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Using DGT to Measure Bioavailable Metals in a Constructed Wetland Treatment System

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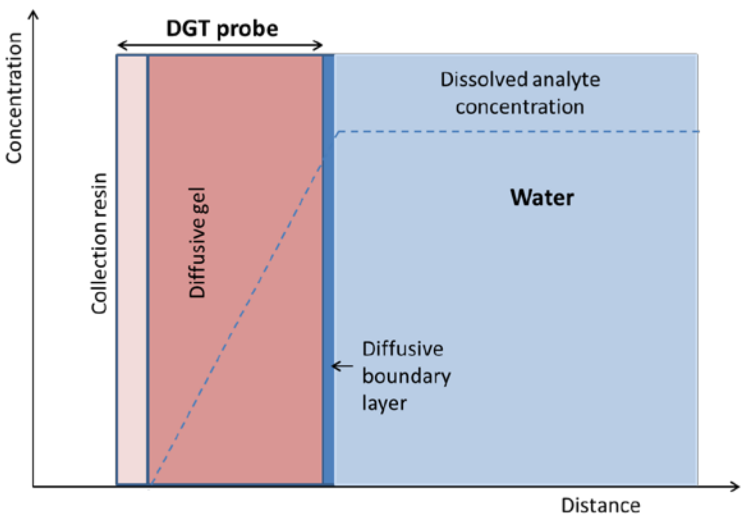
Background – DGT Technology

- Diffusive Gradients in Thin Films (DGT) probes consist of an absorbent layer with a medium that selectively binds to the contaminant of interest and a diffusion gel that selectively admits analyte molecules. They require no electricity, have no moving parts, and are simple to use
- DGT relies on the unassisted molecular diffusion of analytes through the diffusion gel onto the adsorbent layer. After sampling, adsorbed analytes are usually desorbed off the adsorbent and analyzed (e.g., by mass spectrometry)
- Environmental concentrations of elements are calculated from the concentration of the element in the absorbent gel, device configuration, analyte diffusion coefficients, deployment time, and other factors



Schematic cross-section through a DGT probe showing a steady state concentration gradient between an analyte in solution and a collection resin.

$$M = \frac{Ce * (V_{NO3} + V_{gel})}{fe}$$

$$C_{dgt} = \frac{M * \Delta g}{D * t * A}$$

Davison, W. & H. Zhang. 1994. In situ speciation measurements of trace components in natural waters using thin-film gels. Nature. 367, 546 - 548 (10 February 1994); doi:10.1038/367546a0

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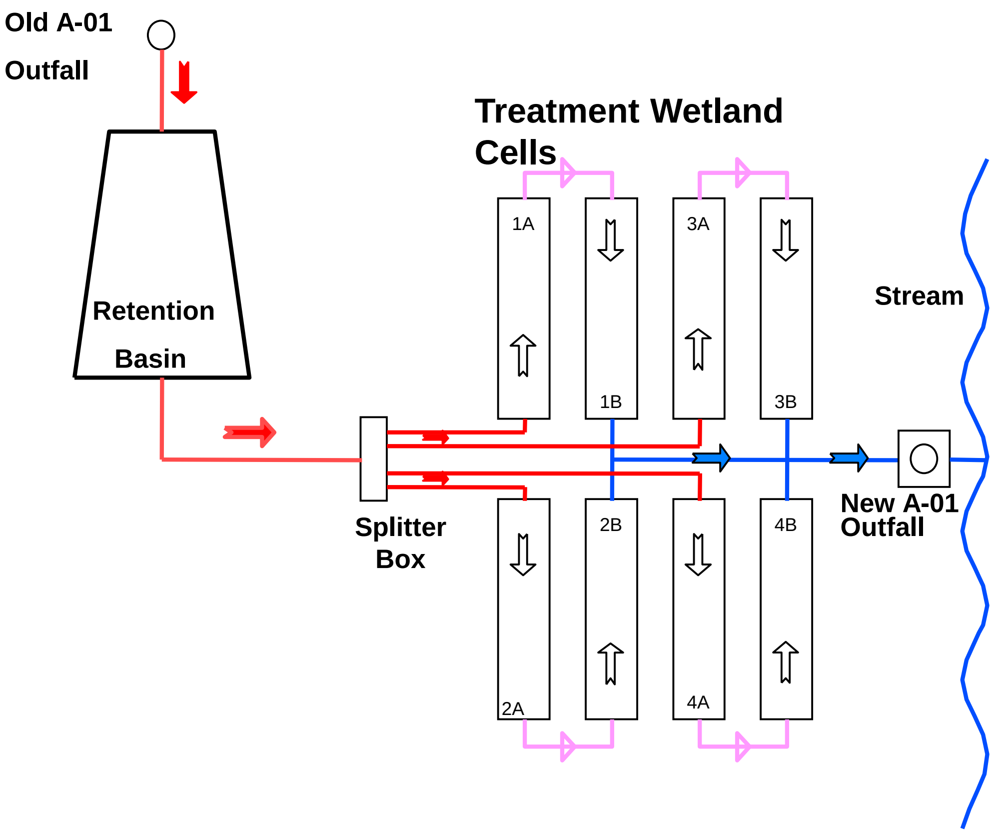
Background – Bioavailability

