

**A Presentation of the**



UNIVERSITY OF MINNESOTA  
**EXTENSION**  
**Driven to Discover<sup>SM</sup>**

*with partners:*

IOWA STATE UNIVERSITY  
University Extension



South Dakota  
Cooperative Extension Service

**November 23, 2010**

**Owatonna, MN**

# Methylmercury production in denitrifying bioreactors: *A preliminary investigation* of hydrologic and biogeochemical controls

Robert J.M. Hudson, NRES

Richard A.C. Cooke, ABE

University of Illinois at Urbana-Champaign



# Acknowledgements

- **Illinois Sustainable Technology Center**
  - Project funding
- **Richard Cooke**
  - Expertise in bioreactor design and operation
  - Access to field sites
- **Graduate Student Researchers**
  - Brian Vermillion (NRES: MeHg analysis work)
  - Siddhartha Verma (ABE: Sampling and sample processing)



# Motivating Question

- Due to the extent to which humans have impacted the environment and the coupling between biogeochemical cycles of N and Hg, cleaning up excess nitrate is not a simple matter.
- Could reducing nitrate levels using subsurface drain bioreactors in agricultural watersheds inadvertently cause the levels of MeHg in the waters downstream to become elevated, and thereby reduce the quality of the fisheries?



# A Tale of Two Elements

Both elements have ***complex biogeochemical cycles*** involving multiple chemical species in different phases and oxidation states:

## Nitrogen

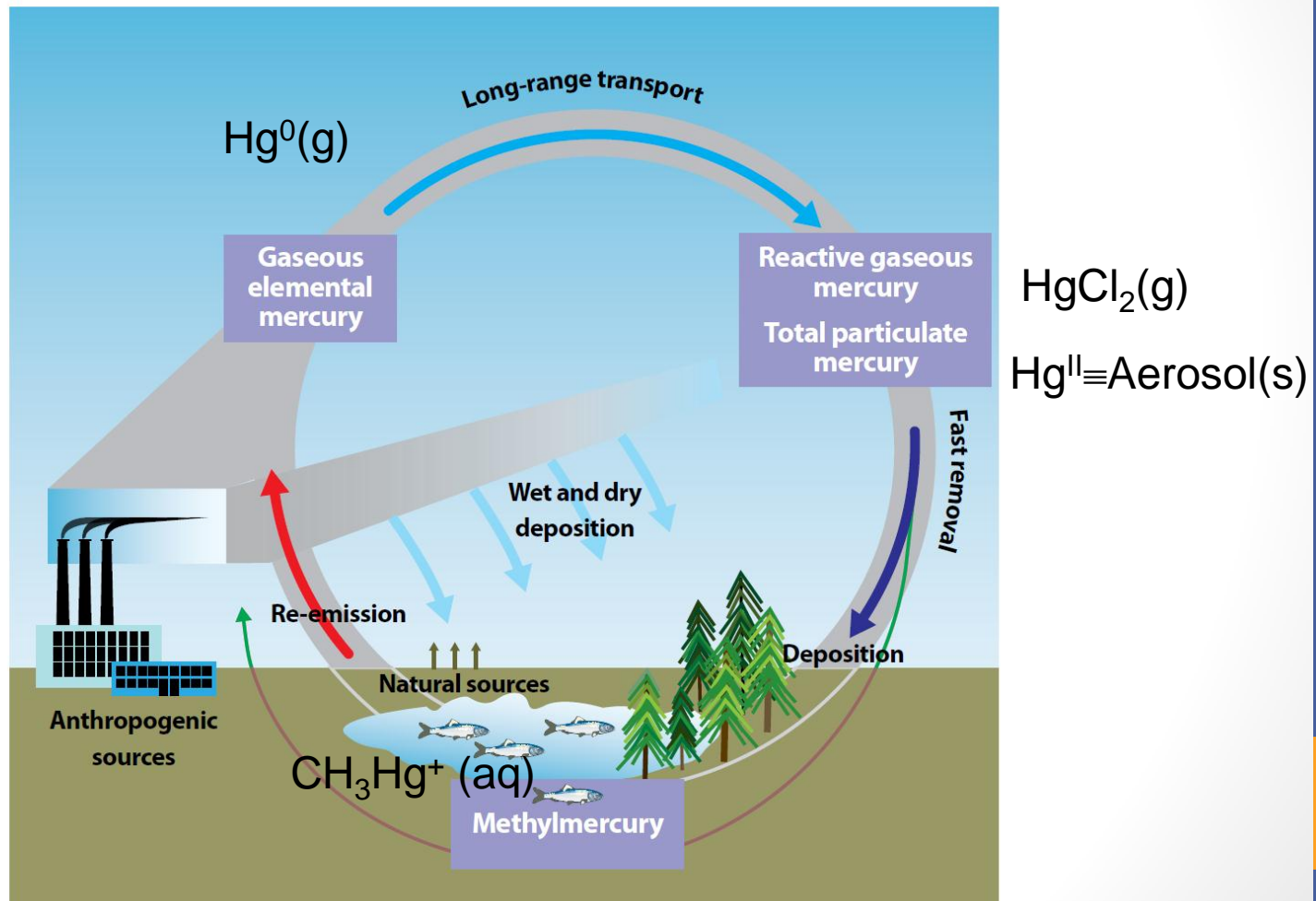
$\text{N}_2(\text{g})$  ,  $\text{NO}_3^-(\text{aq})$ ,  $\text{NH}_4^+(\text{aq})$ , Soil Organic N, etc.

## Mercury

$\text{Hg}(\text{g})$  ,  $\text{Hg}^{2+}(\text{aq})$ ,  $\text{CH}_3\text{Hg}^+(\text{aq})$ , Hg in SOM,  $\text{HgS}(\text{s})$ , etc.



# Hg Cycle in Aquatic Ecosystems



The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport (UN Environment Programme, 2008)

Introduction to Hg Biogeochemistry



# Pollutant Sources and Impacts

## Nitrogen

- Non-point source pollutant derived from fertilizer overuse
- Nitrate exported from agricultural fields impacts:
  - Gulf of Mexico ecosystem (hypoxia)
  - Water quality for communities that obtain drinking water from rivers in agricultural areas

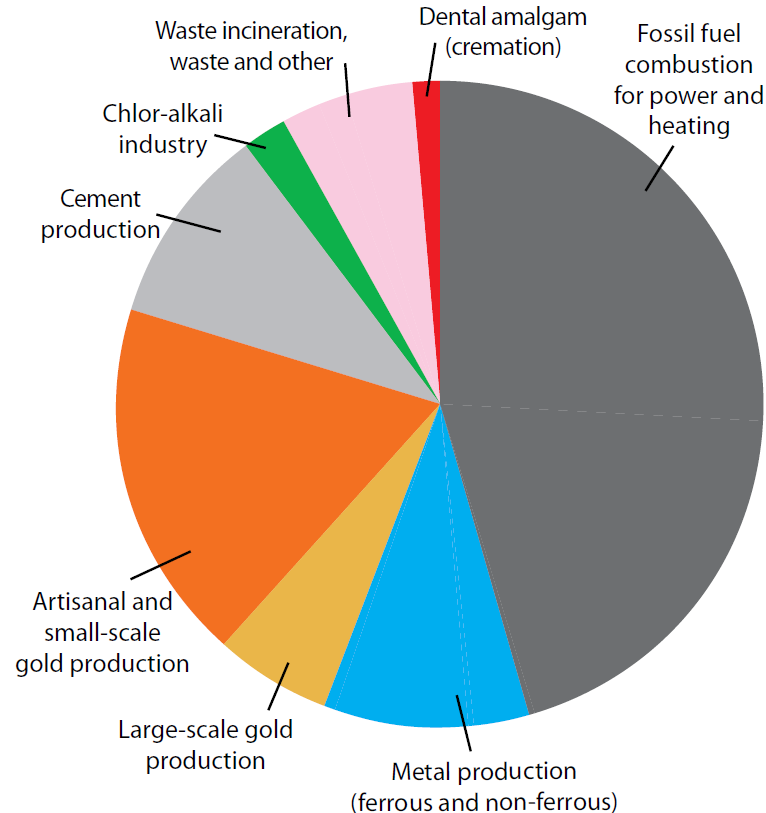
## Mercury

- Effectively a non-point source atmospheric pollutant initially emitted by coal combustion and waste incineration
- Methylmercury strongly bioaccumulates in food webs:
  - Fish consumption is main source of human exposure to Hg.
  - Leading cause of freshwater fish consumption advisories in the U.S.
  - Eight percent of U.S. women of childbearing age have blood Hg higher than the USEPA “Threshold Level” (Schober et al., JAMA, 2003).



# 2005 Global Anthropogenic Atmospheric Emissions

Total:  $1930 \pm 700$  tons



The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport (UN Environment Programme, 2008)



# Global-Scale Hg Transport and Recycling

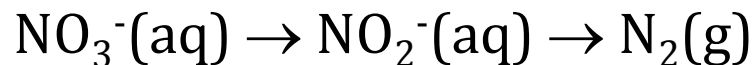


The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport (UN Environment Programme, 2008)

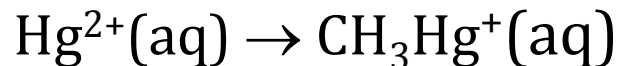
# Anaerobic Processing

Key processes that determine the environmental impacts of each element occur in anaerobic environments:

Denitrification (alleviates impacts)



Mercury methylation (greatly increases impacts)



