Removal of mercury from surface waters using coagulation with metal-based salts:
Laboratory and Field Study Findings

U.S. Environmental Protection Agency's (EPA) Region 9 State-of-the-Science Workshop on Mercury Remediation in Aquatic Environments , January 26-28, 2016

USGS CA Water Science Center and others

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- USGS Cooperative Research Program

Overview of this presentation

I. **PROJECT BACKGROUND**

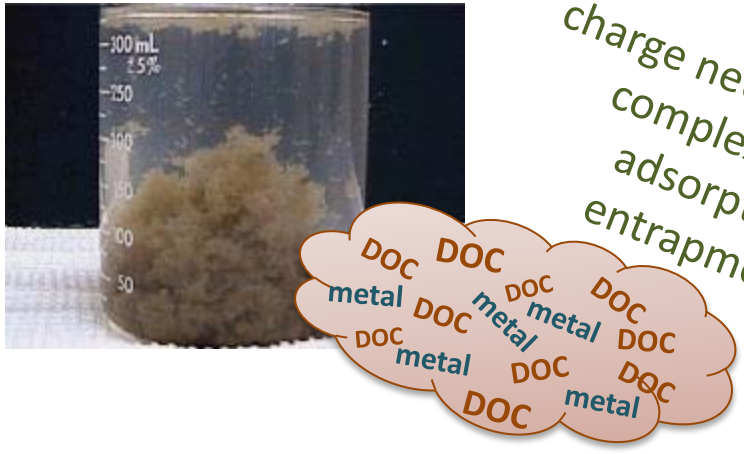
II. **LABORATORY STUDIES**

III. **FIELD STUDY**

IV. **CURRENT, FUTURE WORK**

V. **CONSIDERATIONS, APPLICABILITY**

What is Coagulation & Why are We Even Thinking About It?



charge neutralization
complexation
adsorption
entrapment

Coagulation: the aggregation and subsequent removal of material in the water column through the formation of particles (*flocculate*) which precipitate out of solution

- particles
- dissolved constituents (DOC, PO_4, Hg?)

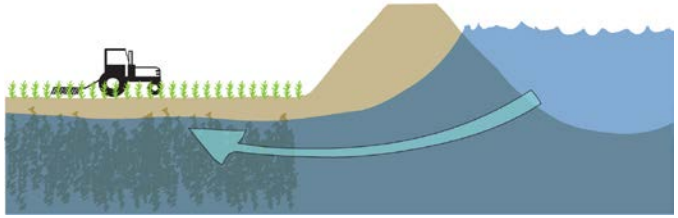
Metal-Based Salts
Aluminum Sulfate (alum)
Polyaluminum Chloride (PAC)
Iron Sulfate
Iron Chloride

- ✓ Drinking Water Treatment
- ✓ Waste Water Treatment
- ✓ Storm Water Treatment
- ✓ Whole Lake Phosphorus Removal

Coagulation-Wetland Project Addresses

1. **Drinking Water Quality**
   - ❑ DOC and DBP precursor removal

2. **Levee Stability**
   - ❑ subsidence mitigation



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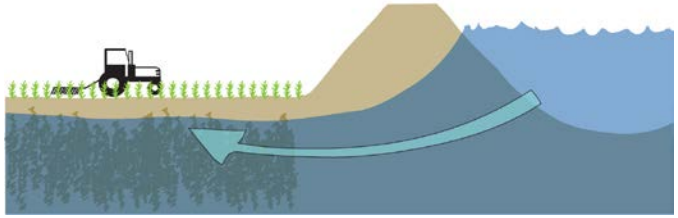
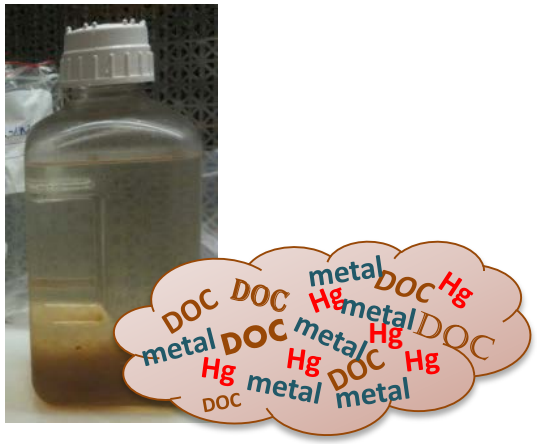


3. **MeHg TMDL****
   - ❑ Hg removal by coagulation alone
   - ❑ MeHg reduction in treated wetlands

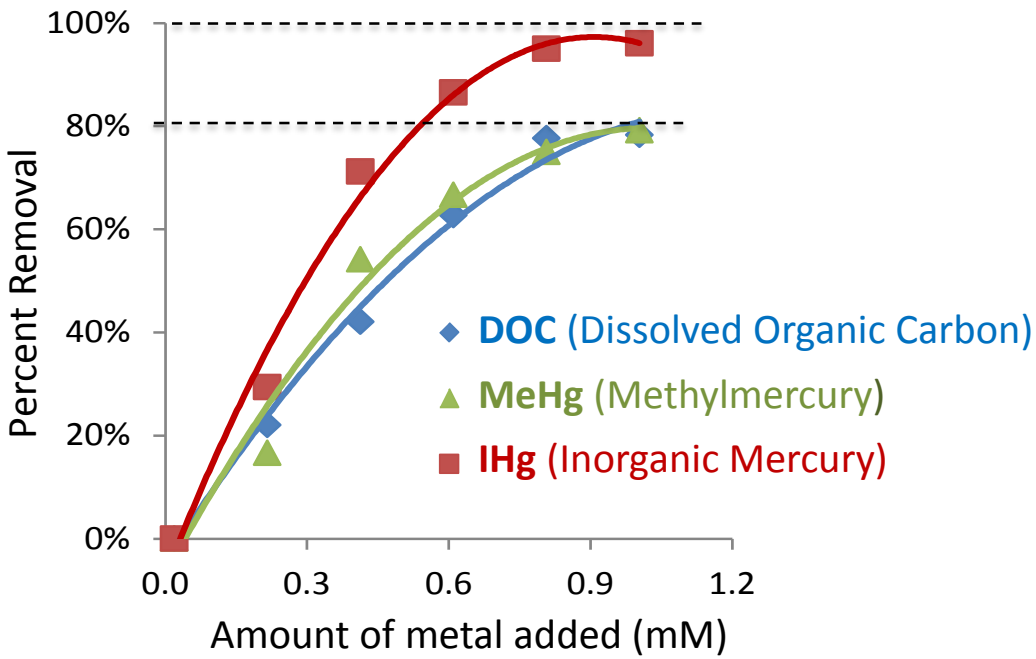


also want to examine

- ❑ Ecosystem Effects (water quality, plants, fish)
- ❑ Feasibility of in situ coagulation systems

First Step: Laboratory Study

1. **Assessed whether coagulants remove <u>dissolved Hg</u> under ambient concentrations of DOC and Hg.**

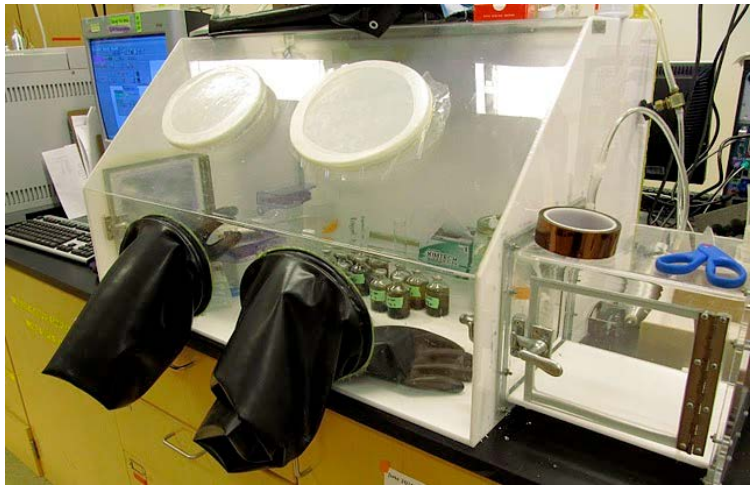


- Coagulation removed up to <u>80</u>% of <u>DOC</u> and <u>MeHg</u> from solution.
- Coagulation removed up to <u>97</u>% of <u>IHg</u> from solution.
- Same trends for 3 coagulants tested

