Methylmercury Cycling in Wetlands Managed for Rice Agriculture and Wildlife: Implications for Methylmercury Production, Transport, and Bioaccumulation

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Methylmercury Cycling in Wetlands Managed for Rice Agriculture and Wildlife: Implications for Methylmercury Production, Transport, and Bioaccumulation

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Methylmercury Cycling in Wetlands Managed for Rice Agriculture and Wildlife: Implications for Methylmercury Production, Transport, and Bioaccumulation

Prop. 40 and Prop. 50 funded ($1.26M) process-based characterization study to guide:
- management practices
- monitoring
- modeling

Special Section of Science of the Total Environment 2014 (editor: Mae Gustin)

1. Synthesis of study results (Windham-Myers et al.)
2. Hydrologic modeling (Bachand et al.)
3. MeHg load calculations (Bachand et al.)
4. MeHg and Water Quality (Alpers et al.)
5. MeHg Photodegradation (Fleck et al.)
6. MeHg Production in Sediment (Marvin-DiPasquale et al.)
7. Plant influence on MeHg Production (Windham-Myers et al.)
8. Role of Plants in MeHg Pools and Fluxes (Windham-Myers et al.)

9. Fish MeHg Bioaccumulation (Ackerman and Eagles-Smith 2010, ES&T)
10. Invertebrate MeHg Bioaccumulation (Ackerman et al. 2010, STOTEN)
Methylmercury (MeHg) is a concern in wetlands.

Scientists + Stakeholders = Solutions

Goals for today’s meeting:

1. Brief stakeholders on scientific results of integrated study (45 minutes)

2. Stakeholder input on research, management implications, and outreach
MeHg is a concern among Delta wetlands.

Why? Wetlands methylate Hg

SRB = Sulfate Reducing Bacteria
FeRB = Iron Reducing Bacteria
MeHg is a concern among Delta wetlands. Why? Wetlands methylate Hg and there are many types in the Sacramento San Joaquin Delta.

0.06 ng/L (Delta Pulse 2012)

0.31 ng/L

How could Yolo Bypass wetlands reduce MeHg loads by >70% to meet the TMDL target?
## YBWA Hg Study Management Timeline

<table>
<thead>
<tr>
<th>Field</th>
<th>MAY</th>
<th>JUN</th>
<th>JUL</th>
<th>AUG</th>
<th>SEP</th>
<th>OCT</th>
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</tbody>
</table>

- **dry field**
- **< 50% flooded**
- **50 - 100% flooded**
- **fully flooded**
- **flooded, no flow**

- **Starter Fertilizer @ 150-210 lbs / acre (18-141 kg SO₄²⁻/ha)**
- **Rice seed applied**
- **Topdressing Fertilizer: (NH₄)₂SO₄ @ 125-200 lbs / acre (101-162 kg SO₄²⁻/ha)**

- **Rice Harvest**
- **Sampling event (all components*)**

* Bioaccumulation evaluated in summer only
YBWA Hg Study Components

SEDIMENT
MeHg Production
Sulfate Reduction
S, Fe & C Chemistry

WATER COLUMN
Hydrology
Water Quality
 Loads
Photodegradation

PLANTS
Experimental Devegetation
Plant metrics
Growth/Decay

BIOTA
Invertebrate sampling
Caged fish studies
Wild fish

USGS
CA DFW
Battelle Labs
Bachand Assoc.
Processes link components – Results of Study

MeHg Conceptual Model

Water, Hydrology, Photodegradation, Sediment, Plants, Biota
**Surface water:** Outflow [MeHg] was highest during wild rice harvest, and for white rice, at initial flood-up (legacy MeHg) and during winter. Permanent wetlands had consistently low [MeHg] at outflows.

![Graph showing MeHg-U levels in surface water over time](image)

Water-quality goal, draft Basin Plan Amendment (Wood and others, 2010b)
**Surface water:** Sulfate concentrations exceeded levels known to limit the activity of sulfate-reducing bacteria (30 mg/L in freshwater). Thus, the addition of sulfate-bearing fertilizer did not simulate MeHg production.

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**Graphical Representation:***

- **Graph 1:**
  - Y-axis: Sulfate (mg/L)
  - X-axis: Date (06/01/07 to 05/01/08)
  - Data points for Supply Canal, White Rice, Wild Rice, Fallow, Seasonal Wetland, and Permanent Wetland.
  - Labels for growing season, drain & harvest, and post-harvest.

- **Graph 2:**
  - Y-axis: % Hg-methylation (d⁻¹)
  - X-axis: Sulfate (mg/L)
  - Data points for Freshwater, Estuarine, and Marine conditions.