**In the environment, these processes are linked!!!**

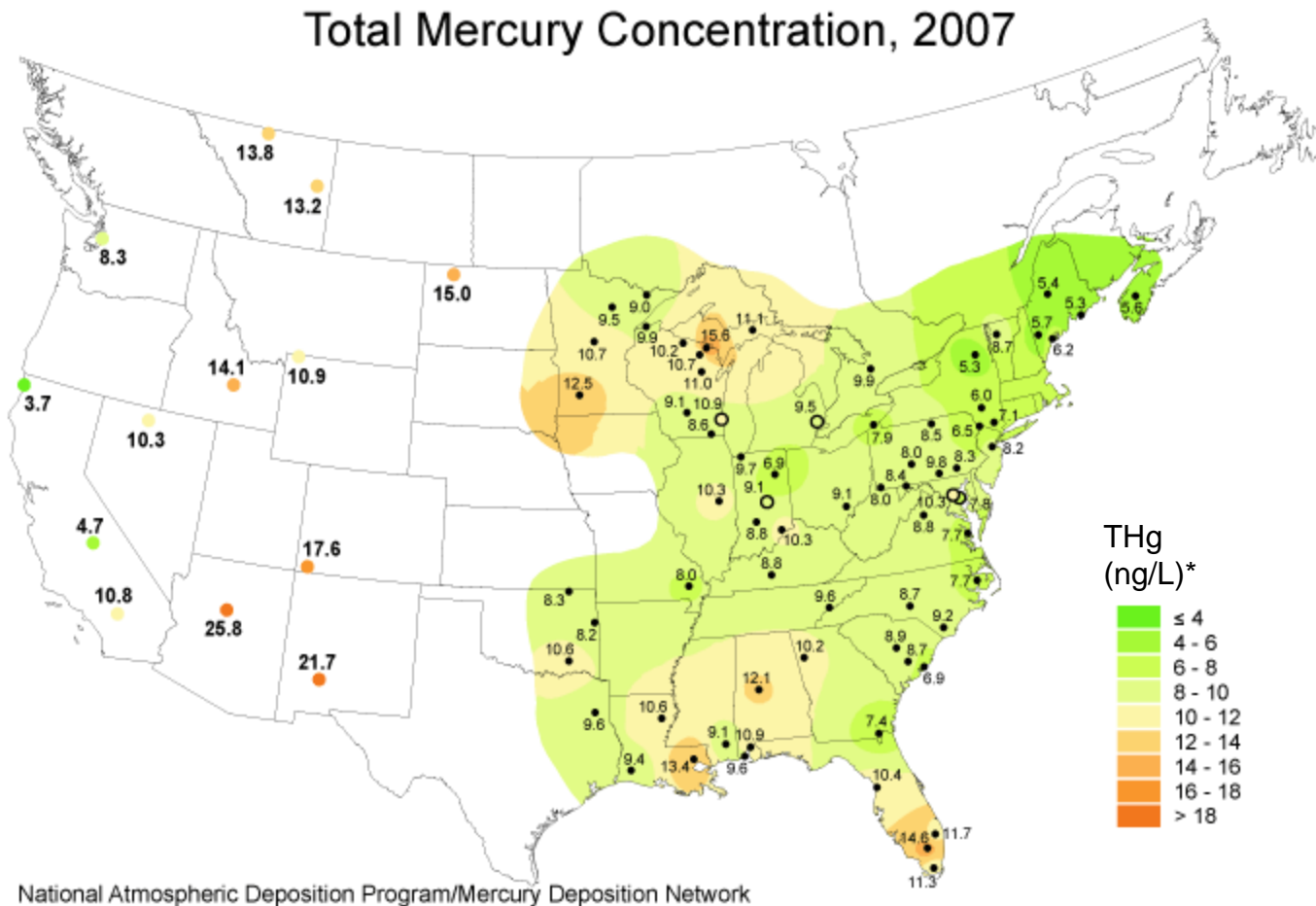
# Typical Levels of Hg in the Environment

Environmental Medium	Total Hg Concentrations*	Fraction of Total Hg Present as Methyl-Hg
Wet deposition	5-50 ppt	Low
Typical surface water – atmospheric source	0.5-5 ppt	5-20% oxic; Up to 100% anoxic
Contaminated Water	>10 ppt	0.5%
Wood/wood products	0.001-1 ppm	??
Sediments	0.1-10 ppm	0.1-5%
Fish and biota	0.1-3 ppm	>90%

\*ppt = parts per trillion; ppm = parts per million



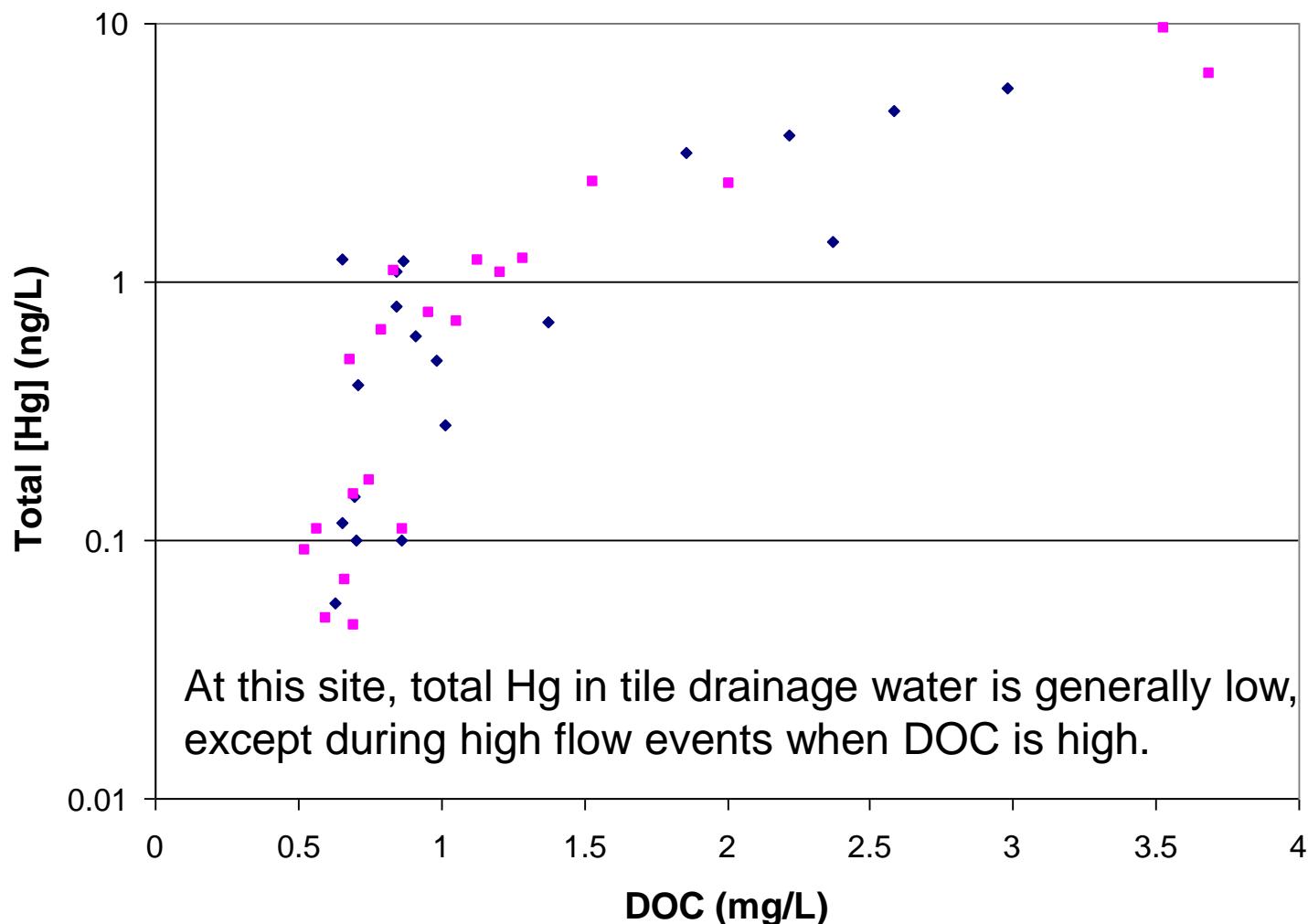
# Mercury in Wet Deposition



\*ng/L = parts per trillion



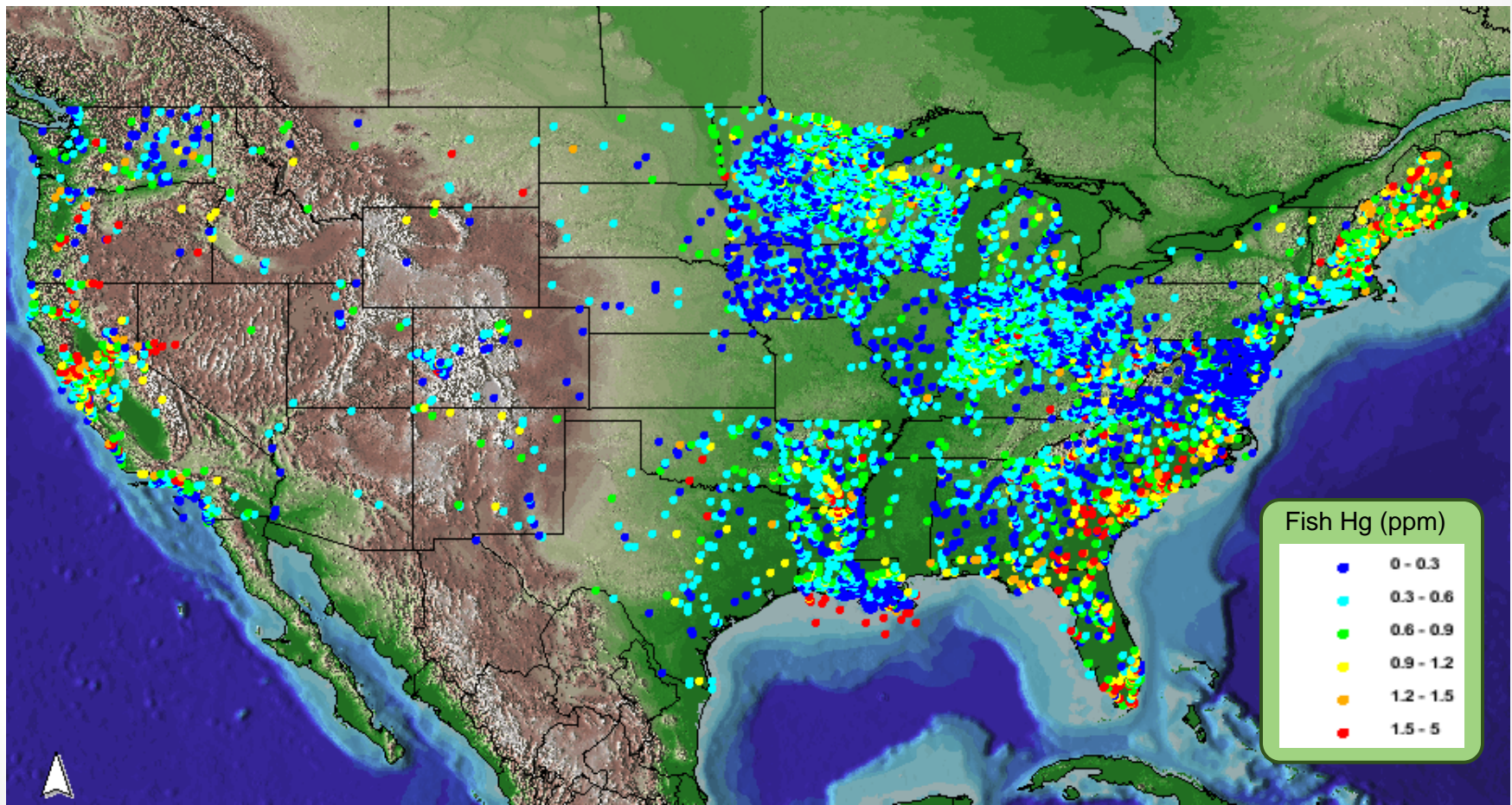
## Hg in Subsurface Drain Discharge: Embarras River Basin, East Central Illinois (1998)