Henneberry et al. 2011
Science of the Total Environment
409:631-637

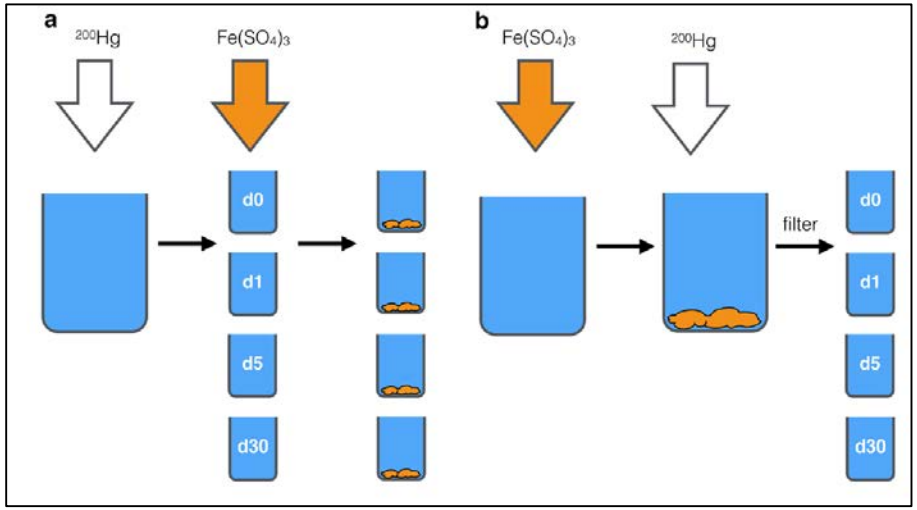
Laboratory Studies

2. **Examined floc stability (iron sulfate) under abiotic reducing conditions**
   (no Hg component)



- Remained non-crystalline
- No evidence of DOC release

3. **Examined (a) time to form metal-DOM-Hg complex; (b) once formed, can additional Hg be removed?**
   (Hg Isotope Spike)



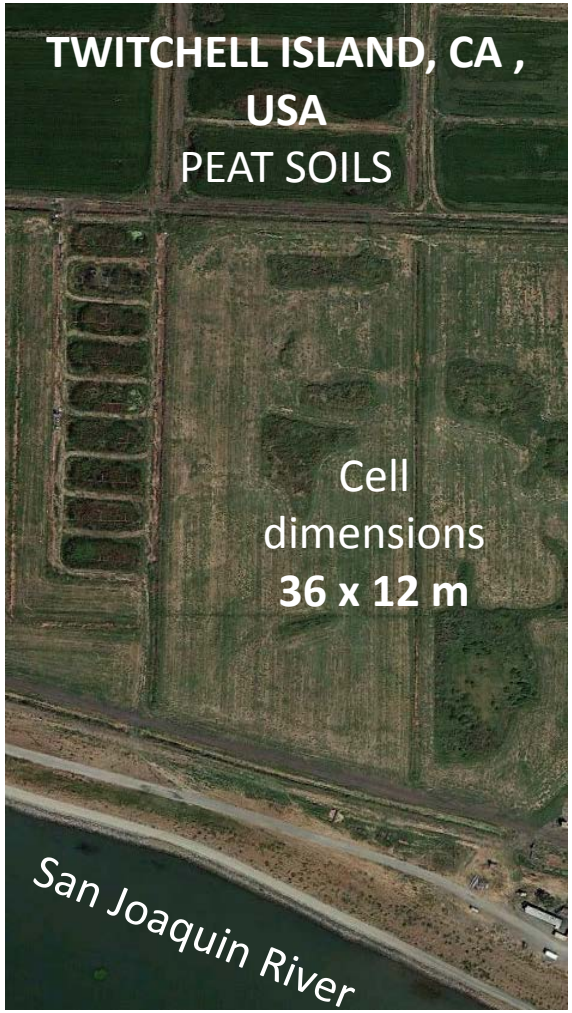
- Rapid association with Floc
- Additional capacity to remove Hg after Floc formed

Henneberry et al. 2012
Organic Geochemistry
http://dx.doi.org/10.1016/j.orggeochem.2012.04.005

Henneberry et al. 2016
Environmental Management
DOI 10.1007/s00267-015-0601-2

Field Study

Coagulation-Wetland System Operating 2012- 2014



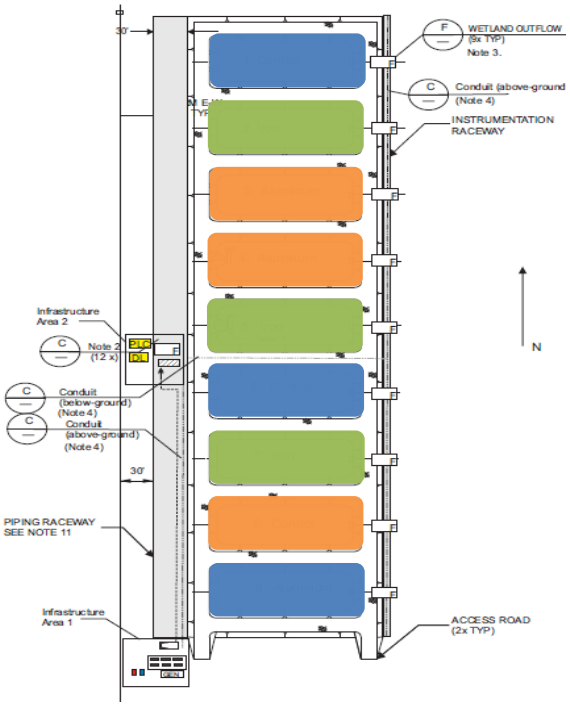
Comparison of 3 treatments

- Co – untreated Control
- Fe – Iron Sulfate
- Al – PolyAluminum Chloride

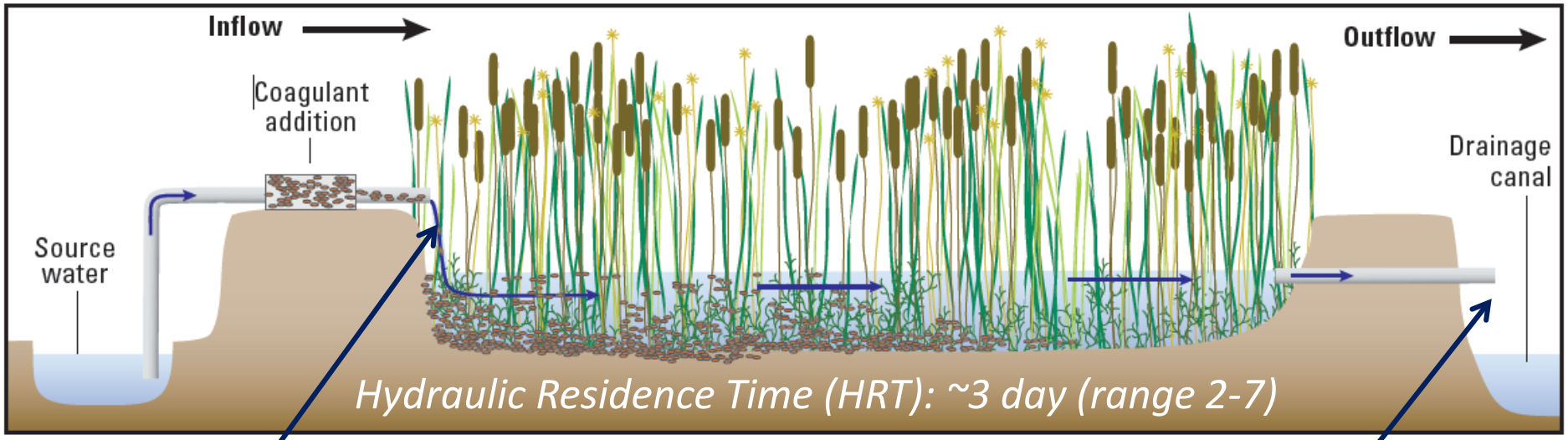
Replicated Design:

