Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

Title: BioAccumulation using Surrogate Samplers (BASS): Evaluation of a passive sampler as an alternative monitoring tool for environmental contaminants at the Savannah River Site

Project highlight:

Department of Energy (DOE) sites conduct traditional environmental monitoring programs that require collecting, processing, and analyzing water, sediment, and fish samples. However, recently developed passive sampling technologies may have the potential to eliminate some of these laborious steps and produce more accurate results by measuring the specific chemical forms that are most toxic to aquatic life. Diffusive Gradient in Thin films (DGT) is a type of passive sampler that consists of a gel-layer that selectively binds to specific contaminants and a diffusion gel that selectively admits molecules that are available and toxic to organisms. Our laboratory showed that dissolved copper concentrations measured by DGT probes were strongly correlated with the uptake of copper by an aquatic worm. Dissolved copper concentrations in DGT probes increased with time of exposure, paralleling the increase in copper with time that ocurred in these organisms. Additional studies with a combination of seven dissolved metals showed similar results. These findings support the use of DGT as a monitoring tool that mimics contaminant uptake by aquatic organisms and provide a basis for refinement of passive sampling methods for cost-effective environmental monitoring. Ultimately, such methods have the potential to modernize and reduce the costs of labor intensive surface and groundwater environmental monitoring programs within the DOE and elsewhere in the nation.

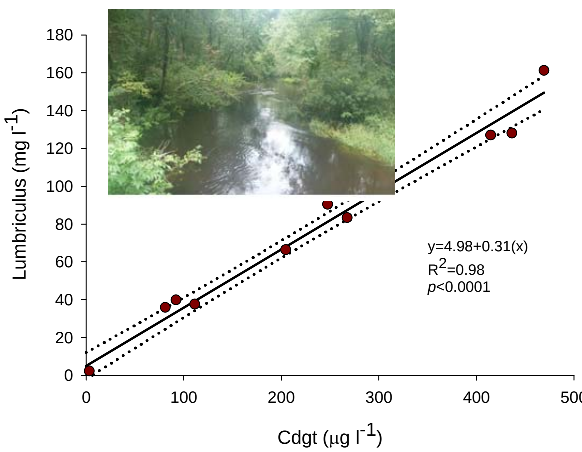

Figure 2. Copper levels in *Lumbriculus* vs. copper levels measured by DGT (Cdgt).

Awards and Recognition

None

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

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Signature **Date**

Title: BioAccumulation using Surrogate Samplers (BASS): Evaluation of a passive sampler as an alternative monitoring tool for environmental contaminants at the Savannah River Site

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Subcontractor: University of Georgia

Thrust Area: (Environmental Stewardship)

Project Type: (Exploratory Quick Hit)

Project Start Date: May 1, 2015
Project End Date: September 30, 2015

Abstract: DOE sites conduct traditional environmental monitoring programs that require collecting, processing, and analyzing water, sediment, and fish samples. However, recently developed passive sampling technologies, such as Diffusive Gradient in Thin films (DGT), may measure the chemical phases that are available and toxic to organisms (the bioavailable fraction), thereby producing more accurate and economical results than traditional methods. Our laboratory study showed that dissolved copper concentrations measured by DGT probes were strongly correlated with the uptake of copper by *Lumbriculus variegatus*, an aquatic worm, and with concentrations of copper measured by conventional methods. Dissolved copper concentrations in DGT probes increased with time of exposure, paralleling the increase in copper with time that ocurred in *Lumbriculus*. Additional studies with a combination of seven dissolved metals showed similar results. These findings support the use of DGT as a biomimetic monitoring tool and provide a basis for refinement of these methods for cost-effective environmental monitoring at DOE sites.

FY2015 Objectives

- Measure biologically available heavy metal concentrations in water with DGT probes
- Compare DGT measurements with results from conventional methods and with metal uptake by aquatic organisms to determine if DGT measures bioavailable contaminants.

Introduction

Traditional environmental monitoring programs require collecting, processing, and analyzing samples from a variety of environmental media. Data interpretation can be difficult because of differences in sample size, heterogeneity within and among media, and failure to measure the chemical species that are bioavailable and toxic. Recently, passive samplers are being investigated as efficient and cost-effective alternatives to traditional methods. They are based on the flow of analyte molecules from the sampled medium to a receiving medium in the sampling device as a result of differences in concentration between the two media. Passive samplers can be viewed as “virtual organisms” that absorb contaminants in a manner analogous to living organisms. Potential advantages include

1. **Cost Savings.** Passive samplers can reduce costs because they combine sampling, sample processing, selective analyte isolation, and analyte pre-concentration.
2. **Realism.** Passive samplers theoretically measure the dissolved and labile chemical species that are available and toxic to organisms (the bioavailable fraction).
3. **Sensitivity.** Passive samplers make it possible to measure very low but significant levels of contaminants because they pre-concentrate and maximize the amount of analyte sampled.
4. **Representativeness.** Passive samplers yield a time-integrated average concentration that is more representative of prevailing contaminant levels than the “snapshot” typically produced by grab samples.