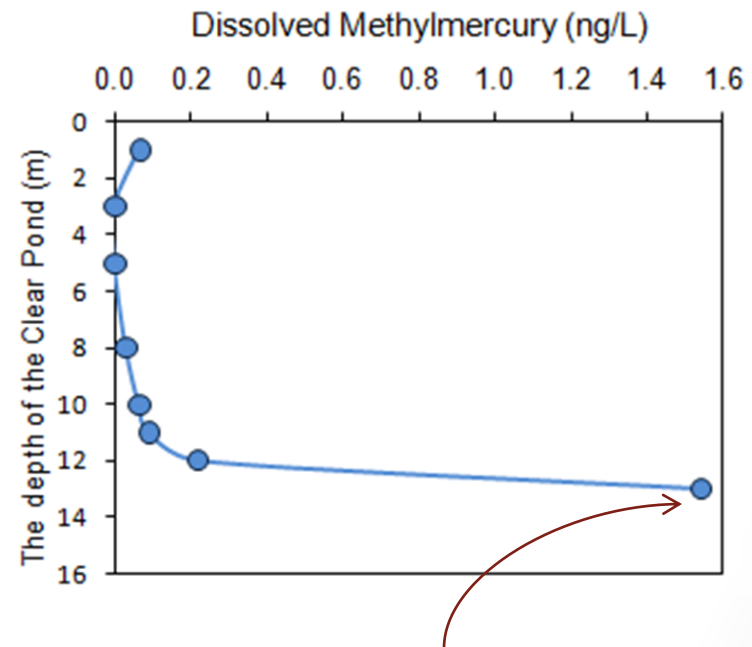
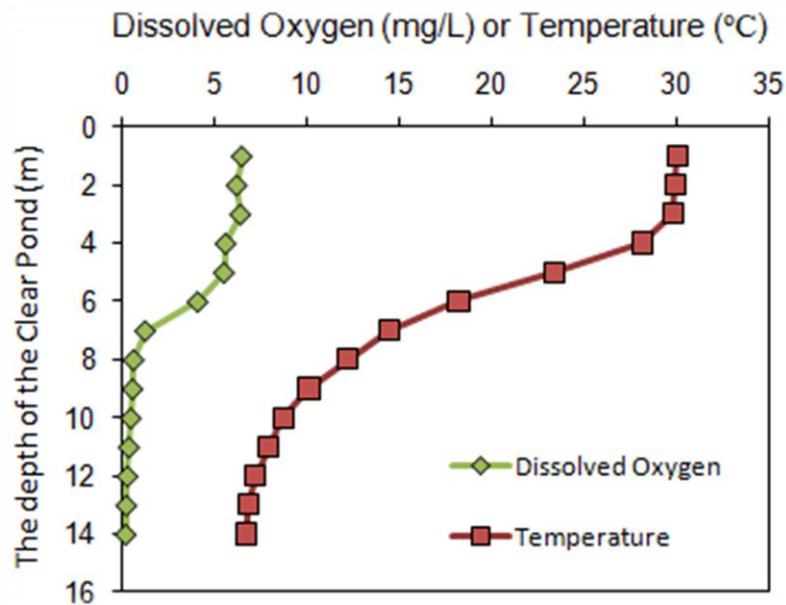
# Hg in Largemouth Bass (14-in)

## National Descriptive Model for Mercury in Fish (USGS)



High degree of spatial variability despite smooth gradients in atmospheric deposition.

# Clear Pond, Kickapoo State Park Profile (August 2010)



MeHg is produced in anaerobic environments, such as lake hypolimnia.



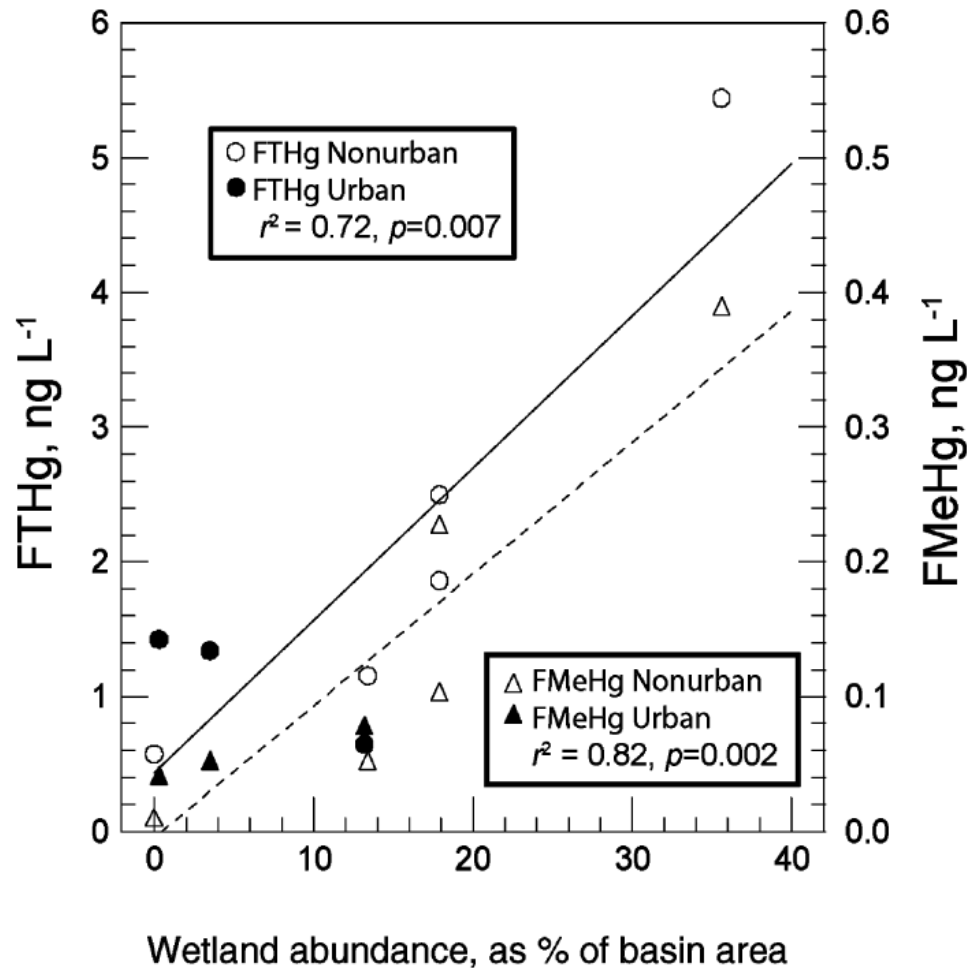


Great Marsh (restored wetland)  
Indiana Dunes National Lakeshore  
Dissolved MeHg 0.4 – 2.0 ng/L

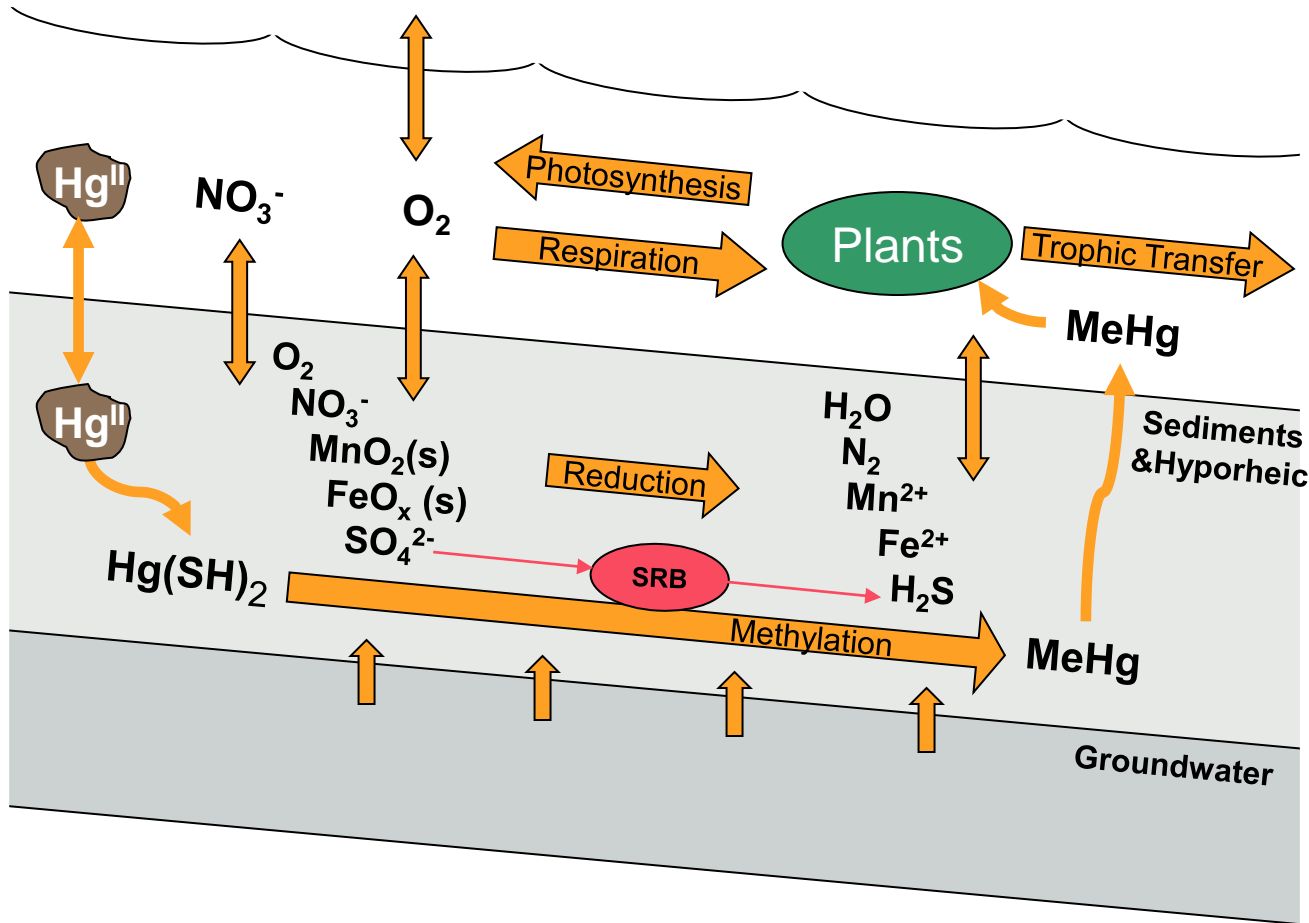


# Landscape-Scale Effects of Natural Anaerobic Ecosystems on Mercury Cycling

Brigham et al. (ES&T 2009)



# Nitrate-Mercury Interactions in Aquatic Ecosystems



Nitrate in surface waters inhibits Hg methylation since denitrifiers can out compete Mn-, Fe- and Sulfate-reducing bacteria for energy (reduced carbon compounds).