3 treatments x 3 replicates = 9 cells

In-situ coagulation system



Coagulation-Wetland Treatment System

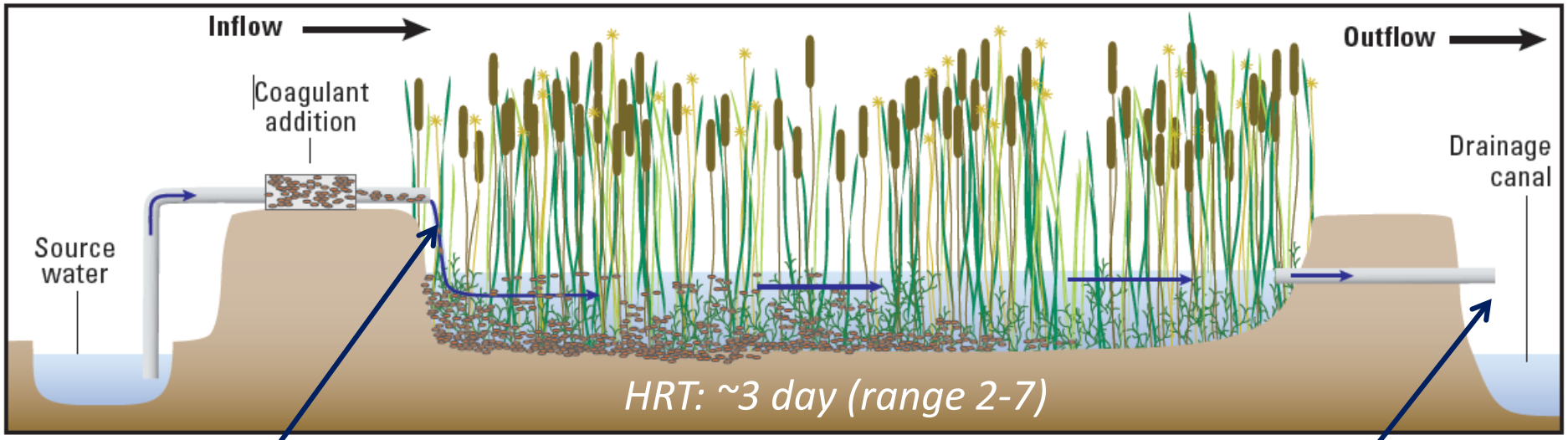


INFLOW
Post coagulation

OUTFLOW
Post Coag + Wetland

***LICD**: **L**ow **I**ntensity **C**hemical **D**osing*

Coagulation-Wetland Treatment System



INFLOW
Post coagulation

WETLAND

OUTFLOW
Post Coag + Wetland

***LICD**: **L**ow **I**ntensity **C**hemical **D**osing*

Water Sample Collection for Hg

INFLOW: post coagulation
OUTFLOW: coagulation + wetland passage

- ✓ Wetlands initially flooded Fall 2011
- ✓ Coagulation-Wetland System Ran **June 2012 – September 2013 (16 m months)**
- ✓ Inflow/Outflow Water for Hg: 1 year **Nov. 2012-Sept. 2013**, 10 samples

TotHg & MeHg

Dissolved & Particulate

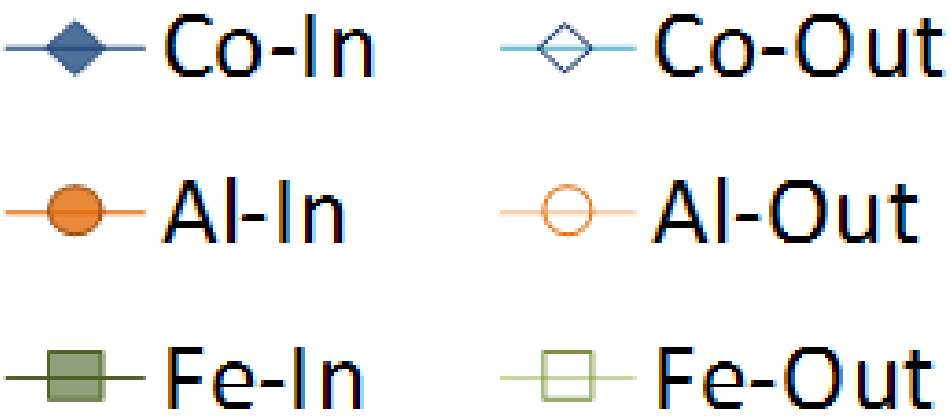
MERCURY ABBREVIATIONS

	Methyl	Total
Filtered Fraction (<0.3 µm)	*f* MeHg	*f* THg
Particulate Fraction (>0.3 µm)	*p* MeHg	*p* THg
Total Fraction (Filtered+Particulate)	*t* MeHg	*t* THg

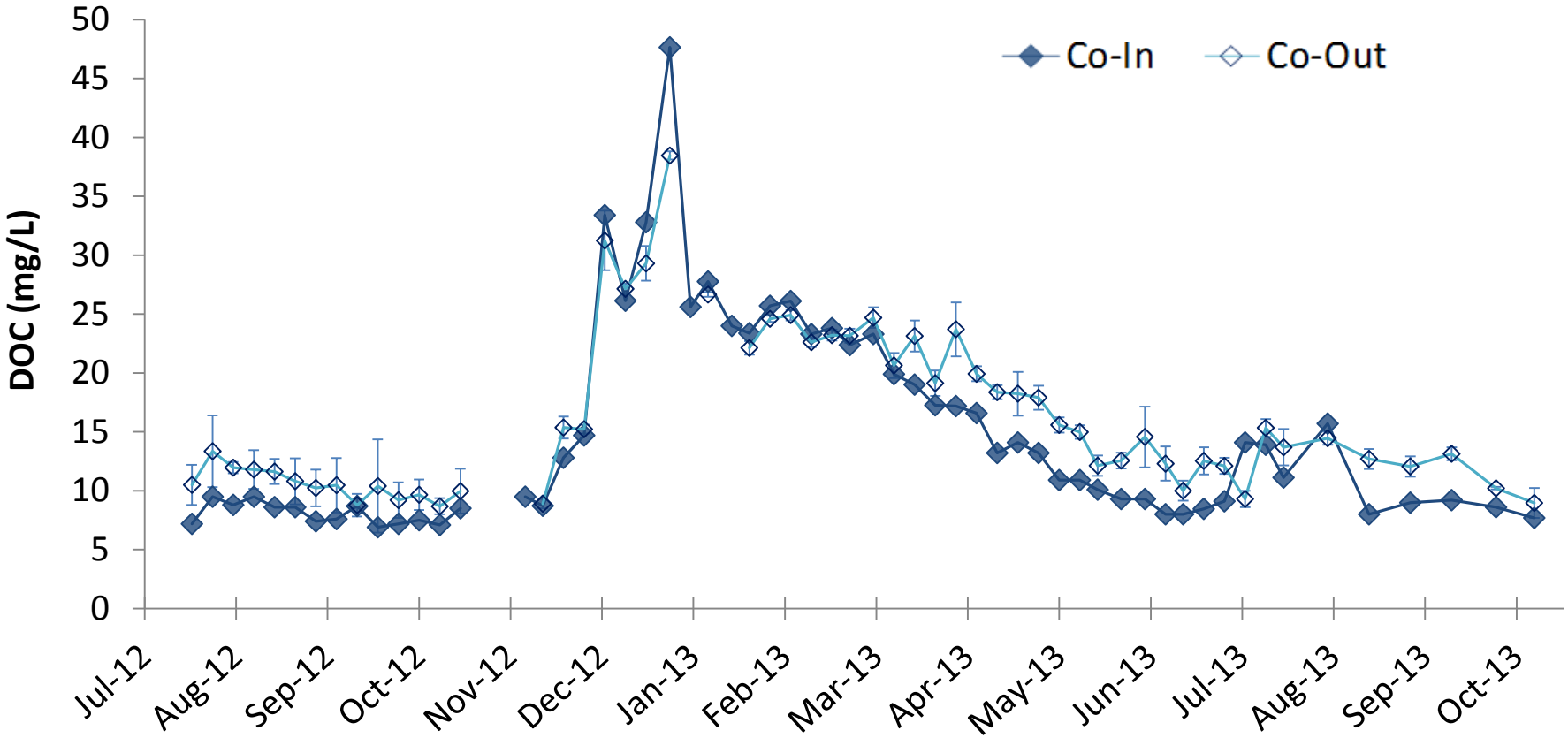
Analyzed by the USGS Wisconsin Mercury Research Lab