- Bioavailability – degree to which chemicals (e.g., metals) are absorbed or metabolized by human or ecological receptors or are available for biological interactions
- Metals exist in different forms in the environment. These forms differ in toxicity because of differences in bioavailability
- Metals strongly bound to organic molecules and metal sulfides are typically unavailable (Di Toro et al. 2001)*
- DGT theoretically measures bioavailable dissolved and labile metal species that readily pass through the diffusion gel but excludes relatively unavailable metals, such as those bound to large organic molecules

* Di Toro DM, Allen HE, Bergman HL, Meyer JS, Paquin PR, Santore RC. 2001. Biotic Ligand Model of the Acute Toxicity of Metals. I. Technical Basis. Environmental Toxicology and Chemistry 20: 2383–2396.

Background – AO1 Wetland Treatment System

- Designed and constructed in 2000 to remove metals, especially copper, from the A-01 effluent.
- Consists of four sets of two sequential treatment cells planted with giant bulrush (*Schoenoplectus californicus*)
- Effluent passes from A cell to B cell in each pair of cells



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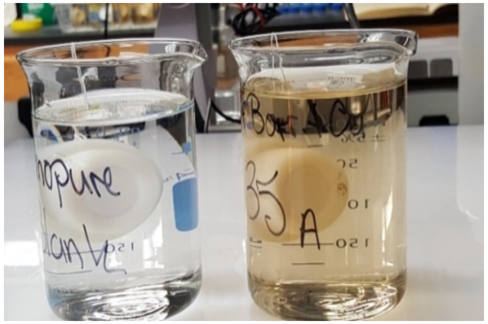
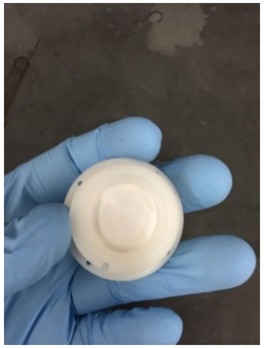
Laboratory Study: Assess Effects of Water Quality on DGT Measurements of Copper and Zinc

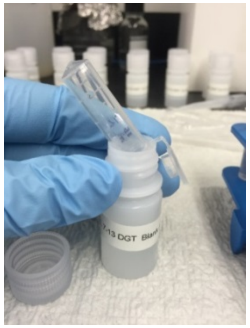
- Four types of water:
  1. Low hardness (10-13 mg/L as $CaCO_3$) and low (<detection limit) dissolved organic carbon (DOC, represented by BorreGRO HA-1™)
  2. Low hardness and high DOC (5 mg C/L)
  3. High hardness (80-100 mg/L as $CaCO_3$) and low DOC (<DL)
  4. High hardness water (80-100 mg/L as $CaCO_3$) and high DOC (5 mg C/L)



Water with and without BorreGRO

- Metals measured with DGT water probes during each 48-hr bioassay
  - DGT probe : APA (polyacrylamide gel cross-linked with agarose) diffusive gel and Chelex binding layer
  - Acid extraction of metals from binding layer and analysis by ICP MS
- Total metal levels in water measured at beginning and end of each 48-hr bioassay by ICP-MS
- 48-hr LC50s for copper (Cu) and zinc (Zn) calculated for *Ceriodaphnia dubia* in four types of water (LC50 = metal concentration that kills half of the *C. dubia* sample population in 48 hrs)





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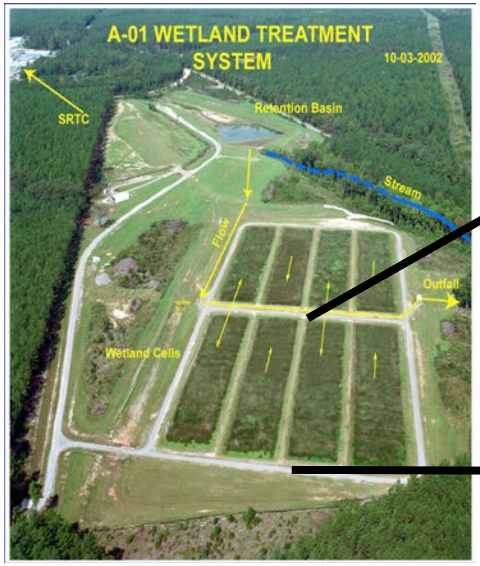
Field Study: Using DGT to Measure Bioavailable Metals in the AO1 Wetland Treatment System

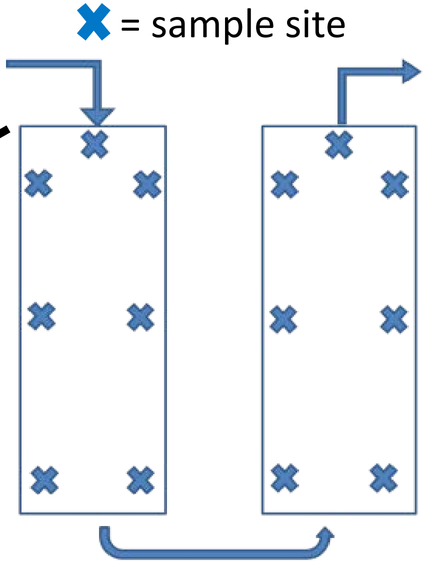
DGT water and sediment probes were placed at intervals in two treatment cells and compared with water and sediment samples collected at the same locations.