# Constructed Anaerobic Ecosystems

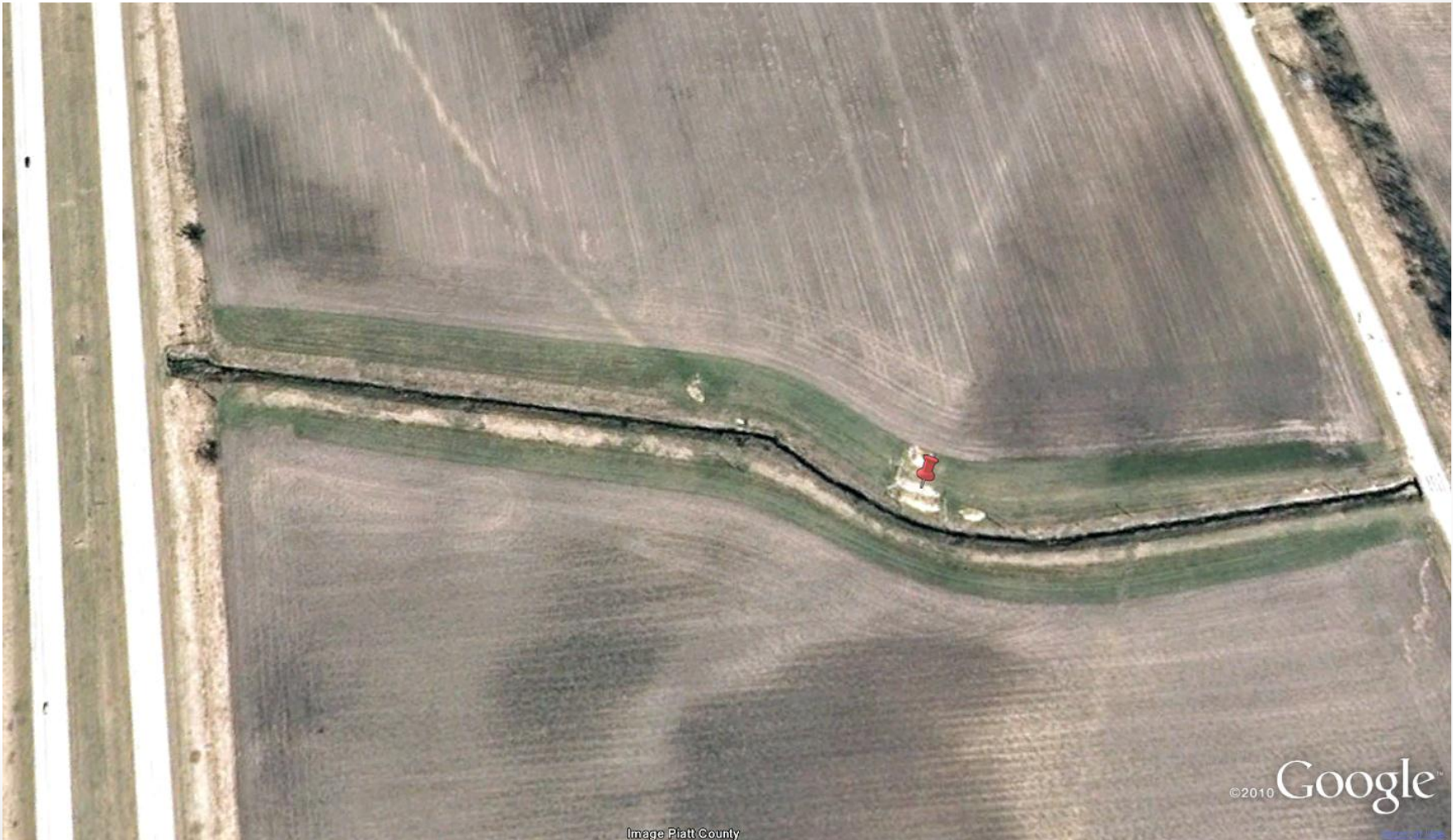


# Denitrifying Bioreactors

- Installed by Richard Cooke, ABE-UIUC.
- Designed to reduce nitrate export from tile-drained fields.
- Economical
  - Small footprint
  - Wood chips are inexpensive
  - Minimal cost of water control structures (<\$10k)
  - Little time required to operate/maintain
- Field tests show their high efficiency at  $\text{NO}_3^-$  removal.