Dissolved Organic Carbon (DOC)

concentrations



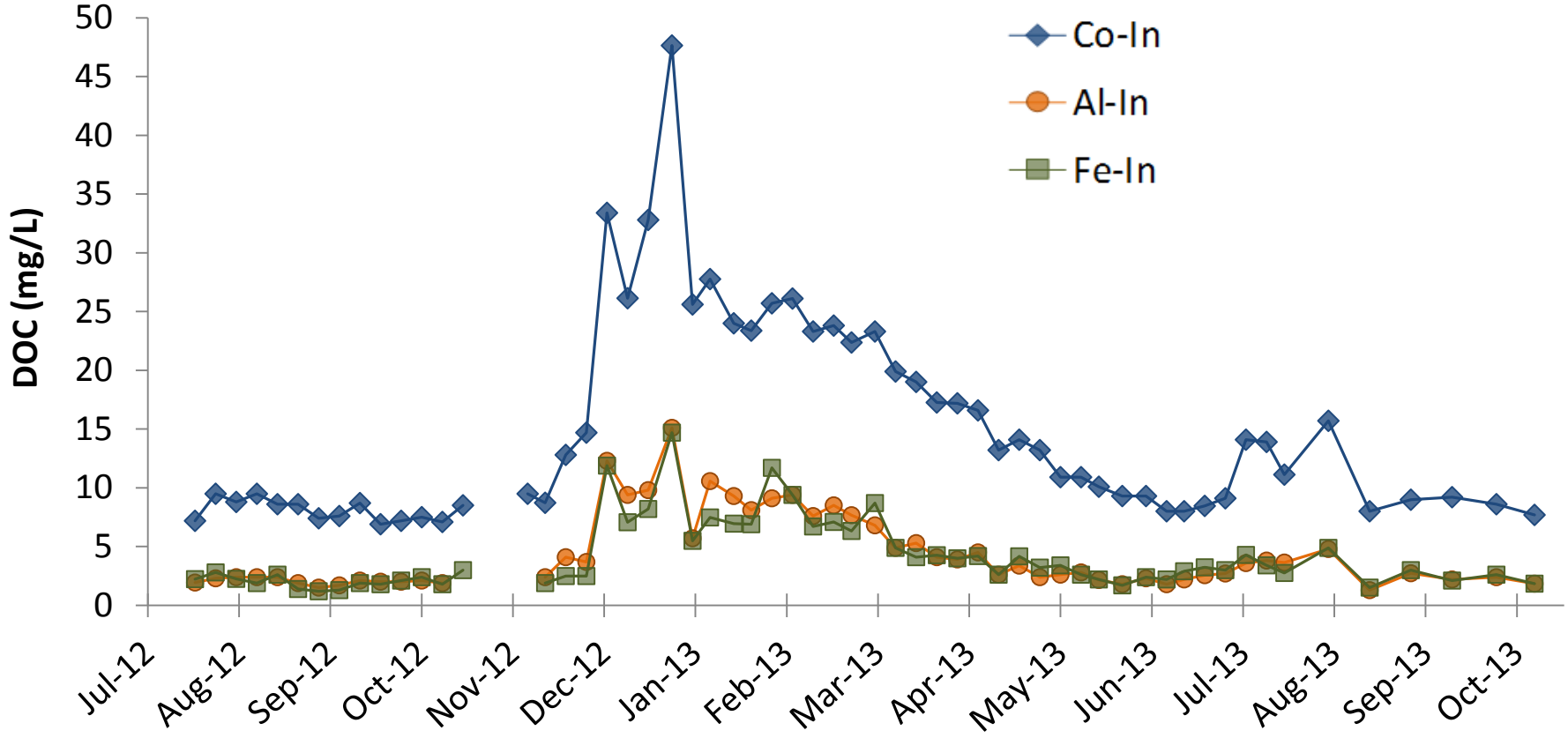
DOC CONCENTRATION



- DOC concentrations in the drainage water were higher during the winter months.
- Wetlands added DOC (except in the winter)

Stumpner et al. 2015
USGS Data Series Report
http://dx.doi.org/10.3133/ds950

DOC CONCENTRATION



- **Coagulation alone** reduced DOC by 65-85% (OUR TARGET)

Stumpner et al. 2015
USGS Data Series Report
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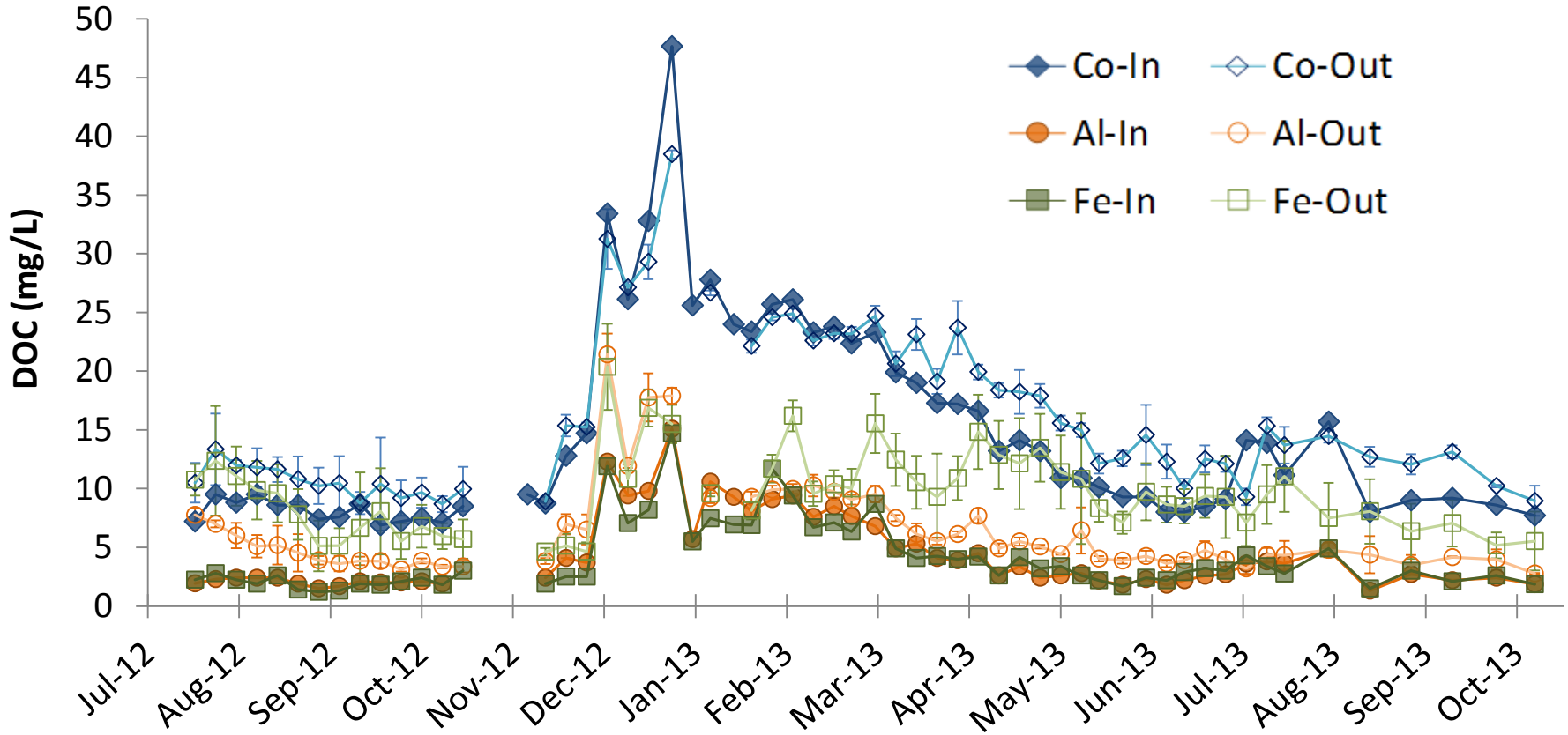
DOC CONCENTRATION