Methods

- DGT water probes (Cu, Zn) suspended in water for 24 hrs and 168 hrs
- DGT sediment probes embedded in sediments for 24 hrs
- Sediment cores –one inch diameter cores to a depth of 3 inches
- Water samples –surface water grab samples

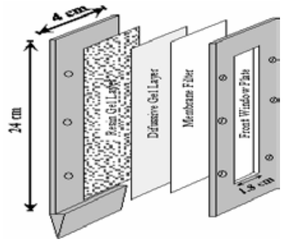


Blue arrows show flow path



Wetland cells 4A and 4B. Sample locations marked with an "X."

Water probe



Sediment probe

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Research Objective and Hypotheses

Objectives:

1) Determine if DOC affects the measurement of Cu and Zn by DGT
2) Determine if the presence of DOC results in differences between DGT-based LC50s and water-based LC50s (i.e., LC50s based on measurement of total metals in water by ICP-MS)
3) Determine if DGT appears to measure bioavailable Cu and Zn within the A-O1 Wetland Treatment System

Hypotheses:

1. DOC will reduce the concentration of metals measured by DGT because metals bound to organic matter will not pass through the DGT diffusion gel
2. DGT LC50s will be lower than water-based LC50s (i.e., LC50s based on total metal concentrations) because DGT will exclude metals bound to organic matter that do not contribute to toxicity
3. DGT concentrations of metals in AO1 water and sediment will be lower than total concentrations of metals because DGT will exclude metals that are complexed with organic matter (i.e., metals that are not bioavailable)

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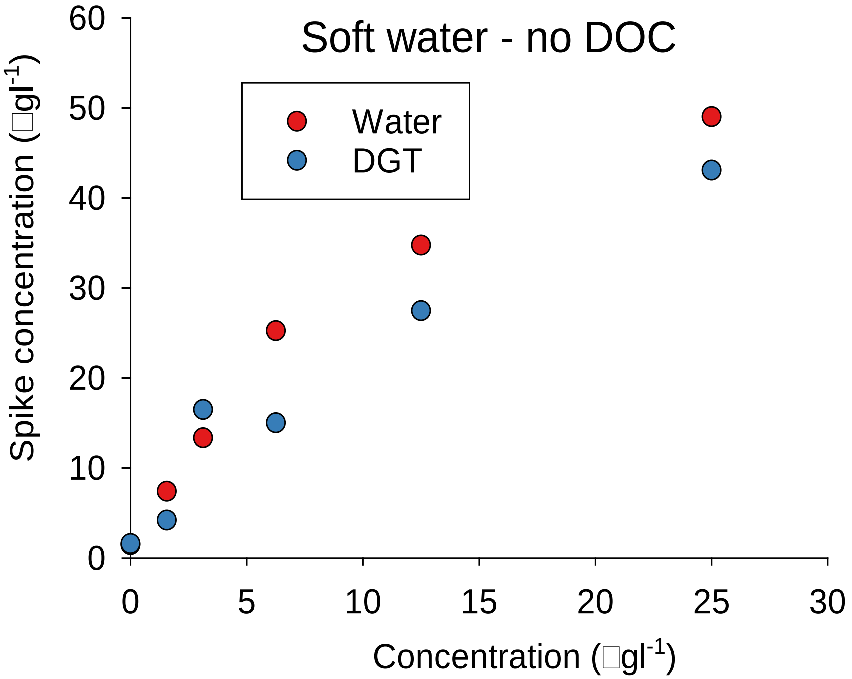
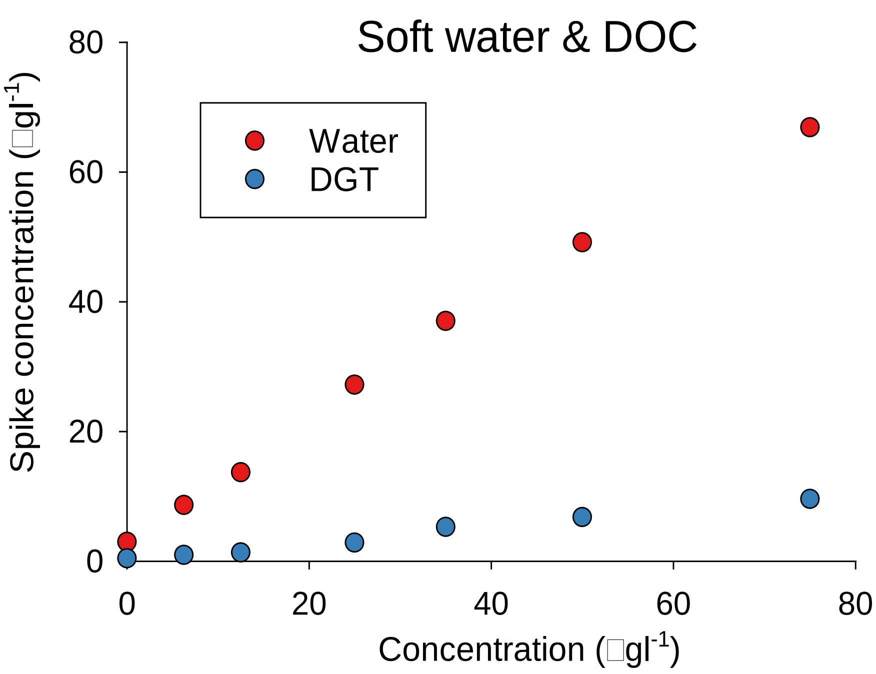
Lab Results: Effects of Dissolved Organic Carbon on Measurement of Cu by DGT

