## Bioavailability of Atmospheric Mercury in Surface Waters of the Great Lakes Western

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Patrick Gorski David Armstrong Jocelyn Hemming Dawn Karner-Perkins Amy Prash Dave Bittrich Helen Manolopoulos Rebecca Moore Shawn Chadwick James Schauer Dave Lewis Barbara Lewis Trevor Schott Abbey Babinat With mercury, bioavailabilty can mean two different things:

(1) Uptake of Hg(II) by sulfate or iron reducing bacteria to produce MeHg

(2) Uptake of MeHg by the lower food web and subsequent biomagnification

## Western Great Lakes regional trends in MeHg concentrations in rain



# Western Great Lakes regional trends in MeHg concentrations in surface water



# MeHg levels in zooplankton were higher in the near-shore mixing zone.





#### **Sediment Trap Data from METAALICUS**

#### Isotopic HgT

Within <u>6 days</u> of spiking, <sup>202</sup>Hg began appearing in particles in sediment traps and by November, comprised <u>almost 50%</u> of all Hg in sinking particles.



### Isotopic MeHg

Within <u>2 weeks</u> of spiking, methyl <sup>202</sup>Hg began appearing in particles in sediment traps, and by November comprised <u>almost 25%</u> of all MeHg in sinking particles.



## Main Objectives:

(1) Compare the bioavailability of MeHg in mixtures of Lake Michigan surface water and environmentally relevant end members, such as wet and dry deposition and runoff.

(2) Compare urban vs. rural influences on bioavailability.

## Algae as the test organism

- Grows well in lab
- Found in nature
- Excellent food source
- Used previously
- EPA test organism



Selenastrum capricornutum

## Site Descriptions

Sample	Purpose
Lake Michigan	Great Lakes Surface Water
Milwaukee Rain	Urban Precipitation
ELA Rain	Rural Precipitation
Milwaukee Street Flow	Urban Runoff
Milwaukee River	Urban-Influenced Runoff
Lake 658	Rural Runoff
Madison Air Particulates	Dry Deposition
Suwannee River HA	DOC gradient
Fraquil Media	Control Matrix

## Typical Bioassay Design

- Acid-leached polycarbonate flasks
- 450 mL of test water added to each flask
- Two to five flasks per site/mixture
- Within each site, there was at least one MeHgspiked flask and one flask without spike.
- MeHg spike ~1 to 2 ng/L
- Fraquil controls run with each batch
- Inoculated with log-phase algal cells at 20,000 cells/mL
- Exposure = 24 hours

Acrylic Frame

## Exterior Lighting 3 sides

### **Plastic Curtain**

### Acid-leached Polycarbonate Flasks



### **Slotted Shelving**

**HEPA Flow Hood** 

# Sampling Each Flask



- Flow Cytometry
- MeHg
  - Particulate
  - Aqueous
- Ancillaries (DOC, pH, Conductivity)



## Calculating the bioconcentration factor

$$BCF = \frac{C_A}{C_W} pL Cell^{-1}$$

## $C_A$ = concentration of MeHg on the Algae in ag cell<sup>-1</sup> $C_W$ = concentration of MeHg in the test solution in ag pL<sup>-1</sup>

Note on units: Assuming cells are spherical and have a cell volume of 4 pL ( $V=1.33\pi$  (0.001cm)<sup>3</sup>), then values reported here are of similar magnitude to traditional calculation methods having units of L kg<sup>-1</sup>. Typical BCFs from literature field data range from 10<sup>^4</sup> to 10<sup>^6</sup>

## Switched from Selenastrum to Chlamydomonas to improve cell counts



## Verify the functionality of Chlamydomonas as a test algae



## Influence of pH on cell growth



# Influence of dissolved organic carbon on bioavailability



## Influence of initial cell inoculation level



## Bioavailability of MeHg as rain mixes with Lake Michigan surface water



## Bioavailability of MeHg as runoff mixes with Lake Michigan surface Water



# Bioavailability of MeHg as air particulates mix with surface water



## Summary

- (1) Chlamydomonas is a robust test algae for mercury bioassays. Performance is best when the initial cell count is 20K, the test waters are circum neutral (pH 6.5 to 8.5), and DOC levels are moderate (less than ~ 5 mg/L)
- (2) Urban Rain appears to inhibit the bioavailability of MeHg compared with rural rain.
- (3) Bioavailability seems to increase as urban rain mixes with LM surface water; bioavailability decreases as rural rain mixes with LM surface water.
- (4) Urban storm-water runoff inhibits the bioavailability of MeHg, and the effect is reflected in waters from urban influenced rivers
- (5) Dry deposition may have a fraction of MeHg that is bioavailable when mixed with surface waters. Better estimates of loading are needed to determine the potential magnitude of this input.

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