- Passage through the wetlands often ADDED DOC

Stumpner et al. 2015
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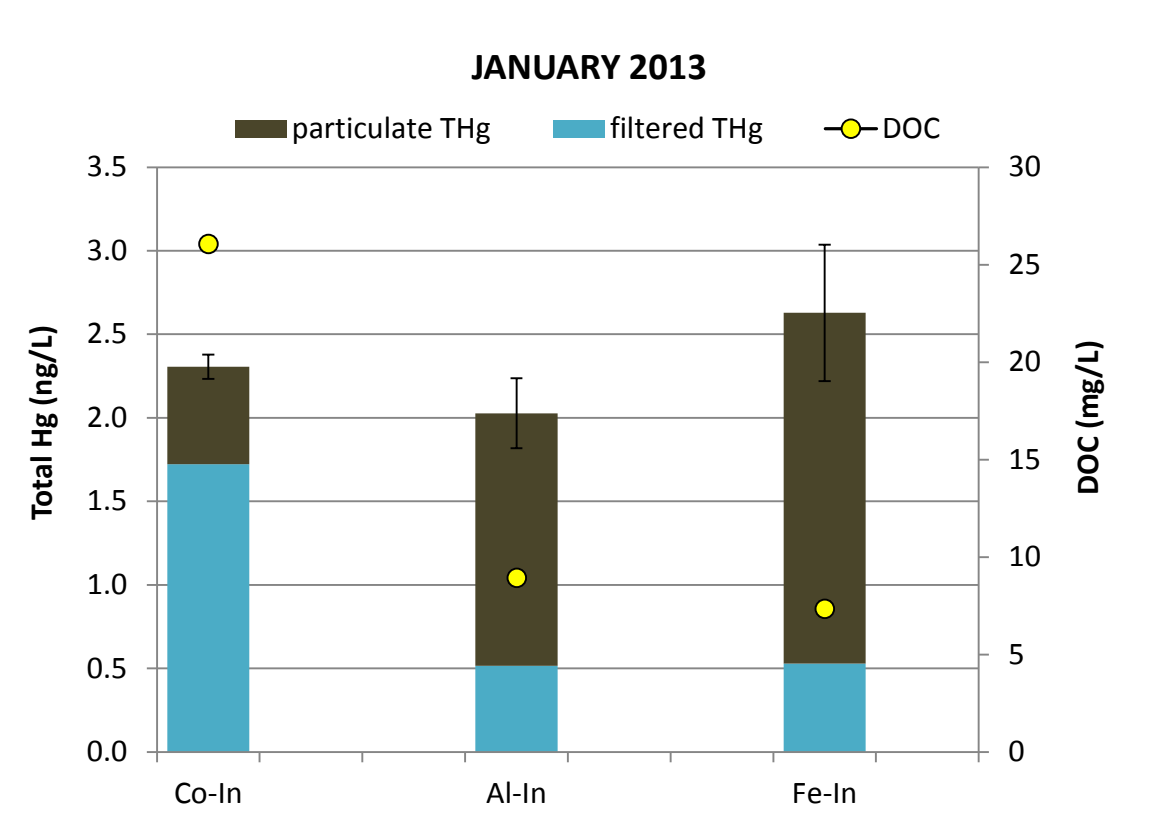
Mercury

Total Hg

Source water
30% particulate
70% dissolved



- coagulant addition converts dissolved (*f*THg) to particulate Hg (*p*THg).

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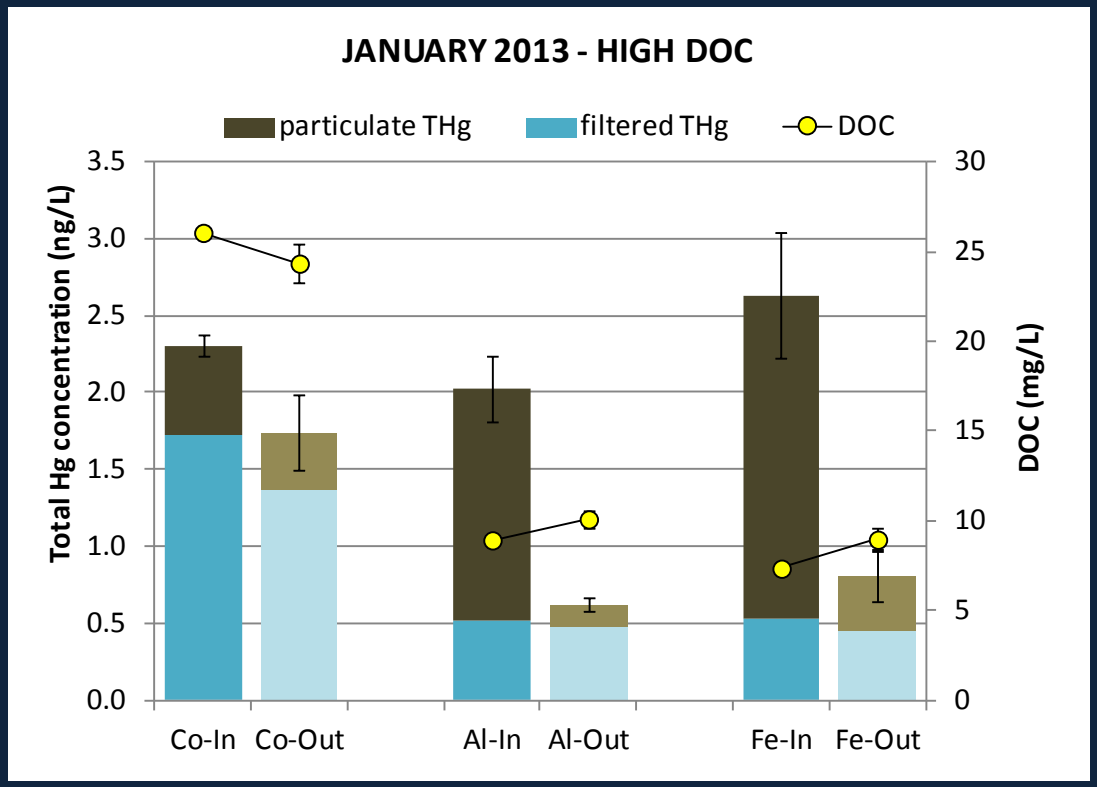

- coagulant addition immediately converts dissolved (*f*THg) to particulate Hg (*p*THg).
- particulate material is retained in the wetlands, resulting in significantly lower THg (*f* + *p*) concentrations at the outflows.