- Cu concentrations measured by DGT were fairly similar to Cu concentrations in water when no DOC was present
- Cu concentrations measured by DGT were much lower than Cu concentrations in water when DOC was present, presumably because DGT did not measure Cu bound to organic matter





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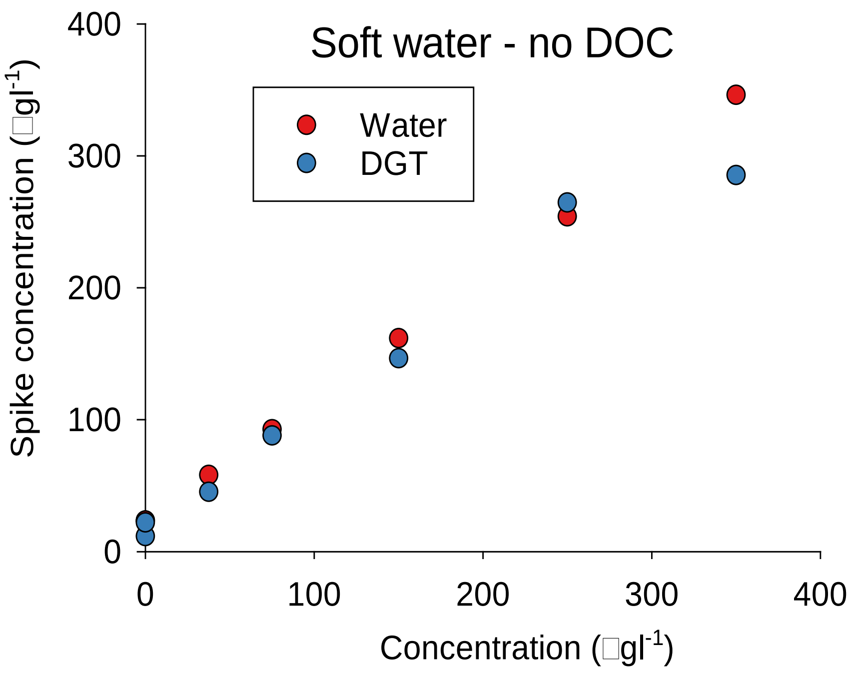
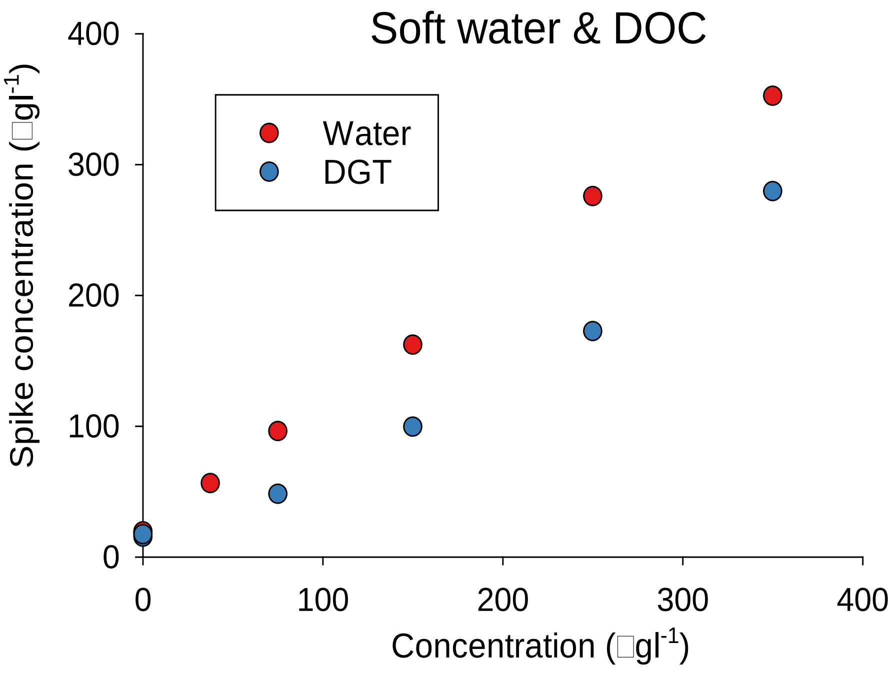
Lab Results: Effects of Dissolved Organic Carbon on Measurement of Zn by DGT