# Monticello Bioreactor Site

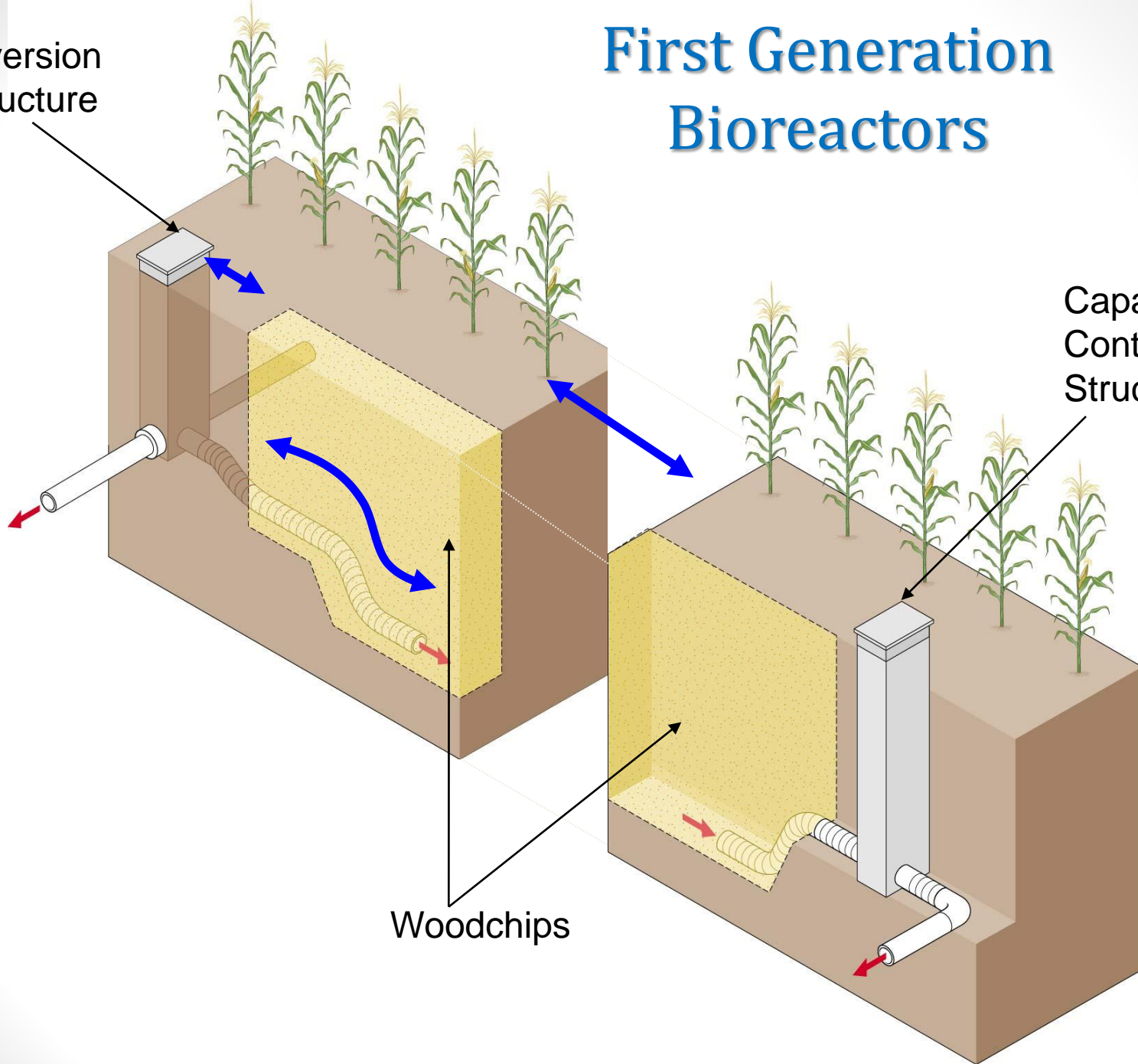


# First Generation Bioreactors

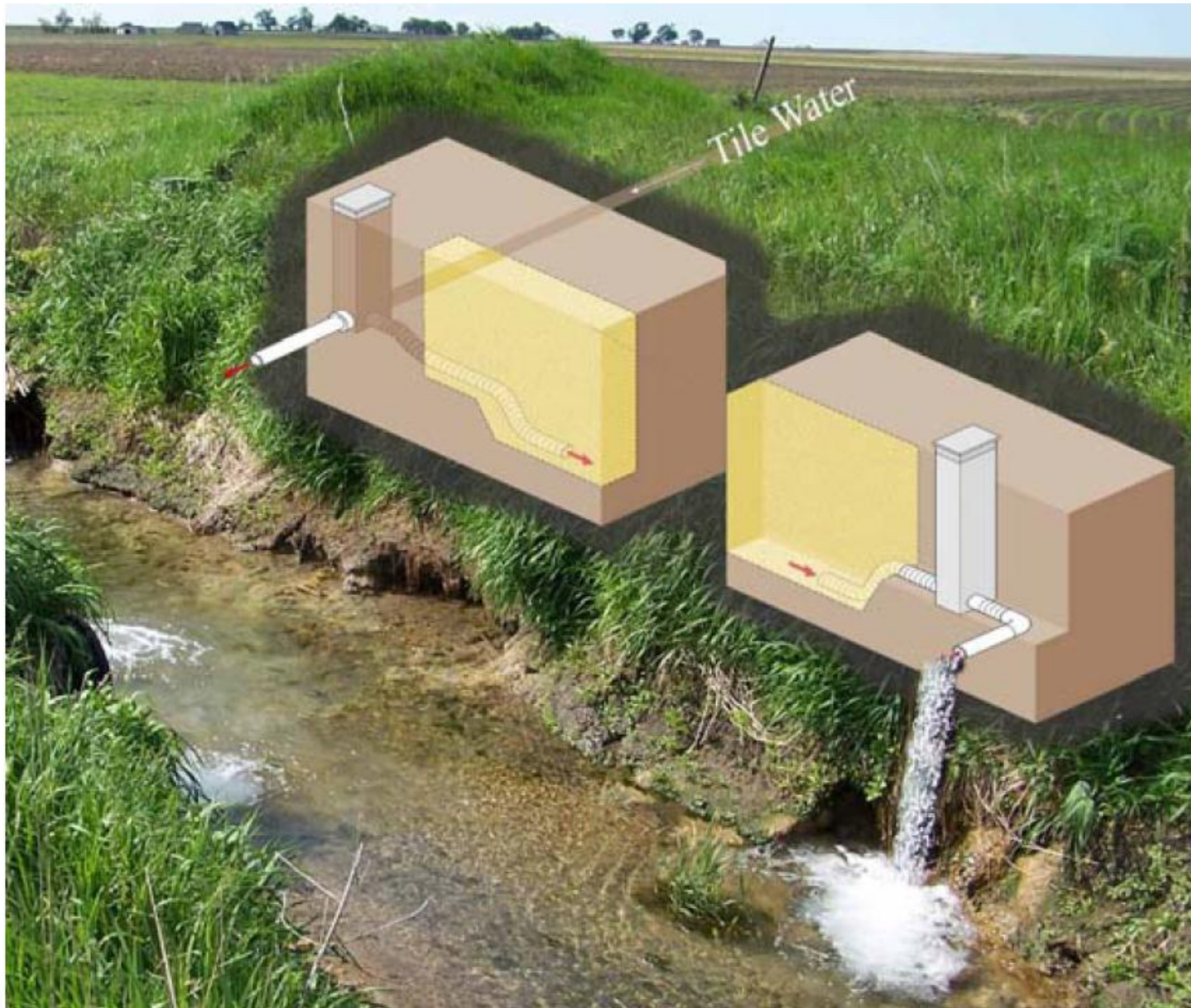
Diversion Structure

Capacity Control Structure

Woodchips

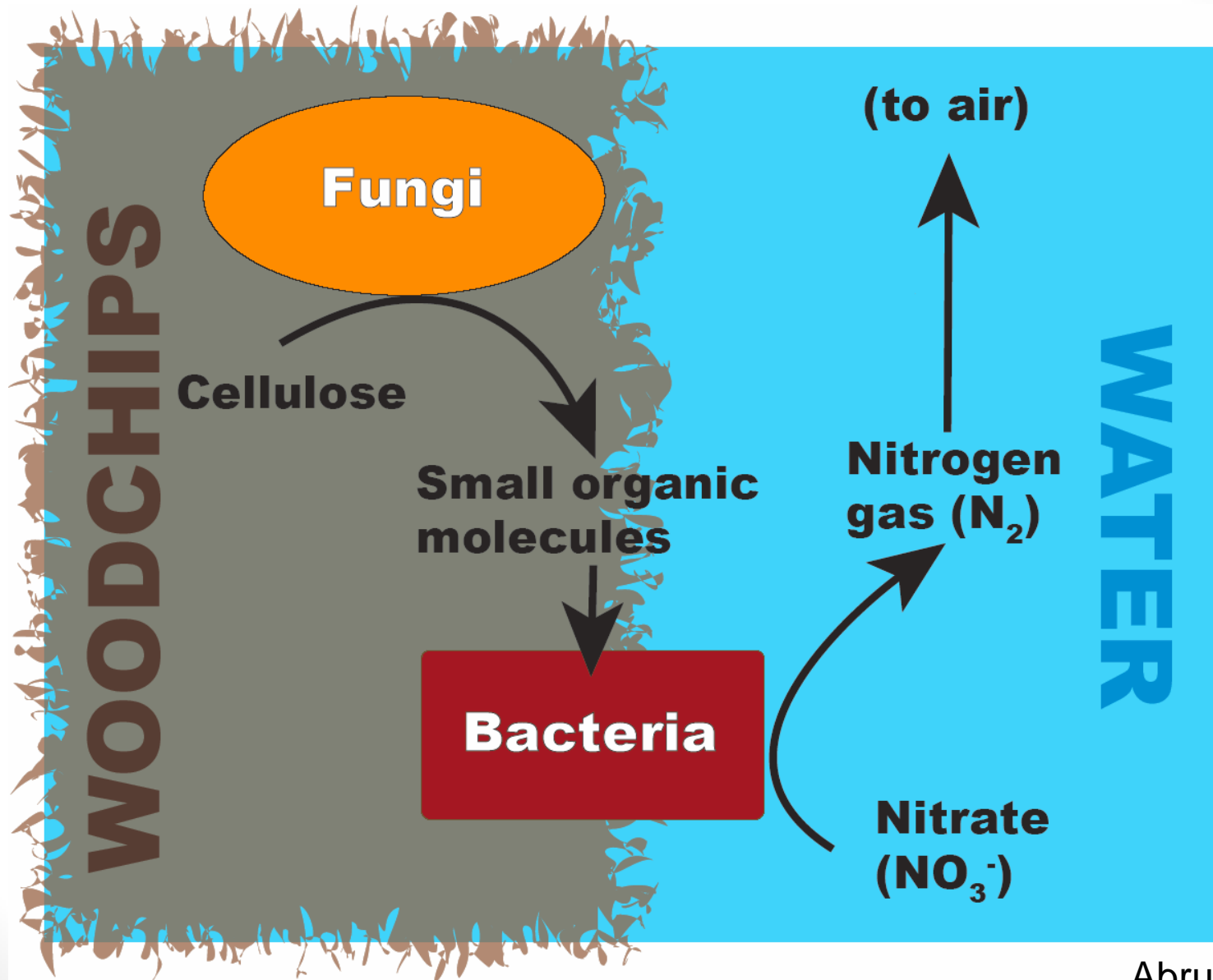






Andrus et al. (2010)

# Biogeochemistry





# Bioreactor Methylmercury Study Objective

1. Determine whether denitrifying bioreactors produce methylmercury due to anoxic environments formed within bioreactor.
2. Determine MeHg export flux.
3. Compare to natural levels in environment.



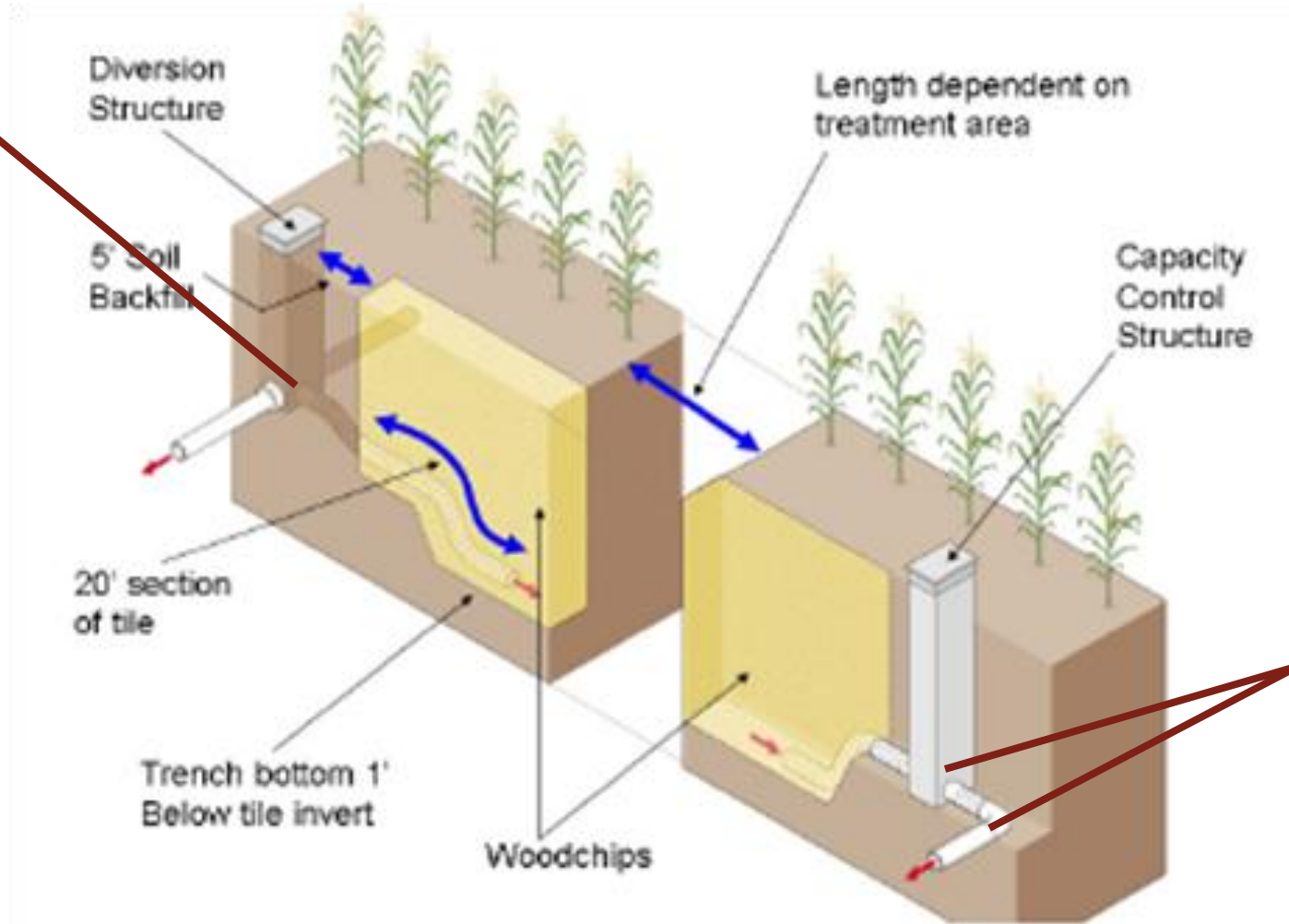
# Bioreactor Methylmercury Study Design

- Synoptic sampling design
  - Collect samples after storm events and other periods when tiles are flowing
  - Inlet and outlet sampled simultaneously
  - Sampled periodically from summer 2008-June 2009
  - Sampled again in summer 2010.
  - Preserved by filtration/acidification or freezing.
- Analyze
  - Dissolved Methylmercury (MeHg)
  - Dissolved organic carbon
  - Sulfate, nitrate, chloride
  - Only a limited number of samples have been analyzed to date.