Stumpner et al. 2015
USGS Data Series Report
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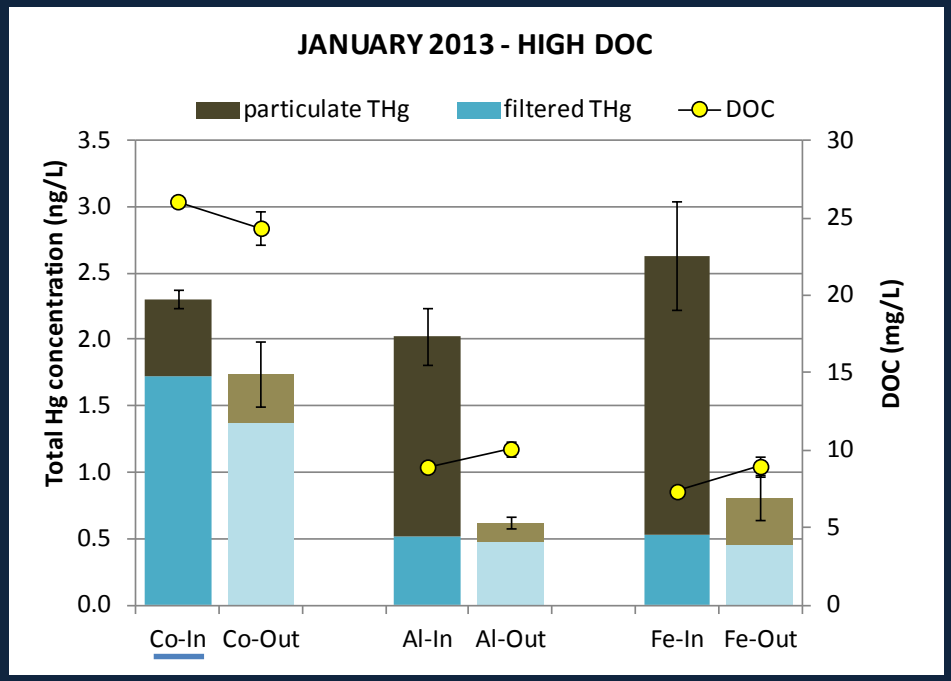
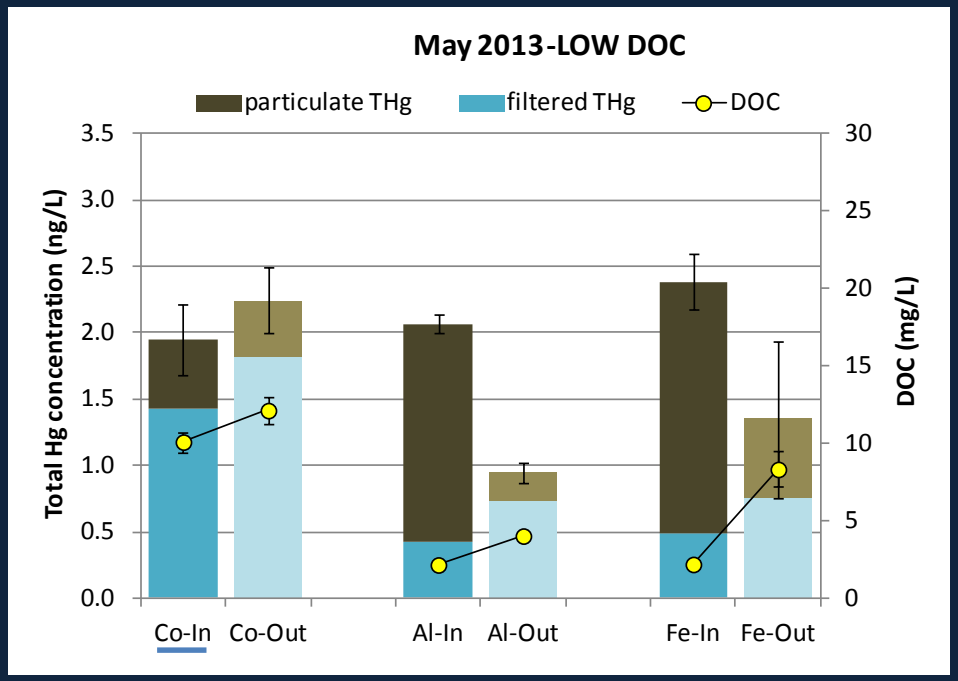
Total Hg





- Seasonal effects
- Wetland passage increased *f*THg concentrations during spring/summer.
- Overall, both Fe and Al Coagulation-Wetland systems are lowering surface water Total Hg concentrations.

Stumpner et al. 2015
USGS Data Series Report
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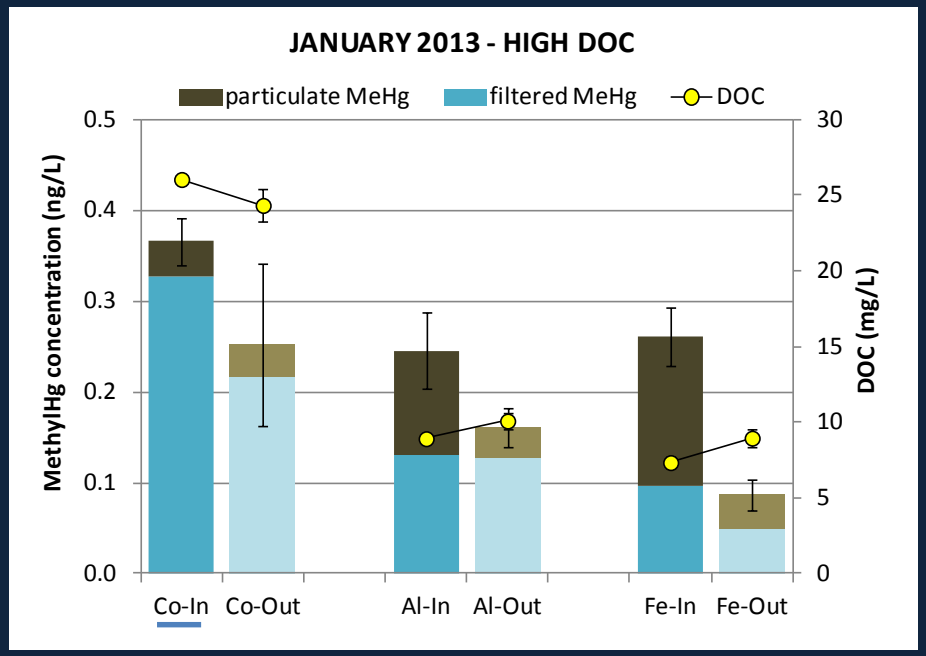
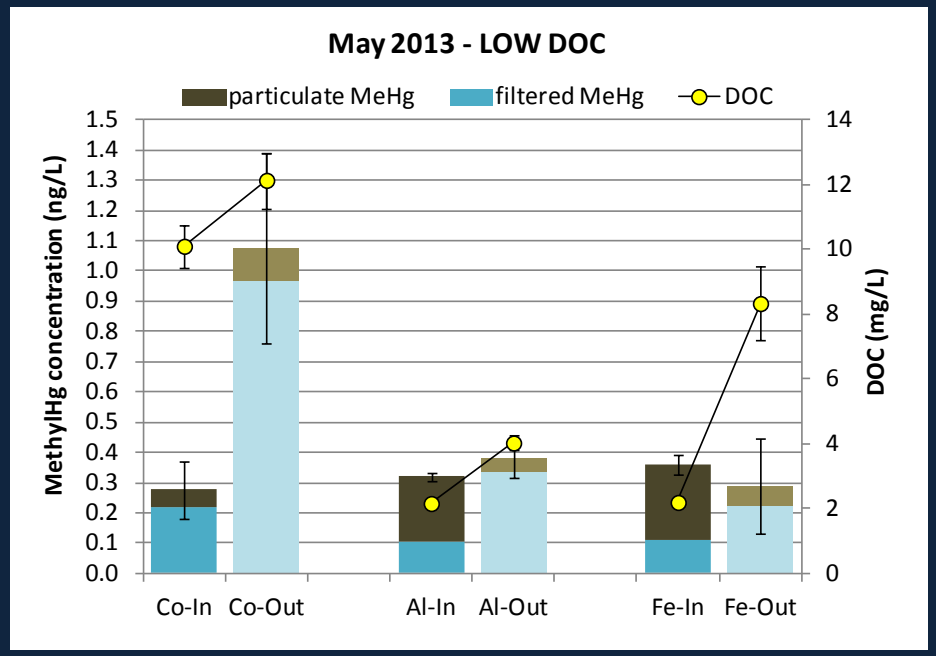
MethylHg