In contrast to Cu, Zn concentrations measured by DGT were only slightly lower than Zn concentrations in water across different levels of DOC, presumably because Zn did not form strong bonds with organic matter that prevented the passage of Zn through the diffusion gel





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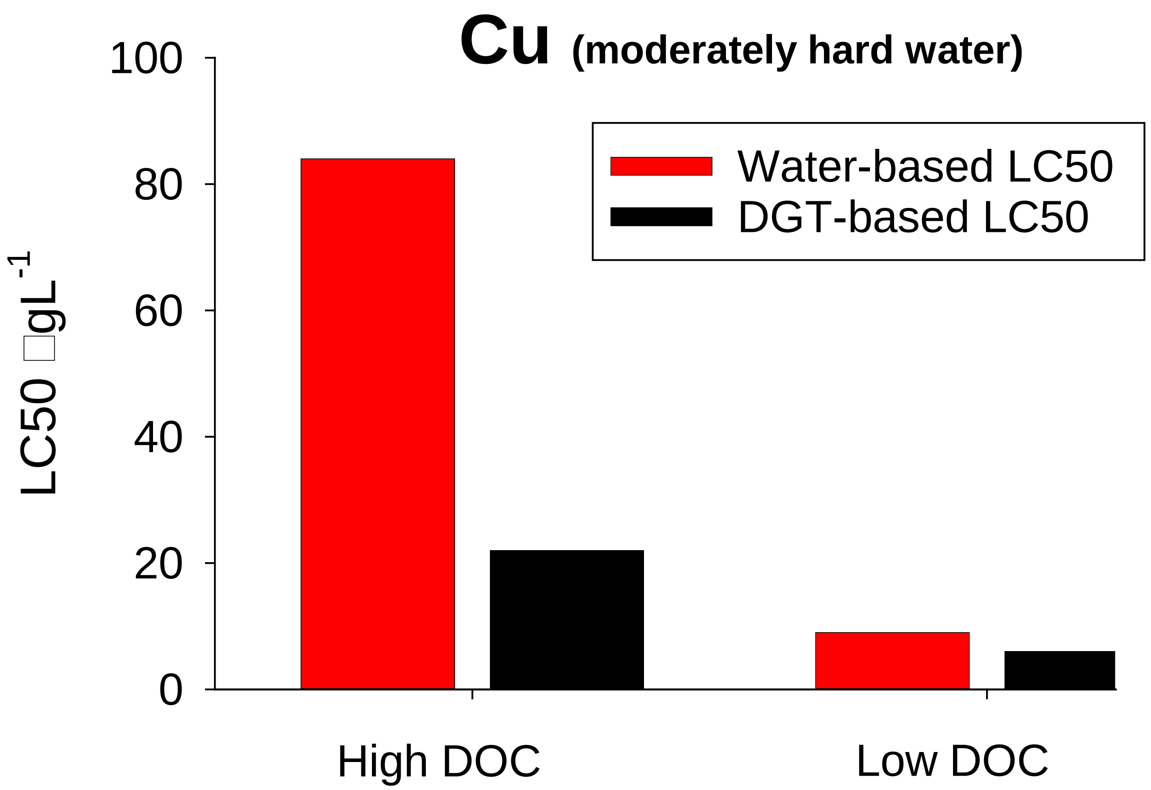
Lab Results: LC50s for Cu



- DGT-based LC50s for Cu were much lower than water-based LC50s in high DOC waters but only slightly lower than water-based LC50s in low DOC water
- DGT did not measure Cu bound to the organic matter. This resulted in a lower DGT-LC50 than water-based LC50 because DGT excluded Cu bound to DOC that did not contribute to toxicity