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**Table:**

<table>
<thead>
<tr>
<th>Supply</th>
<th>White Rice</th>
<th>Wild Rice</th>
<th>Fallow</th>
<th>Seasonal Wetland</th>
<th>Permanent Wetland</th>
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</table>

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**Legend:**

- Yolo Bypass
- “Goldilocks curve” adapted from Gilmour and Henry (1991)

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**Source:**

Alpers et al. 2014
Surface water: In areas with lower sulfate, the addition of sulfate-bearing fertilizer may cause increased MeHg formation (e.g. upstream in the Sacramento River).

data from this study and Domagalski et al. (2000)

“Goldilocks curve” adapted from Gilmour and Henry (1991)

Alpers et al. 2014
Hydrology: Load calculations are not based on concentration alone. Assuming Evaporation (E) dominates water loss leads to inaccurate calculation of hydrologic loads, AS WELL AS constituent transport.

Over growing season, 75% of water loss is through plant transpiration (T).
Hydrology: Transpiration dominates ET in summer, but not in winter.

- Chloride and conductivity (conservative tracers) showed importance of flowpaths.
  - Evaporation (E) concentrates constituents in surface water
  - Transpiration (T) transports dissolved constituents into shallow root zone

- Relative effect of transpiration changes over growing season and day
**Hydrology:** Soil MeHg is retained and accumulated in summer via transpiration-advection and released to surface water in winter.

Summer transpiration limits MeHg export in 2 ways:
- Physically pulls water downward, which
- Prevents upward diffusion of porewater MeHg

---

**Legend**
- Distance at which...
- Hydrology: Soil MeHg is retained and accumulated in summer via transpiration-advection and released to surface water in winter.
- Summer transpiration limits MeHg export in 2 ways:
  - Physically pulls water downward, which
  - Prevents upward diffusion of porewater MeHg

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**Bachand et al. 2014b**
**Hydrology:** All fields made MeHg, but summer storage and degradation of incoming MeHg made northern fields more of a sink than a source.

Outlet Load – Inlet Load for **Northern** and **Southern** Block Fields (ng MeHg m\(^{-2}\) d\(^{-1}\))

Davis Drain/Greens Lake: = 5x Toe Drain [MeHg]

Bachand et al. 2014b
**MeHg Photodegradation:** Solar radiation degraded water column MeHg (up to 50% in 2 days) and the total amount of MeHg lost was primarily a function of initial MeHg concentrations and cumulative light exposure.

\[
\frac{[\text{MeHg}]_t}{[\text{MeHg}]_0} = -0.0049 \times \text{PAR} + 0.99
\]

\[r^2 = 0.87, \ p < 0.001\]

\*PAR = Photosynthetically Available Radiation (sunlight)

Fleck et al. 2014
MeHg Photodegradation: Rice plants can shade surface water during the summer growing season to PAR flux levels comparable to winter.

**Summer (Growing Season)**
- AVG. PAR flux w/ 0% shading = 50 mol m\(^{-2}\) d\(^{-1}\)
- May-June = 40% shading = 30 mol m\(^{-2}\) d\(^{-1}\)
- July-Sept = 90% shading = 5 mol m\(^{-2}\) d\(^{-1}\)

**Winter (Post Harvest Period)**
- AVG. PAR flux w/ 0% shading = 10 mol m\(^{-2}\) d\(^{-1}\)

Fleck et al. 2014
**MeHg Photodegradation**: Sunlight degrades both MeHg and dissolved organic matter (DOM). fDOM is becoming a useful tool for future monitoring with *in situ* optical measurements.

\[
Y = 3.11 \times \text{ABS}_{280} - 2.1
\]
\[
r^2 = 0.76, \ p < 0.001
\]

\[
Y = 1 \times \%\text{FDOM}
\]
\[
r^2 = 0.68
\]

\[
Y = 1.62 \times \%\text{FDOM} - 0.68
\]
\[
r^2 = 0.91
\]

Fleck et al. 2014
**Sediment**: Controls on MeHg Production? A Conceptual Model.

MeHg Production = \( K_{\text{meth}} \times \text{Hg(II)}_R \)

- **Hg(II)-Methylating Bacteria Activity (K_{\text{meth}})**
  - Low
  - Moderate
  - High

- **Hg(II)\(_R\) Concentration**
  - Low
  - Moderate
  - High

Marvin-DiPasquale et al. 2014
**Sediment:** MeHg production rates were comparable between rice fields and managed wetlands, but for different reasons.

MeHg Production = $K_{meth} \times Hg(II)_R$

Data from Marvin-DiPasquale et al. 2014
**Sediment:** MeHg concentrations were higher in rice fields than in managed wetlands.

Data from Marvin-DiPasquale et al. 2014
Sediment: MeHg concentrations in rice fields were higher during the post-harvest season compared to the growing season.

Data from Marvin-DiPasquale et al. 2014
**Sediment:** The addition of sulfate based fertilizer did **NOT** result in an increase in sediment MeHg concentration.
Vegetation: Sediment MeHg production was reduced by devegetation.

Data from Windham-Myers et al. 2014a
**Vegetation:** MeHg Production is enhanced by plant carbon exudates. Plant effects may also include rhizo-concentration and rhizo-oxidation.

Data from Windham-Myers et al. 2014a
Vegetation: Plant carbon drives MeHg in summer AND winter.