- *f*MeHg is coverted into *p*MeHg – settles in the wetlands

In the <u>WINTER</u> months:

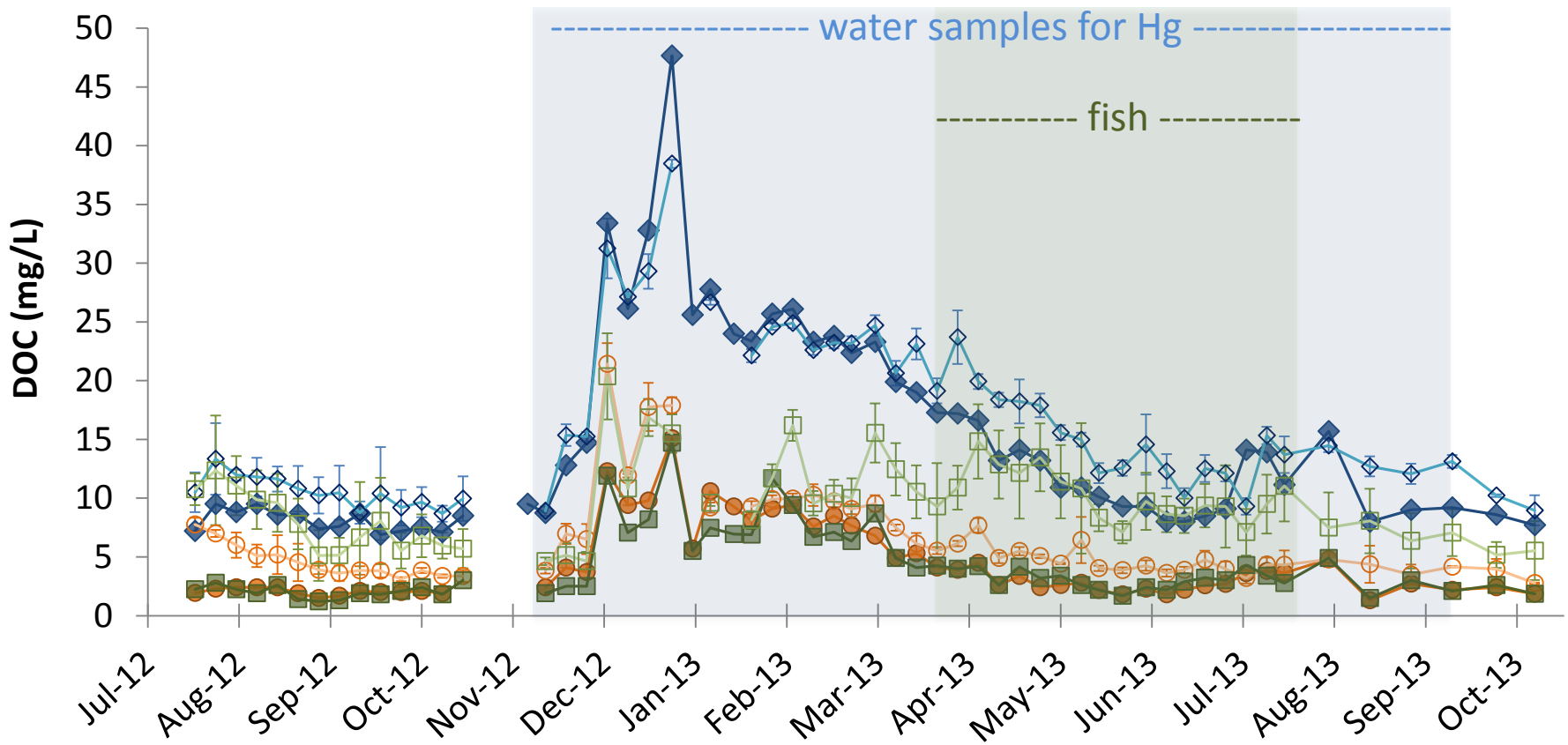
- There is no indication passage through the wetlands increases MeHg concentrations.

In the <u>SUMMER</u> months:

- wetlands are sources of *f*MeHg (and DOC).

Stumpner et al. 2015
USGS Data Series Report
http://dx.doi.org/10.3133/ds950

Water and Fish Collection



Stumpner et al. 2015
USGS Data Series Report
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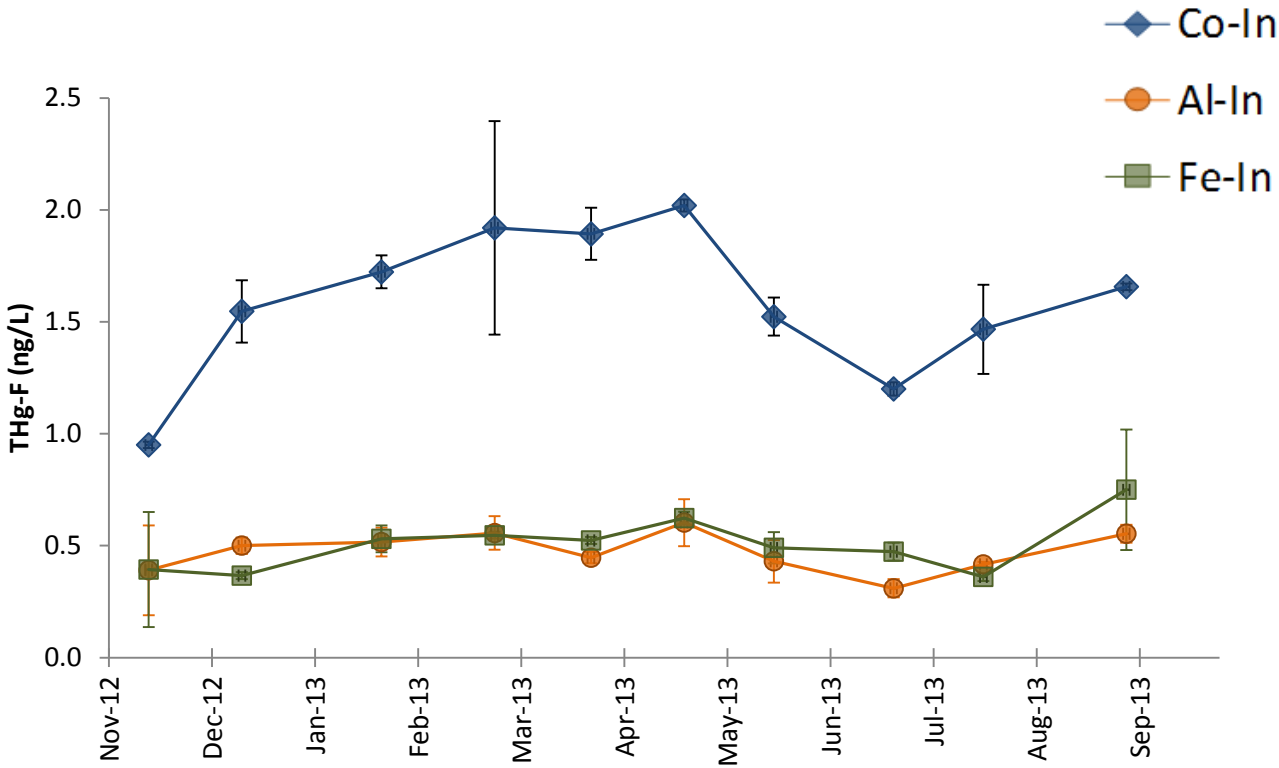
Filtered THg



- fTHg concentrations reduced by 60-76%.