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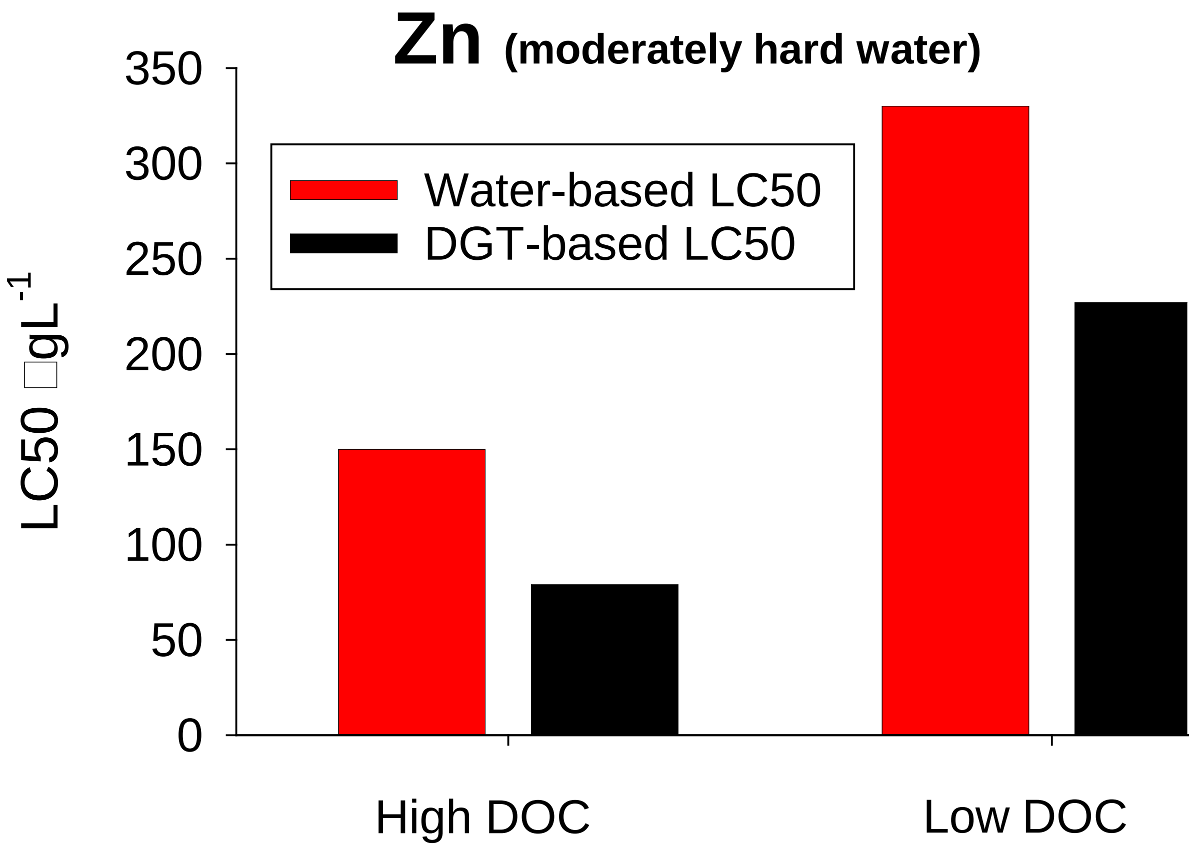
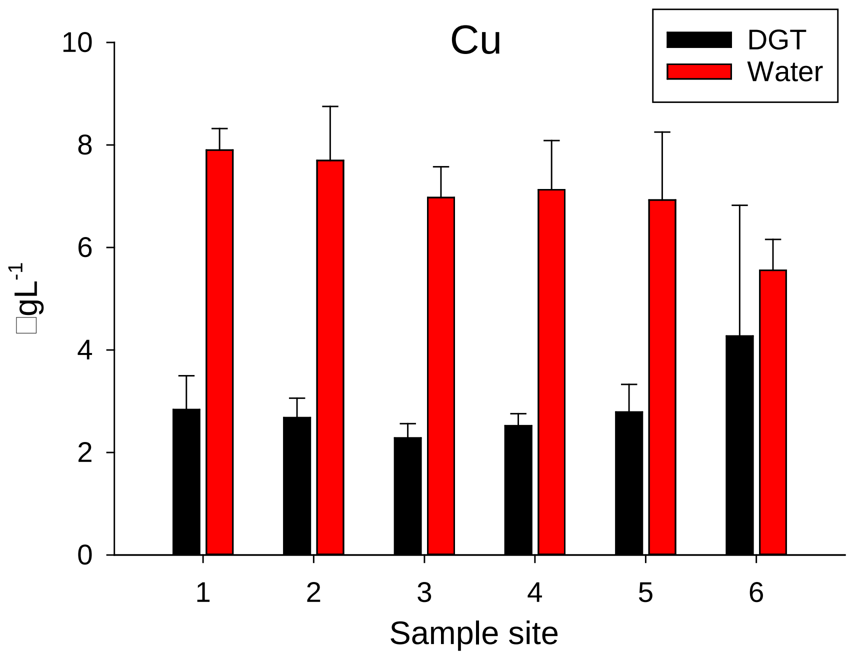
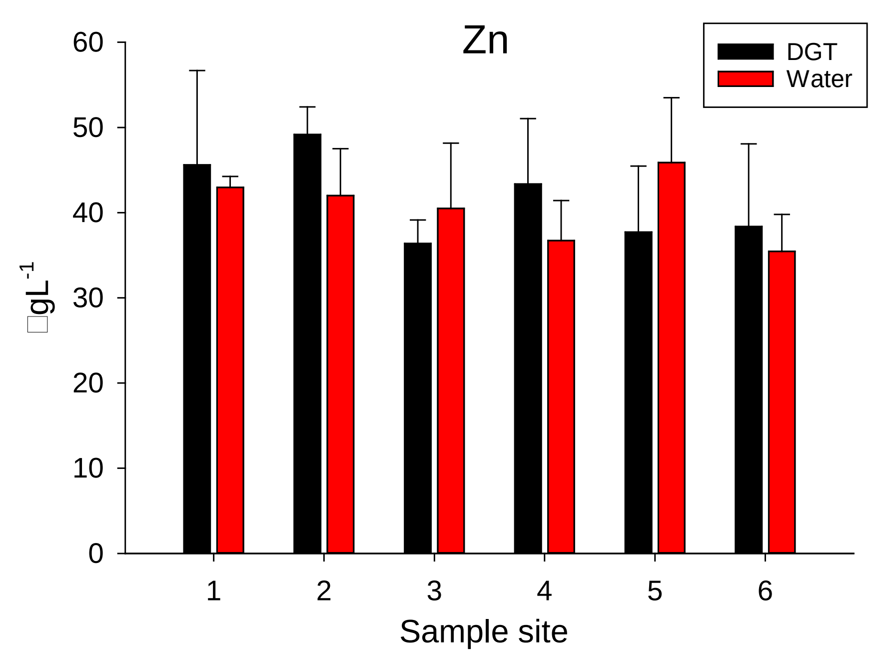
Lab Results: LC50s for Cu and Zn