5. **Quality Assurance.** Data from passive samplers are consistent and comparable, which facilitates spatial comparisons, trend assessment, and adequate replication for robust statistical testing.

Approach

DGT is a type of passive sampler that consists of a gel-layer with a medium that selectively binds to the contaminant of interest and a diffusion gel that selectively admits analyte molecules (Davison and Zhang 1994, Van der Veeken et al. 2010). DGT can be deployed in surface water, ground water, submerged sediments, and saturated soils to measure metals and radionuclides.

We evaluated DGT in the laboratory by performing the following tasks:

Task 1: Surface water was collected from two sources and spiked with heavy metals to produce different levels of contamination. Each level (plus controls) was represented by three replicate beakers (Figure 1). Experiments were conducted with dissolved copper alone and with combinations of dissolved metals (cadmium, chromium, cobalt, copper, lead, nickel, and zinc).

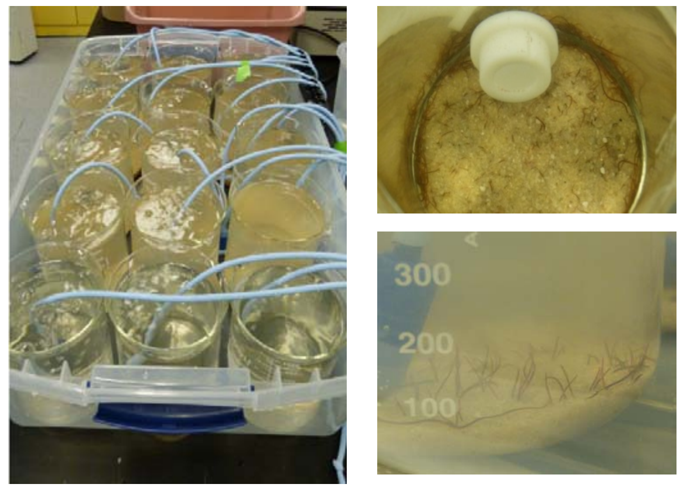

Figure 1. Experimental setup (left). DGT probe (top right). *Lumbriculus* (bottom right)

Task 2: Multiple individuals of *Lumbriculus variegatus,* an aquatic worm, were added to each beaker for a 10 day exposure period.

Task 3: Metal levels were measured with commercially available DGT probes that were placed in the beakers and with conventional methods of water analysis. Other water chemistry variables, pH, hardness, alkalinity,etc. were also measured.

Task 4: *Lumbriculus variegatus* were harvested and analyzed for body burdens of metals.

Task 5: Data were analyzed to answer the following questions: 1) how do DGT measurements compare with measurements made by established methods, 2) how do metal measurements made by both methods compare with biological uptake by aquatic organisms?

Results/Discussion

Copper concentrations measured by DGT probes were strongly correlated with copper uptake by *Lumbriculus* held in the beakers for 10 days (Figure 2). This relationship persisted over dissolved copper concentrations ranging from several parts per billion (ppb) to 800 ppb and occurred in relatively hard Savannah River water as well as soft, acidic Tinker Creek water. Copper accumulated in the DGT probes over time paralleling the accumulation in copper over time that occurred in *Lumbriculus* (Figure 3). Copper concentrations measured by DGT were strongly correlated with copper concentrations in water

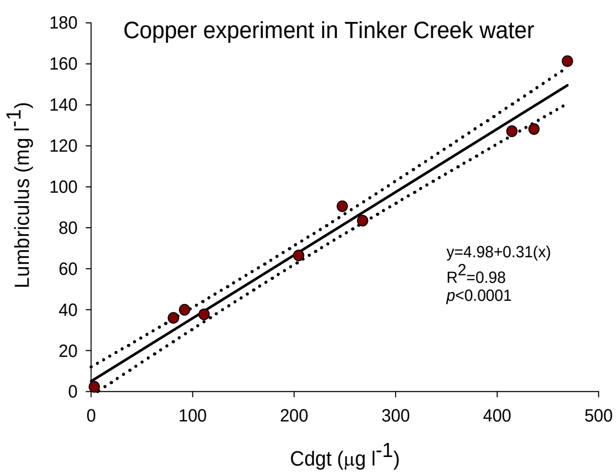

Figure 2. Copper levels in *Lumbriculus* vs. copper levels measured by DGT (Cdgt).

measured by traditional methods of analysis.