# Sampling Bioreactors

**Inlet  
Samples**



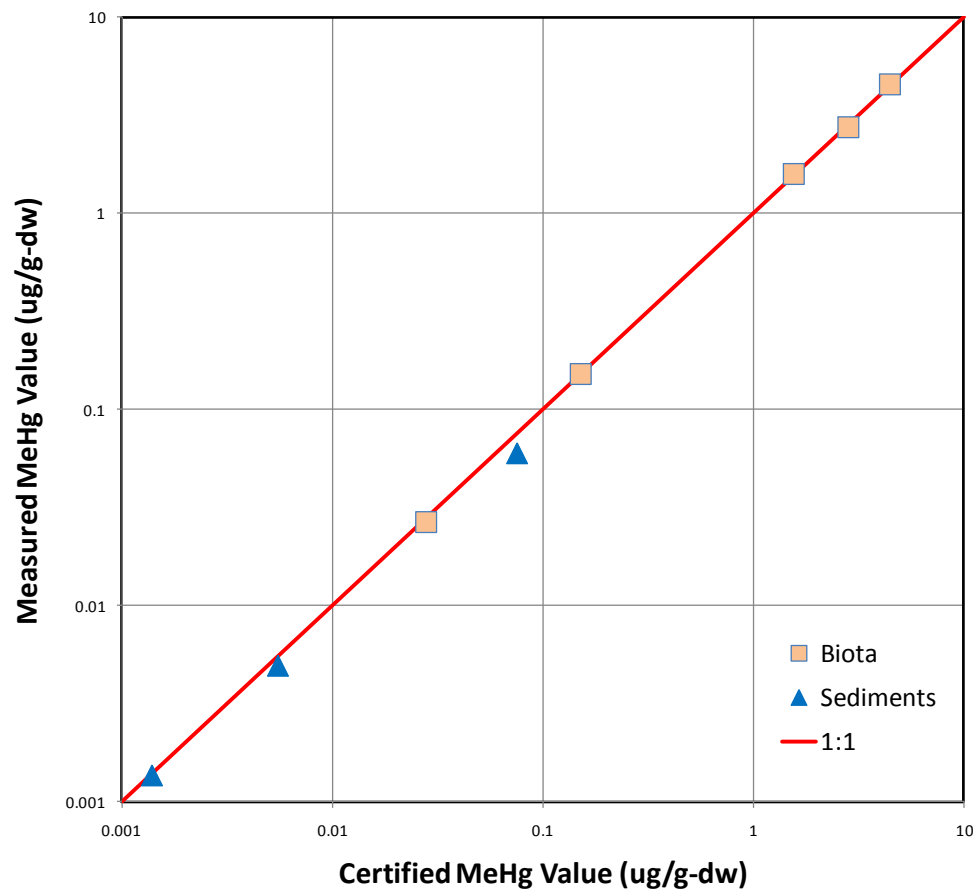
**Outlet  
Samples**

# UIUC Method for Hg Speciation Analysis

- Shade and Hudson (2005) *Environmental Science and Technology*
- Shade, Hudson, et al. patent (2007)
- Vermillion and Hudson (2007). *Analytical and Bioanalytical Chemistry*. Preparation method for water samples.



# Validation of Sediment and Biota Sample Preparations



Biota: Leaching of tissues in acidic TU  
(Shade, ES&T 2008)

Sediments:  $\text{H}_2\text{SO}_4 + \text{KBr}$   
Digestion/Toluene Extraction  
(Vermillion, Shade, and Hudson, in prep)

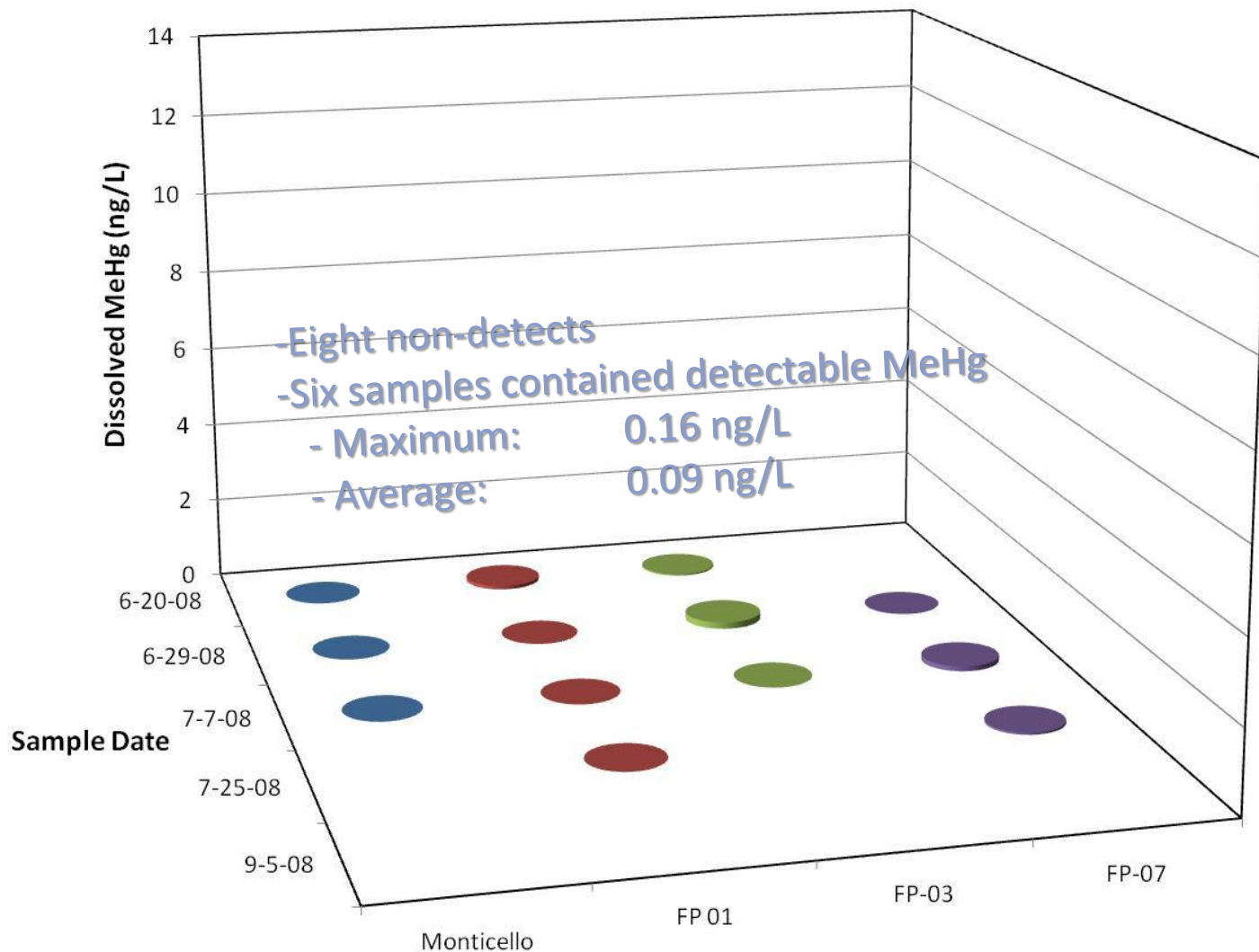
Water: Novel method



# Bioreactor Field Study Results

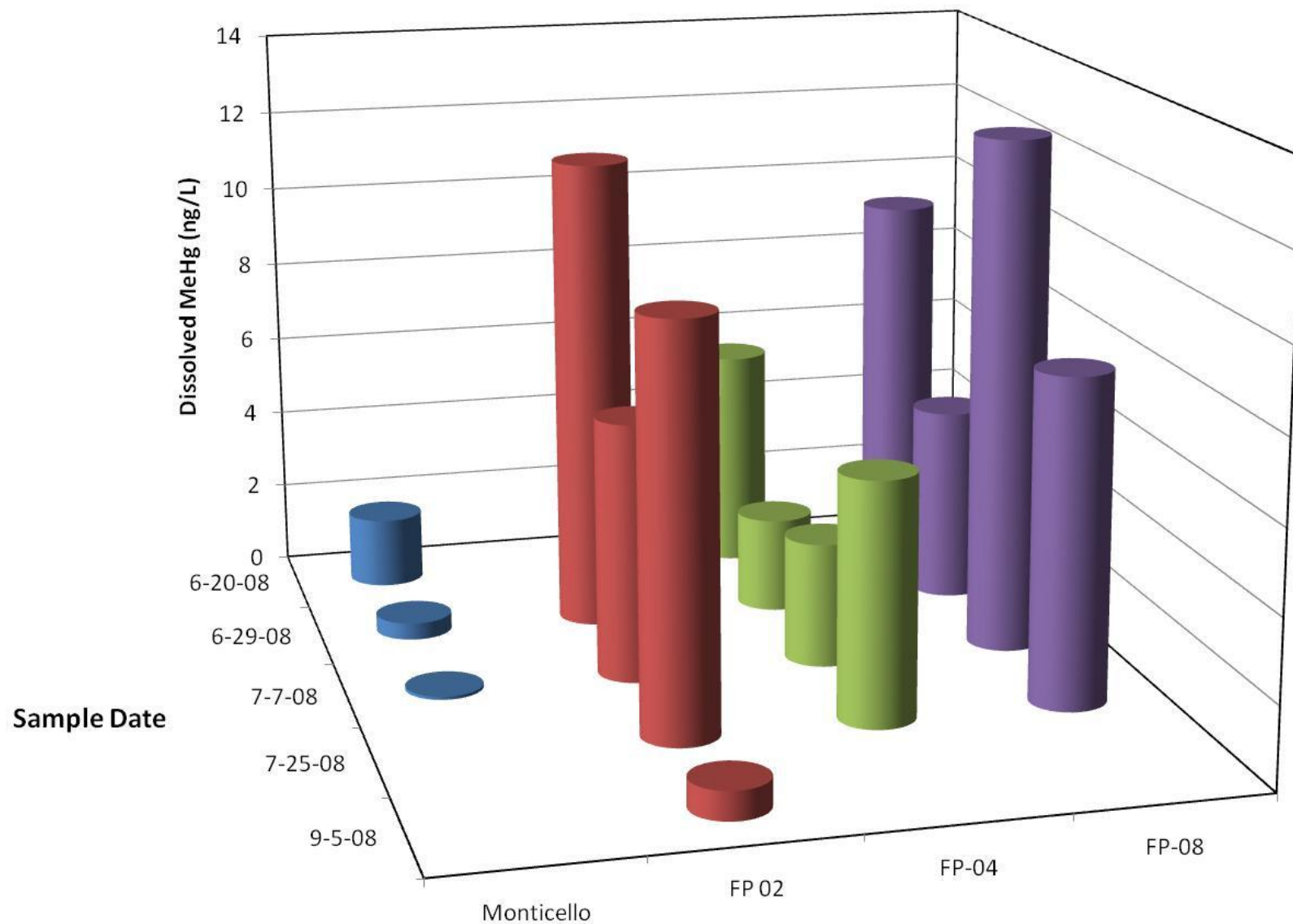


# Dissolved MeHg in Bioreactor Inlets



# Dissolved MeHg in Bioreactor Outlets

(Results for Original Design)