- The difference between water-based and DGT-based LC50s in high DOC water was smaller than observed with Cu
- DOC did not affect the DGT-LC50 for Zn as strongly as Cu because Zn was less likely than Cu to form strong complexes with organic matter that were excluded by DGT

Field Results: Cu and Zn in AO1 Water as Indicated by DGT and Total Metals in Water



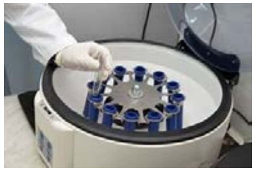


DGT measurements were lower ($P<0.05$) than total metals in water for Cu but not Zn (24 hr deployment)

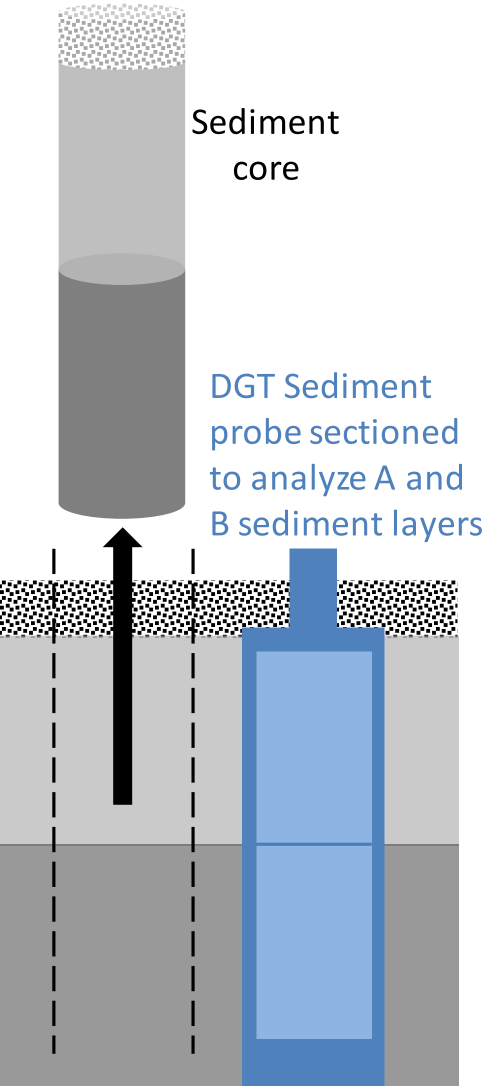
- Cu bound to DOC is included in water measurements but not DGT measurements.
- Assuming Cu bound to DOC is not bioavailable, DGT measured bioavailable Cu while water measurements included bioavailable Cu plus nonbioavailable Cu bound to DOC
- DGT- and water-based measurements of Zn did not differ much because Zn did not form strong complexes with DOC (as also observed in the lab)

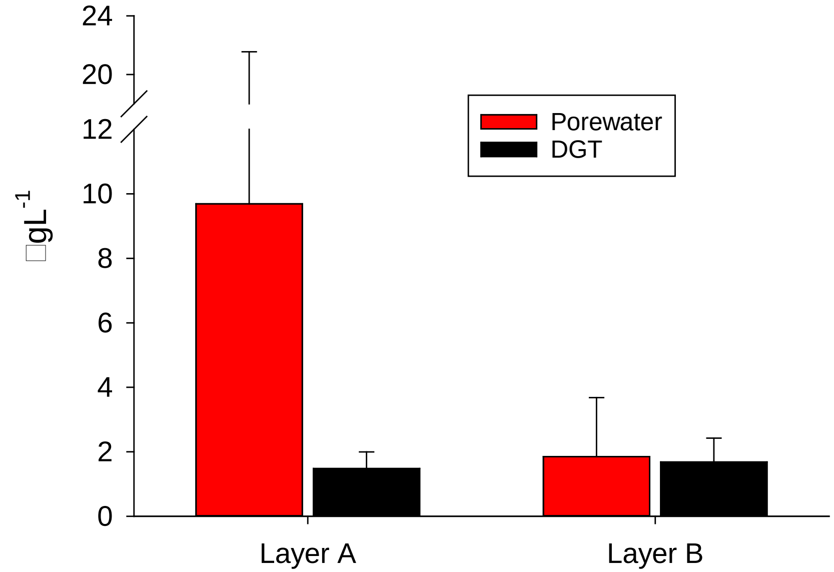
Field Results: Comparison of Cu Measurements Made by DGT Sediment Probes (24 hr deployment) with Measurements of Total Cu in Sediment Porewater