Results with mixtures of seven dissolved metals were generally similar to those reported for copper: Pearson correlations between metal uptake by *Lumbriculus* and metal concentrations measured by DGT probes were strong and statistically significant, ranging from 0.68 to 0.94 ($p<0.05$). DGT probes and *Lumbriculus* exhibited similar affinities for different metals, with the exceptions of cobalt and nickel, which were taken up more strongly by the DGT probes than by *Lumbriculus*.

These results show that the metal concentrations measured by DGT are strongly correlated with metal uptake by the aquatic invertebrate, *Lumbriculus*, and that metals accumulate in DGT probes over time paralleling their accumulation in aquatic organisms. This supports the use of DGT as a biomimetic monitoring tool and provide a basis for refinement of these methods for cost-effective environmental monitoring.

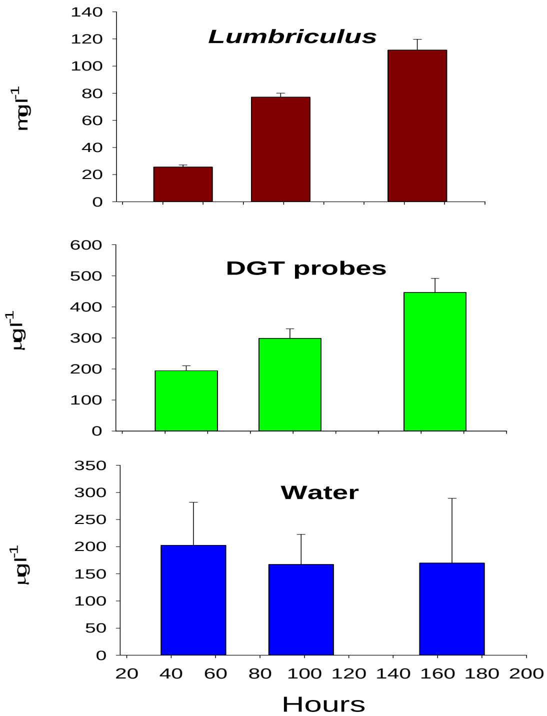

Figure 3. Uptake of copper over time in *Lumbriculus* and DGT probes.

FY2015 Accomplishments

- Showed that metal concentrations measured by DGT water probes were strongly related (R^2 as high as 0.98) to metal uptake by an aquatic invertebrate.
- Showed that metal uptake over time by DGT probes paralleled metal uptake over time by an aquatic invertebrate.

Future Directions

- Evaluation of DGT as an alternative monitoring tool for metals. Passive samplers such as DGT could be incorporated into monitoring programs at the SRS and throughout the DOE with the potential to accurately measure contaminants at less cost.
- Task 2 – Environmental risk assessment for mercury (Hg) using Hg-DGT. Mercury is a potent neurotoxin and widespread environmental contaminant in the nation's waters. Hg-DGT can be used to measure and map water and sediment Hg concentration and speciation in SRS environs.
- Development and application of DGT for assessment of environmental contamination by radionuclides. The application of DGT to radionuclides is experimental and has not seen widespread use. DGT probes could be developed for the cost-effective measurement of environmental contamination with radionuclides.
- Establishment of SRNL as a center of excellence for the application of passive sampling methods.

FY 2015 Publications/Presentations

1. LDRD External Report Summary: BioAccumulation using Surrogate Samplers (BASS): Evaluation of a passive sampler as an alternative monitoring tool for environmental contaminants at the Savannah River Site.
2. Use of Diffusive Gradients in Thin films (DGT) to predict whole-body metal concentrations in the aquatic macroinvertebrate, *Lumbriculus variegatus*. In preparation

References

1. Davison, W., Zhang, H. 1994. In situ speciation measurements of trace components in natural waters using thin-film gels. Nature 367: 546-548.
2. Van der Veeken, P.L.R., Van Leeuwen, H.P., 2010. DGT/DET gel partition features of humic acid/metal species. Environ. Sci. Technol., 44: 4253-4257.

Acronyms

BASS: Bioaccumulation Using Surrogate Samplers
DGT: Diffusive Gradients in Thin films
Hg: mercury
Hg-DGT: mercury-Diffusive Gradients in Thin Films
SRS: Savannah River Site
DOE: Department of Energy

Intellectual Property

None

Total Number of Post-Doctoral Researchers

None