(Total and) Methyl Mercury Export from Denitrifying Bioreactors in Tile-Drained Fields of Central Illinois

Robert J.M. Hudson, NRES
Richard A.C. Cooke, ABE
University of Illinois at Urbana-Champaign
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• Illinois Sustainable Technology Center
  • Funding for the project
  • Patience with our pace

• Brian Vermillion (formerly NRES)
  • MeHg analysis

• Richard Cooke group
  • Access to field sites and assistance with sampling
  • Expertise
A Tale of Two Elements

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

**Nitrogen**

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

**Mercury**

\[ \text{Hg}(\text{g}) , \text{Hg}^{2+} (\text{aq}), \text{CH}_3\text{Hg}^+ (\text{aq}), \text{HgS(s)}, \text{etc.} \]
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**
- Non-point source pollutant generated via 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.
  - Significant percentage of U.S. women of childbearing age have blood Hg higher than the USEPA “Threshold Level”. 
Anaerobic Processing

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

**Denitrification (alleviates impacts)**

\[
\text{NO}_3^-(aq) \rightarrow \text{NO}_2^-(aq) \rightarrow \text{N}_2(g)
\]

**Mercury methylation (greatly increases impacts)**

\[
\text{Hg}^{2+}(aq) \rightarrow \text{CH}_3\text{Hg}^+(aq)
\]
Nitrate in surface waters inhibits Hg methylation since denitrifiers can out compete Fe- and Sulfate-reducing bacteria for energy (reduced carbon compounds).
Methylation Theoretical Considerations

**Bioavailability of Hg^{II} in Natural Ecosystems**

\[ \text{RSH} + \text{Hg(OH)}_2 + 2 \text{H}^+ \leftrightarrow \text{RS-Hg (unavailable)} \]

\[ \text{H}_2\text{S} + \text{RS-Hg} \leftrightarrow \text{Hg(SH)}_2 \]

Sulfate-reducing bacteria control this reaction by producing H2S. SRB also have the right enzymes to methylate. Fe reducers do as well, but may depend on SRB to make Hg^{II} bioavailable.
Clear Pond, Kickapoo State Park Profile (August 2010)

MeHg Analysis at UIUC by W.Y. Chen
Landscape-Scale Effects of Natural Anaerobic Ecosystems on Mercury Cycling

Brigham et al. (2009)
Constructed Anaerobic Ecosystems
Denitrifying Bioreactors: Constructed Anaerobic Ecosystems

- Pioneered 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 NO$_3^-$ removal.
Monticello Bioreactor Site
Denitrifying Bioreactors
Second Generation Bioreactors

Diversion Structure

Capacity Control Structure

Woodchips

Denitrifying Bioreactors
Denitrifying Bioreactors

Capacity control structure

Up to soil surface

Side View

Trench bottom 1’ below tile invert

5’ section of non-perforated tile

5’ Soil backfill

10’ Wide

Top View

Length dependent on treatment area

Diversion structure
LR = 95.524 LD^{-0.361}

R^2 = 0.93

BIOREACTOR EFFICACY CURVE

Load Reduction, LR (%)

Loading density, LD (Acres per 100 sq. feet of the bioreactor)
Bioreactor Methylmercury Study Objective

1. Determine whether denitrifying bioreactors produce methylmercury due to anoxic environments formed within bioreactor.
2. Determine total Hg 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

Figure 1. Schematic diagram of a sub-surface bioreactor (R. Cooke).

Inlet
Samples

Outlet
Samples
UIUC Method for Hg Speciation Analysis

- Shade and Hudson (2005) *Environmental Science and Technology*

- Shade, Hudson, et al. patent (*circa* 2007)

**pH-Modulated Thiol-Thione Switch**

After Laws (1970)

\[ \text{Thiol Resin} + \text{Thiol Resin} \]

pH < 2: Desorption Favored

pH > 3: Adsorption Favored

University of Illinois at Urbana-Champaign
Thiourea Complexes of $\text{Hg}^{2+}$ and $\text{CH}_3\text{Hg}^+$

MeHg$^+$

$\text{Hg}^{2+}$
Mercury-thiourea complex ion chromatography

Shade and Hudson, ES&T 2005
Dissolved methylmercury: Thiourea-catalyzed solid phase extraction

Vermillion and Hudson
Analytical and Bioanalytical Chemistry (2007)

Brian Vermillion
Validation of Sediment and Biota Sample Preparations

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

Sediments: H$_2$SO$_4$+KBr Digestion/Toluene Extraction (Vermillion, Shade, and Hudson, in prep)
Comparison of Methods for Analysis of Dissolved MeHg

- Ultraclean sample collection
- Sample preservation
- Distillation
  - TU-Catalyzed SPE
- Ethylation/Purge & Trap
  - Elute SPE/Online Trap
- Gas Chromatography
  - Ion Chromatography
- AFS
- AFS
Intercomparison with Distillation/Ethylation ICP-MS
Trent University (Hintelmann)
Intercomparison with USGS
Wisconsin District Mercury Lab (Krabbenhoft)
Bioreactor Study Results
Dissolved $\text{MeHg}$ in Bioreactor Inlets

- Eight non-detects
- Six samples contained detectable $\text{MeHg}$
  - Maximum: 0.16 ng/L
  - Average: 0.09 ng/L
Dissolved MeHg in Bioreactor Outlets
Farm Progress City Bioreactor
Nitrate Removal
“Typical” Hg Levels

• **Groundwater**
  - Total Hg is very low (<0.5 ng/L)
  - MeHg is often non-detectable.

• **Surface Waters**
  - Total Hg is usually 1-5 ng/L in unpolluted systems
  - MeHg is usually <0.5 ng/L in unpolluted systems
Possible Relationship between Methylmercury Production to Sulfate Consumption in Bioreactors

\[ y = 0.7017x \]

\[ R^2 = 0.7299 \]
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 seasonality
Summary of Results to Date

• Levels in bioreactor discharge are much higher than in tile drain water entering bioreactors.
• Methylmercury is clearly produced in bioreactors.
• Some combination of increase in DOC and decrease in sulfate may be responsible.
• Levels in bioreactor discharge are much higher than typical surface water values (0.1-0.3 ng/L).
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 high flow conditions

- Wood chips:
  - Trees accumulate Hg from air and soil water in the wood
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Sulfate-reducing bacteria control this reaction by producing H2S. SRB also have the right enzymes to methylate. Fe reducers do as well, but may depend on SRB to make Hg$^{II}$ bioavailable.
Questions

What controls the extent of methylation?
  – Amount of sulfate in tile drainage?
  – Extent of anoxia?
  – Flow rate?

Can reactors be designed to minimize MeHg formation?
Denitrifying Bioreactors

Capacity control structure

Trench bottom 1' below invert

Length dependent on treatment area

5' section of non-perforated tile

Up to soil surface

5' Soil backfill

Top View

10' Wide

Side View

Diversion structure
Implications

• MeHg is produced in some bioreactors.

• Effect on MeHg fluxes in watersheds needs to be considered

An apparent trade-off:

Reducing nitrate levels to make water drinkable may make the waters downstream unfishable.
Implications (cont.)

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