Sediment cores divided into two layers (A & B) for porewater extraction and analysis by DGT sediment probes



Sediment porewater extracted by centrifugation

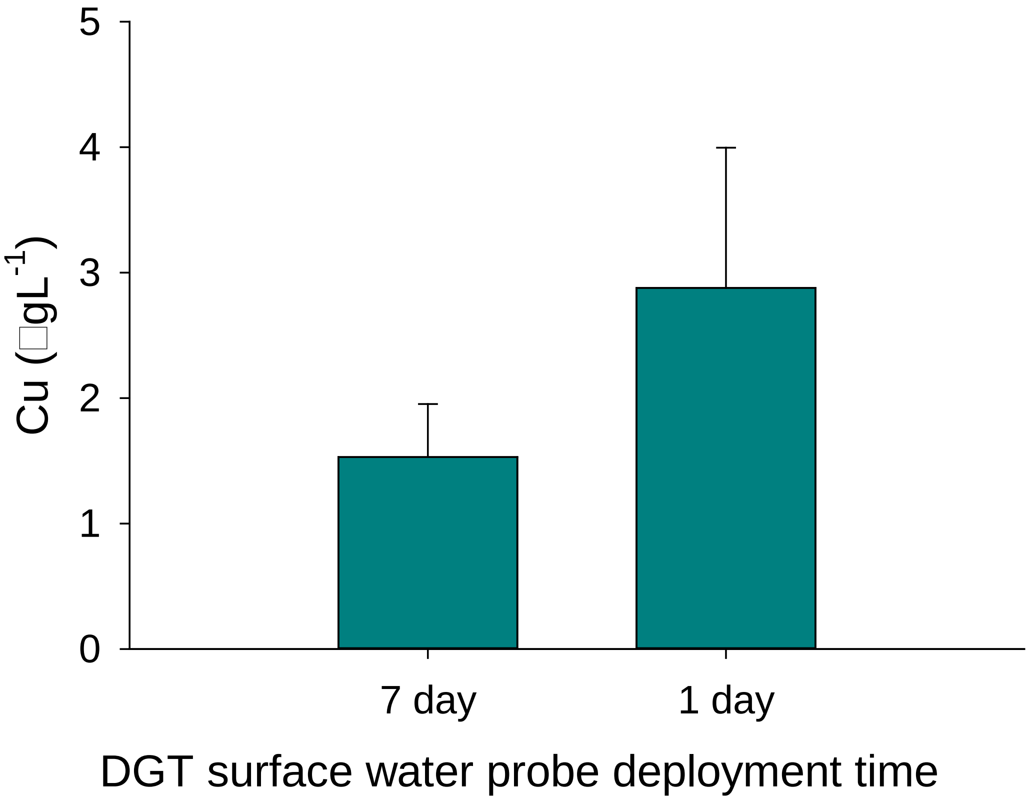




Comparison of porewater Cu with DGT

- Total Cu concentrations in porewater were higher than DGT concentrations in layer A but not layer B
- There was a large difference between porewater and DGT measurements in Layer A where organic matter was present in high concentrations (Knox et al., JEQ, 35, 1948-1959, 2006)
- There was little difference between porewater and DGT measurements in Layer B where organic matter was present in low concentrations

Field Results: Effects of Deployment Time on DGT Surface Water Cu Measurements (1 vs 7-day deployment)



- 7-day DGT deployment resulted in lower concentrations than 1-day DGT deployment
- Localized areas of stagnant flow, biofouling, or other factors might compromise DGT accuracy with longer deployment times in wetland environments

Summary and Conclusions

- DOC strongly affected the measurement of Cu by DGT in the lab because DGT formed strong complexes with DOC that were not measured by DGT
- In the presence of DOC, DGT LC50s for Cu were much lower than water LC50s for Cu because DGT excluded non-bioavailable Cu strongly bound to organic matter
- DOC did not affect DGT measurements of Zn in the lab or DGT LC50s as strongly as Cu because Zn did not form strong bonds with the organic matter under study
- DGT measurements of Cu in AO1 surface waters were significantly lower than measurements of total Cu because Cu bound to DOC (and/or other ligands) was excluded by the DGT probes
- DGT- and water-based measurements of Zn in AO1 surface waters did not differ much because Zn did not form strong complexes with DOC or other ligands
- DGT measurements of Cu in sediment were lower than measurements of total metals in sediment porewater in surface sediments where DOC was plentiful but not in deeper sediments where DOC was relatively scarce
- DGT has potential to measure bioavailable metal fractions in wetland treatment systems and discriminate bioavailable metals from nonbioavailable metals
- Methodological issues can compromise DGT accuracy