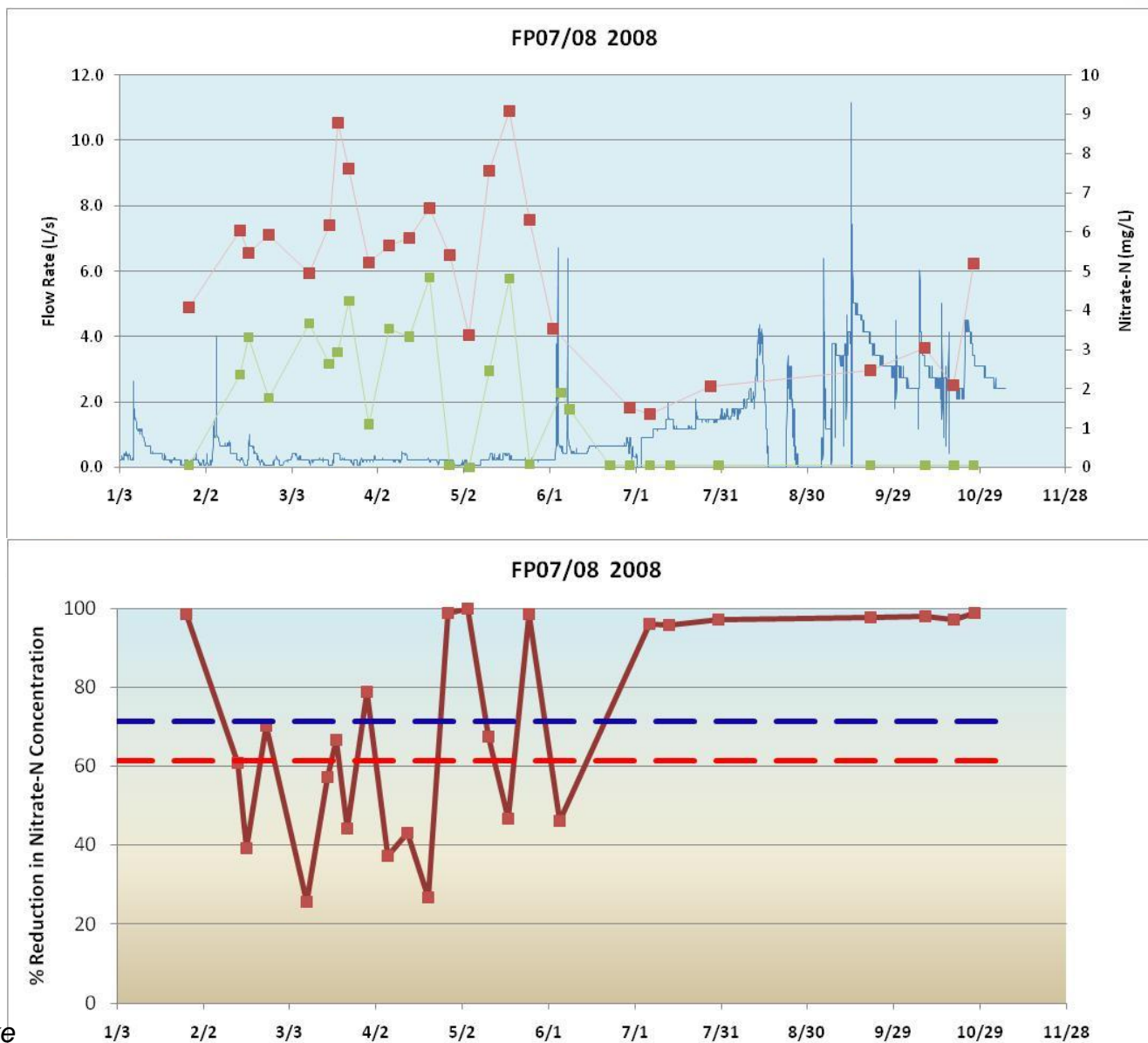




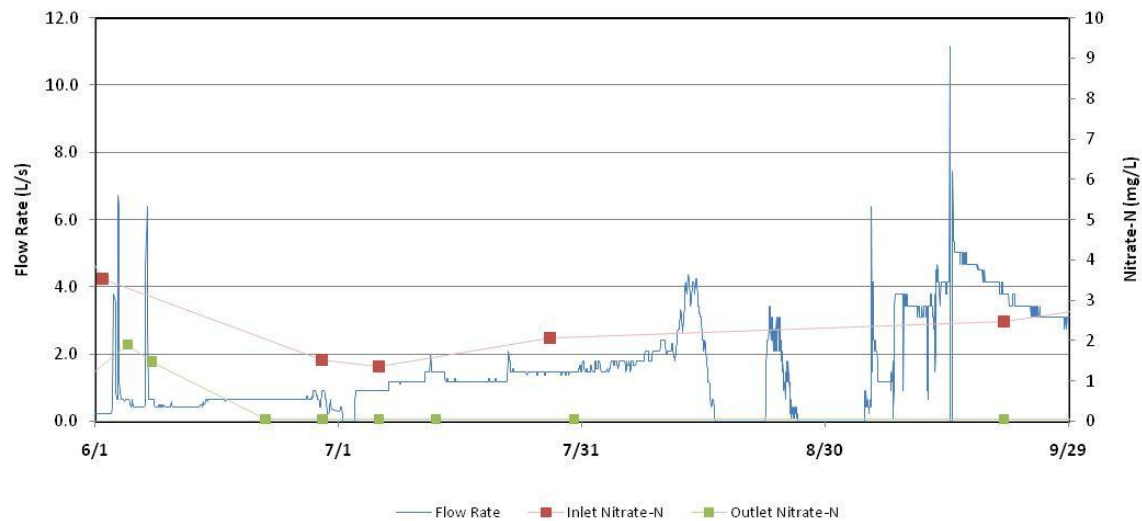
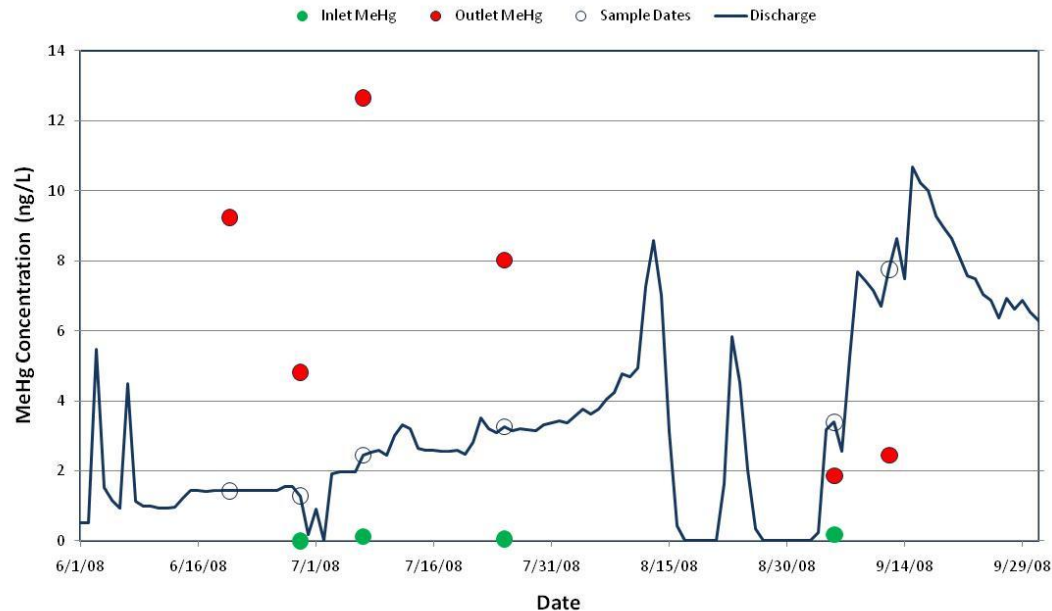
# Decatur West Bioreactor



# Nitrate Removal



# MeHg in Decatur West Bioreactor



*This work.*



# “Typical” Hg Levels

- Groundwater
  - Total Hg is very low ( $<0.5$  ng/L)
  - MeHg is often non-detectable.
- Tilewater
  - Total Hg is lower than rainwater, but can be quite high (10 ng/L) under high flow conditions.
- Surface Waters
  - Total Hg is usually 1-5 ng/L in unpolluted systems
  - MeHg is usually  $<0.5$  ng/L in unpolluted systems



# What is source of Hg?

- Tile water:
  - Groundwater is typically very low except when preferential flow occurs
  - Could accumulate on wood chips during high flow (aerobic conditions) and be released under low flow conditions
- Wood chips:
  - Trees absorb Hg from the air and some accumulates in wood

