciation – Hg^{2+} vs. MeHg

Results





Deployment ⇨ **Accumulation** ⇨ **IC-ICP-MS**

Water detection limits:

- CH_3Hg^+ : 0.1 ng/L
- Hg^{2+} :0.7 ng/L

	Freshwater	Estuarine	Saline
DOC (mg/L)	2.6	4.4	1.1
Cl^- (mM)	0.0375	18.5	560
filtered water THg (ng/L)	4.1	3.3	<10
DGT THg (ng/L)	6.8	1.2	5.6
CH_3Hg^+ (ng/L)	0.25	<0.07	0.13
% free CH_3Hg^+	3.1	<11	2.6

Mercury Speciation – Hg^{2+} vs. MeHg

Study Conclusions

- The DGT estimated total Hg values were within a factor of 2 to 3 of the total Hg concentrations determined by grab sampling and ICP-MS analysis.
- Cl^- & OH^- complexes did not impact overall results:
  - At constant pH, OH^- complexes were stable
  - Effective diffusion coefficient established at ambient pH
  - Cl- concentrations has no significant effect on Hg-species diffusion (Hg-species either bound to Cl^- or not produced similar results)
  - No impact of marine vs. freshwater expected
- DOM complexes (humic/fulvic acids) significantly impacted diffusion
  - Effective diffusion coefficients determined
  - Data analysis approach developed to deal with variable DOM

Mercury Speciation – Hg^{2+} vs. MeHg

Technology Conclusions

- Provides a sound approach to in-situ speciation of bioavailable Hg
- The DGTs used may not be commercially available at present
  - Resin is commercially available, not expected to be a long-term issue
- Other authors noted at the same time that significant clogging of the filter membrane may occur, particularly in eutrophic water
  - In such case metal uptake is significantly or completely eliminated
  - No problems observed in oligotrophic water
  - Int. J. Environ. Anal. Chem. 2011, 92(15): 1689-1698.
- Current recommendation is to avoid eutrophic water, monitor biofilm formation, flag data where significant biofilm is seen

Mercury Speciation Extended

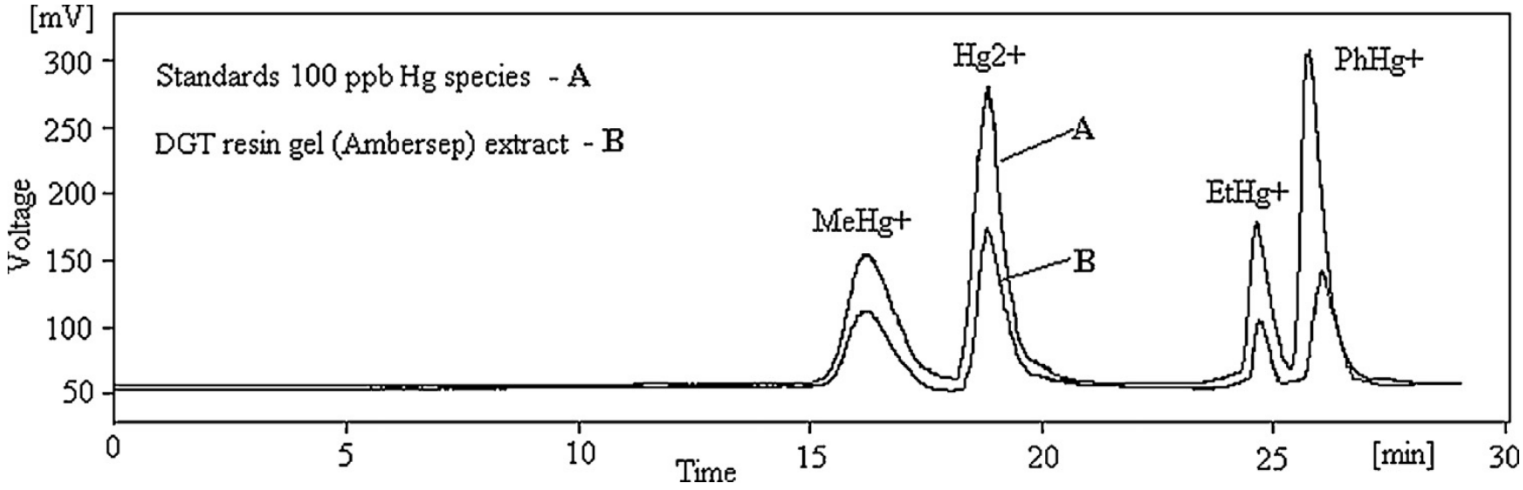
Pelcova, P. et al. 2015, Anal. Chim. Acta 866: 21-26
-Czech Republic

- **Objective**: Demonstrate more complete speciation of Hg species
  - Four species measured; Hg^{2+}, CH_3Hg^+, $C_2H_5Hg^+$, and $C_6H_5Hg^+$ plus total bioavailable Hg
- **Approach**: lab studies and spiked river water
  - Comparison of DGT performance vs direct measure
- **Diffusion gel**: agarose
- **Resin**: Duolite GT73 and Ambersep GT74
- **Elution & Analysis**: 6M HCl, LC-CV-AFS

Mercury Speciation Extended

Results

Preservation of Species Distribution in Resin Digest



Comparison of DGT data with conventional

Mercury species	C_{DGT} [$\mu g L^{-1}$]	C_{direct} [$\mu g L^{-1}$]
Hg^{2+}	5.3 ± 0.2	5.0 ± 0.3
CH_3Hg^+	5.4 ± 0.1	5.1 ± 0.3
$C_2H_5Hg^+$	5.0 ± 0.4	5.1 ± 0.4
$C_6H_5Hg^+$	4.7 ± 0.3	4.9 ± 0.3

Mercury Speciation Extended

Results (cont.)

- Diffusion coefficients in agarose verified
- Species distribution maintained in digest relative to ambient
- Detection limits high (24 h DGT accumulation):
  - Hg^{2+}: 13 ng/L, CH_3Hg^{+}: 38 ng/L, $C_2H_5Hg^{+}$: 34 ng/L, $C_6H_5Hg^{+}$: 30 ng/L
  - Lower DLs possible with a longer deployment &/or ICP-MS analysis
- DGT Water concentrations compared well to conventional analysis
  - Different diffusion coefficients used for different species
- Limitations :
  - Effect of DOM not evaluated
  - Field deployment not demonstrated

Mercury Speciation Extended

Technology Conclusions

- New commercially available resins shown as fit-for-purpose
- Analysis extended to anthropogenic Hg-species
- Poor DL primarily related to the instrumental detection used
- Spike concentrations were high (~5 µg/L), should repeat at relevant concentrations

Summary

- Through careful DGT selection and appropriate lab processing & analysis, speciation of bioavailable mercury is technically feasible
  - No regulatory acceptance as of yet
  - Care must be taken in the selection of diffusion gel and diffusion coefficients to obtain meaningful results
  - Biofilm formation still problematic, need to avoid
  - Still largely an R&D exercise, but mostly applied R&D now

The time is right for properly designed field studies at appropriate sites!

Thank You!

Contact

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