Data from Windham-Myers et al. 2014b
**Vegetation:** Rice seed [MeHg] is elevated beyond native wetland seeds.

*Photo: Sandhill Cranes, Cosumnes River Preserve*

Data from Windham-Myers et al. 2014b
**Bioaccumulation:** Fish mercury increased 12-fold in rice fields in summer.

Ackerman and Eagles-Smith, 2010a
### Bioaccumulation:

All caged and wild fish in summer agricultural fields exceeded the TMDL target, with 26-82% of consumers at risk.

<table>
<thead>
<tr>
<th>TMDL</th>
<th>Caged Mosquitofish</th>
<th>Wild Fish</th>
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</thead>
<tbody>
<tr>
<td>&gt;0.03 µg/g ww</td>
<td>100%</td>
<td>100%</td>
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<tr>
<td>&gt;0.20 µg/g ww</td>
<td>82%</td>
<td>59%</td>
</tr>
<tr>
<td>&gt;0.30 µg/g ww</td>
<td>52%</td>
<td>26%</td>
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</tbody>
</table>

- 0.03 µg/g ww for Trophic Level 2 fish (<50 mm); Central Valley Water Board’s TMDL target to protect wildlife and humans\(^1\)
- 0.20 µg/g ww impairs fish health\(^2\)
- 0.30 µg/g ww causes reduced reproduction in birds\(^3\)

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\(^1\)Wood et al. 2008.  
\(^2\)Beckvar et al. 2005  
\(^3\)Albers et al. 2007

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Ackerman and Eagles-Smith, 2010a
**Bioaccumulation:** Bird Hg risk from invertebrates was high in all wetlands. Invertebrate [MeHg] was highest in permanent wetlands.

MeHg dietary effect levels for birds

- 75% of water boatmen >0.50 µg/g dw\(^1\)
- 48% of water boatmen >0.70 µg/g dw\(^2\)

\(^1\)0.50 µg/g dw caused reduced reproduction in mallards (Heinz 1979)
\(^2\)0.70 µg/g dw caused reduced reproduction in kestrels (Albers et al. 2007)
**Summary:** Processes are interconnected, but temporally lagged. In summer, MeHg production was medium, export was low, and biotic uptake was high.

MeHg Conceptual Model

- Hydrology
- Residence Time
- Water Quality
- Vegetation
- Sediment Flux
- Biota
If MeHg is a problem, what can we do about it?

**Minimize Production**
- Carbon control in fall/winter
  - disking
  - baling
  - grazing
  - mowing
- Reduce sulfate additions where possible in upstream sites

**Minimize Export**
- Maximize aqueous MeHg “loss” by increasing residence time
  - recycle outflows
  - slow water flows
  - route water to permanently flooded openwater ponds
- Apply controls at “hot moments” (disturbances, initial floodup)

**Minimize Bioaccumulation**
- Minimize MeHg concentrations in surface water by reducing production
  - OR
- preventing evapoconcentration
  - NOT slowing flows
  - NOT re-using “dirty water”
Ongoing Research and Future Opportunities

1. **Openwater cells**
   - “Tailwater ponds” MLML, Yolo Bypass
   - “Integrated ponds” USGS/BLM, Cosumnes River Preserve

2. **Carbon control**
   - Mesocosms: MLML, Yolo Bypass
   - Field Scale: USGS/BLM/MLML, Cosumnes River Preserve

3. **Low Intensity Chemical Dosing** (USGS/EPA, Twitchell Island)

4. **Aerobic rice growing** (Wang et al. 2014)


6. **Genotypic strains** (Rothenberg et al. 2012)

7. **Greater global coverage of MeHg in rice grains** (ICMGP 2013, Scotland)
For more information, please visit these websites:

PEER REVIEWED PUBLICATIONS:
Journal: Science of the Total Environment, published by Elsevier
Website: www.sciencedirect.com/science/journal/00489697 (click on Articles in Press)

USGS WEBSITES:
For more information, please visit these websites:
http://www.usgs.gov/mercury
http://ca.water.usgs.gov/mercury
http://ca.water.usgs.gov/mercury/riceFields.html

Open-Forum Question and Answer with Co-Author Panel:
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Mark Marvin-DiPasquale, USGS (Microbial Ecology, Sediment Chemistry)
Charlie Alpers, USGS (Water Chemistry)
Jacob Fleck, USGS (Organic Chemistry)
Josh Ackerman, USGS (Bioaccumulation)
Phil Bachand, Tetra Tech (Hydrology)
Mark Stephenson, Moss Landing Marine Laboratories (Water Chemistry)
(WEBEX) Wes Heim, Moss Landing Marine Laboratories (Water Chemistry)
(WEBEX) Collin Eagles-Smith, USGS (Bioaccumulation)
Full Citations for YBWA related journal publications


Science of the Total Environment (Volume 484) Special Section: Methylmercury cycling in wetlands managed for rice agriculture and wildlife: Implications for methylmercury production, transport, and bioaccumulation (Guest Editors: Mae Sexauer Gustin and Lisamarie Windham-Myers)