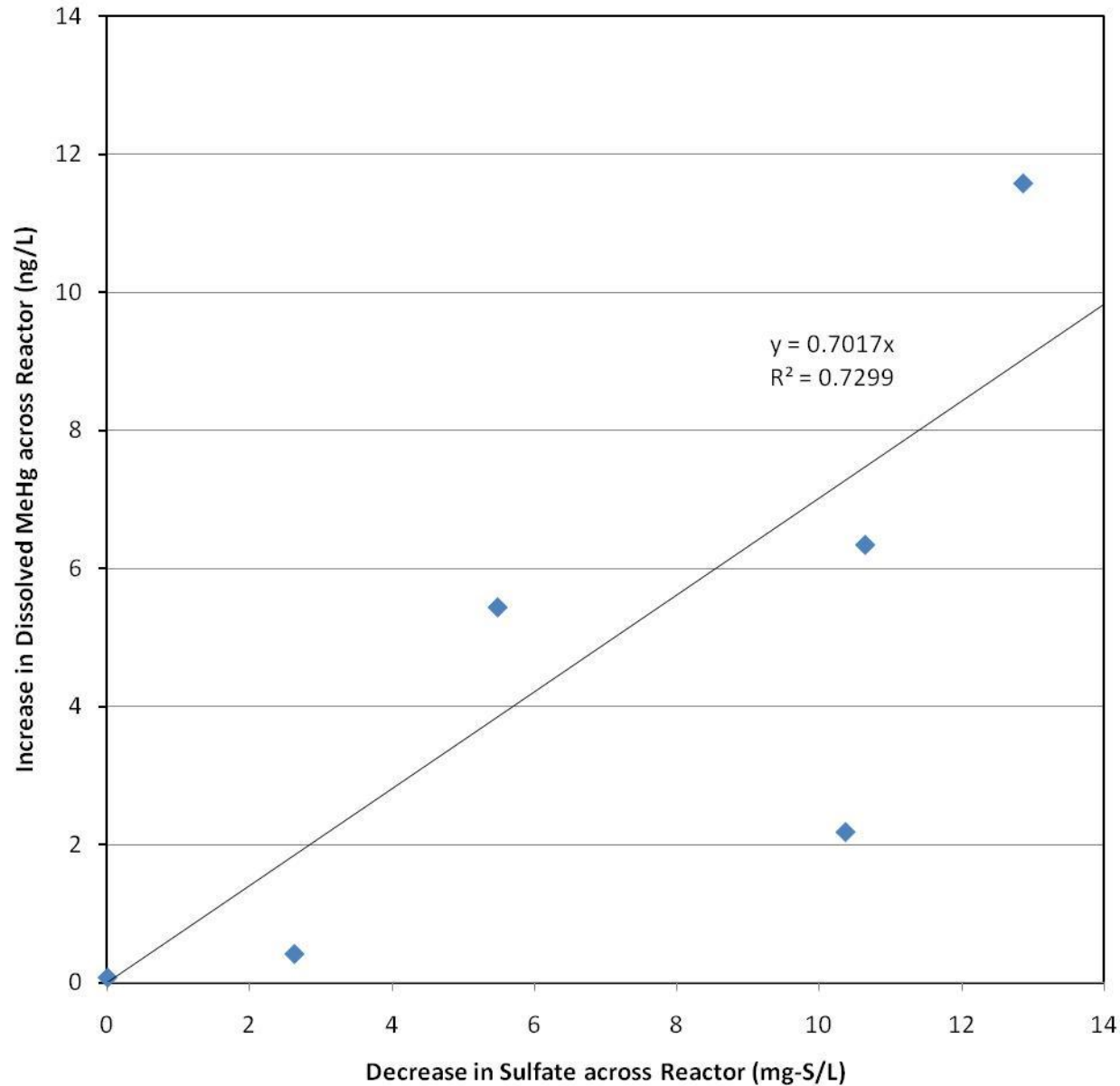


# Dissolved Organic Carbon

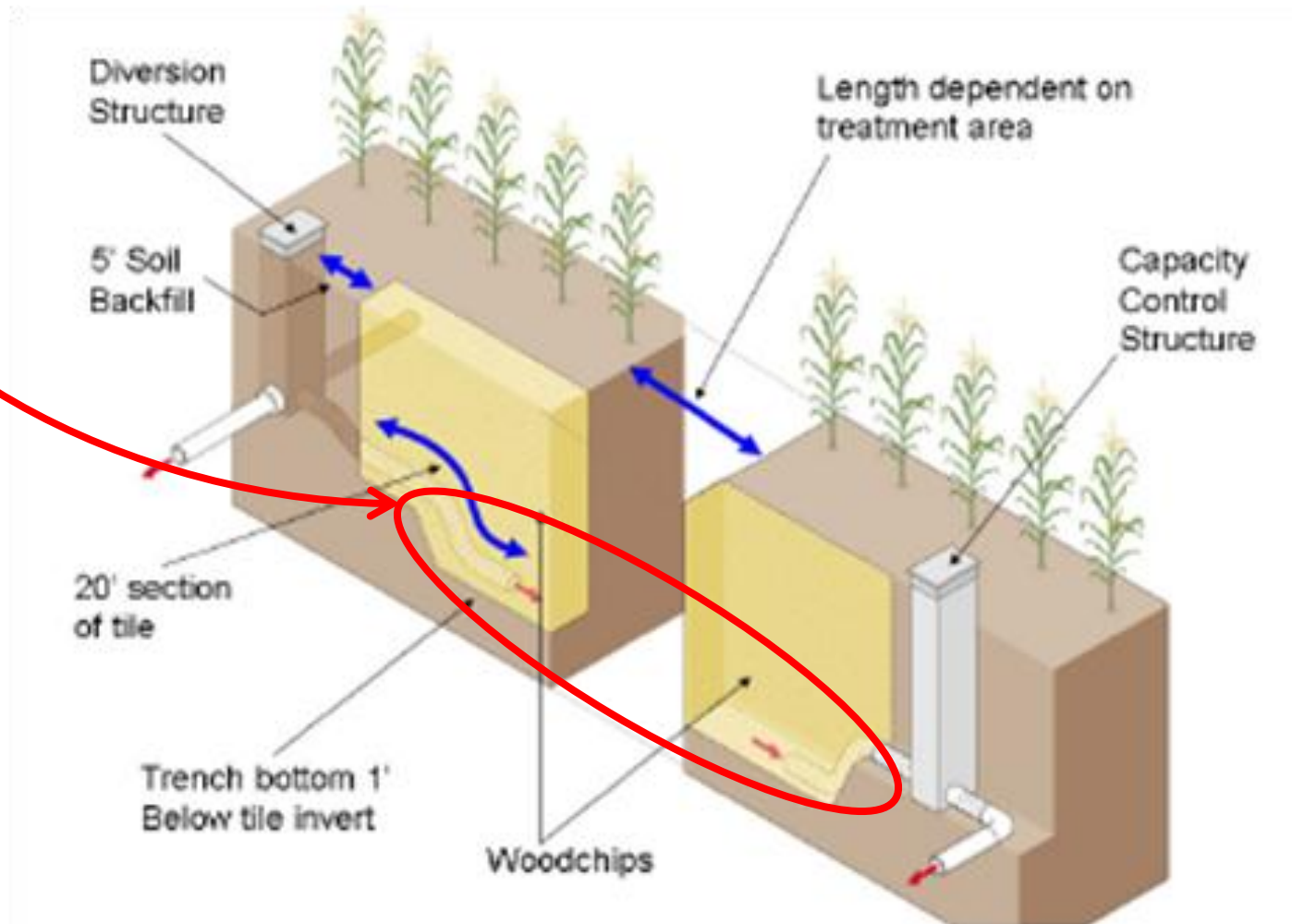
- Dissolved organic carbon is known to be a carrier of mercury and methylmercury.
- DOC in inlets:
  - Geometric mean of 1.6 mg-C/L
- DOC in outlets:
  - Geometric mean of 16 mg-C/L
  - Exhibits strong seasonality



# Possible Relationship between Methylmercury Production and Sulfate Consumption in Bioreactors



# Design Revision: Eliminate Reactor-Bottom Depression to Decrease Likelihood of Strongly Anaerobic Conditions Forming.





# MeHg Discharge from Second Generation Bioreactors

- Results from survey of bioreactors during summer of 2010.
- Inlet MeHg concentrations were all 0.1 ng/L or less (ND).
- The MeHg values are preliminary results subject to revision.
- MeHg not detected in bioreactors with when denitrification was not occurring.
- NA: Sample not yet analyzed.
- ND: MeHg not detected in sample.

Outlet MeHg (ng/L) (Preliminary results)			
	5/14/2010	6/29/2010	7/21/2010
Decatur East		NA	
Decatur West		2.1	2.7
Deland North	ND	ND	
Deland South	NA	0.7	
Monticello		NA	1.8
Mt Zion	ND		
Nitrate Removal			
	5/14/2010	6/29/2010	7/21/2010
Decatur East		43%	
Decatur West		100%	NA
Deland North	24%	1%	
Deland South	100%	100%	
Monticello		8%	NA
Mt Zion	15%		
Sulfate Removal			
	5/14/2010	6/29/2010	7/21/2010
Decatur East		0%	
Decatur West		20%	NA
Deland North	0%	1%	
Deland South	84%	84%	
Monticello		8%	NA
Mt Zion	1%		



# Summary of Results to Date

- Methylmercury is clearly produced in some bioreactors during the summer (June-September).
- Based on limited samples analyzed so far, MeHg production appears to be negligible in May.
- Levels in bioreactor discharge can be much higher than in tile drain water entering bioreactors during the warm summer period.
- Levels in bioreactor discharge are much higher than typical surface water values (0.1-0.3 ng/L).
- Increases in DOC and decreases in sulfate appear to be correlated with MeHg export.
- **Preliminary results suggest that a significant reduction in MeHg production was attained by eliminating ponded bottom zone of bioreactor.**



# Implications

- Just as in natural and constructed wetlands, MeHg is produced in some bioreactors under reducing conditions.
- Effect on MeHg fluxes in watersheds needs to be considered if bioreactors are deployed extensively.
  - Where are the bioreactors relative to water bodies with active fisheries?
  - Do the water bodies have high enough DOC to make MeHg less bioavailable?



# Implications (cont.)

- Reduced MeHg production likely can be attained by adjusting design:
  - Eliminate ponding zones
  - Use low-Hg wood (hypothesis)



# Future Plans

- Analyze more preserved samples for MeHg, especially from spring, high flow periods.
- Analyze total Hg in outlet water
- Analyze Hg in wood chips.  
Depth profile may indicate gain/loss of Hg while in place.
- Study nitrate-methylation connection in lab bioreactors.
- Investigate what ORP is needed before bioreactors start yielding MeHg.

# Contact Information

Please contact the authors if you have questions related to this work.

Robert Hudson

Department of Natural Resources and Environmental Sciences  
University of Illinois

[rjhudson@illinois.edu](mailto:rjhudson@illinois.edu)

217-333-7641

Richard Cooke

Department of Agricultural and Biological Engineering  
University of Illinois

[rcooke@illinois.edu](mailto:rcooke@illinois.edu)

217-333-0944