Stumpner et al. 2015
USGS Data Series Report
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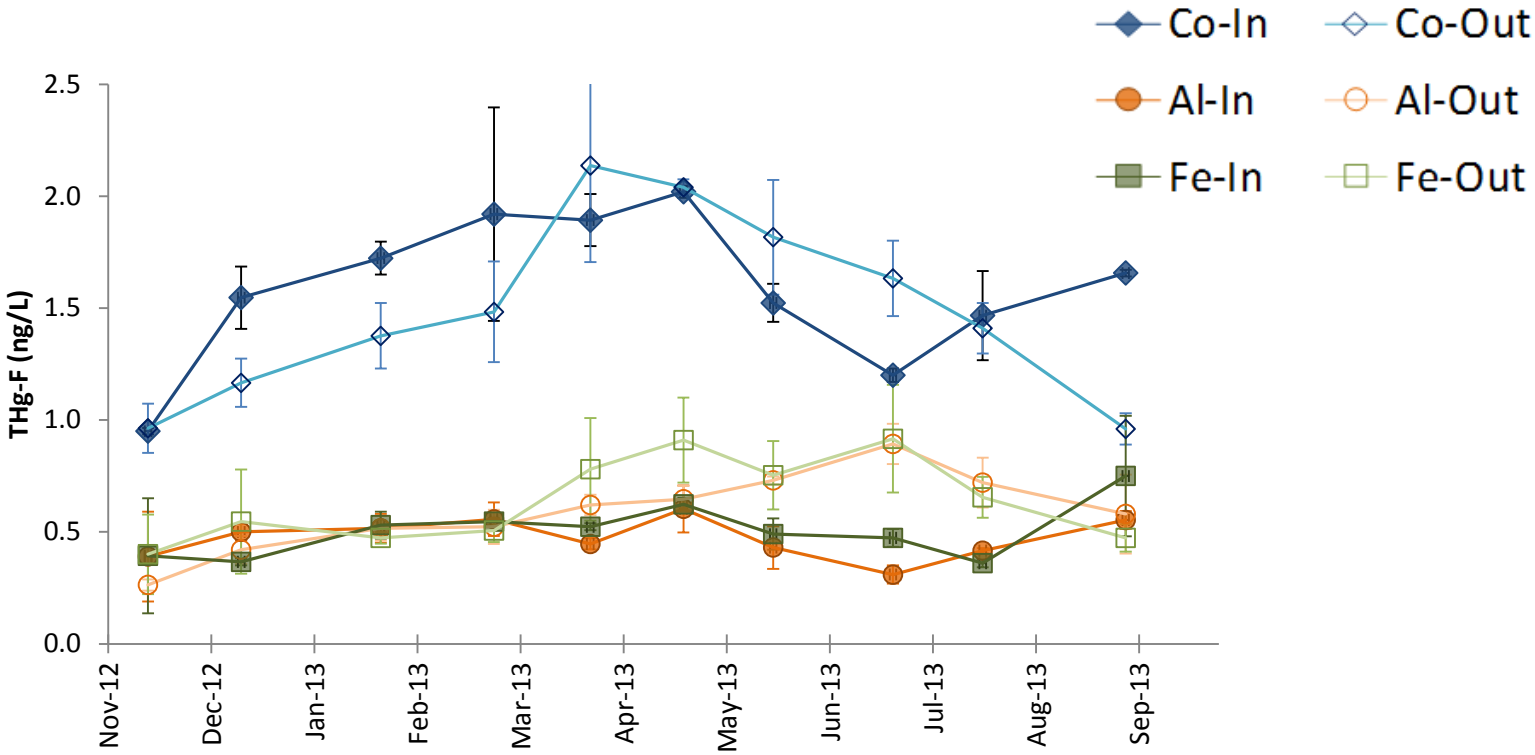
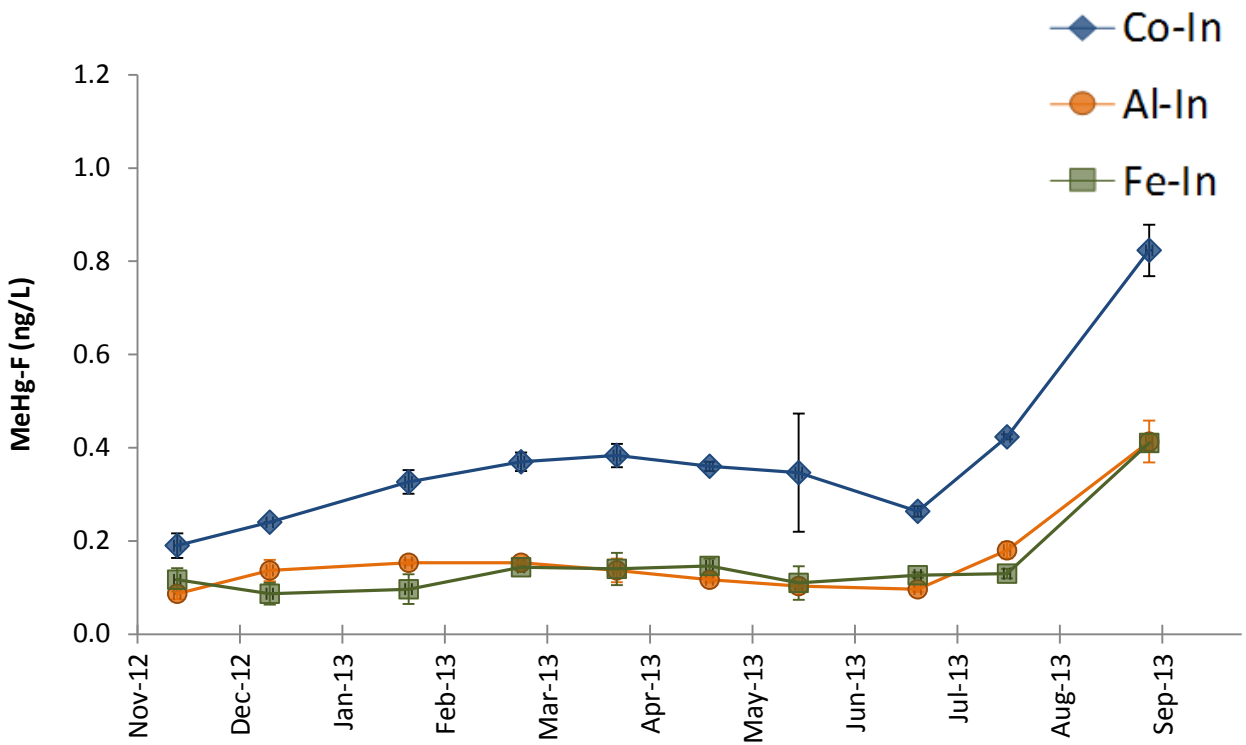
Filtered THg



- effects of wetland passage differed by season (winter vs. summer) and by coagulation treatment (Co vs Al and Fe)

Stumpner et al. 2015
USGS Data Series Report
http://dx.doi.org/10.3133/ds950

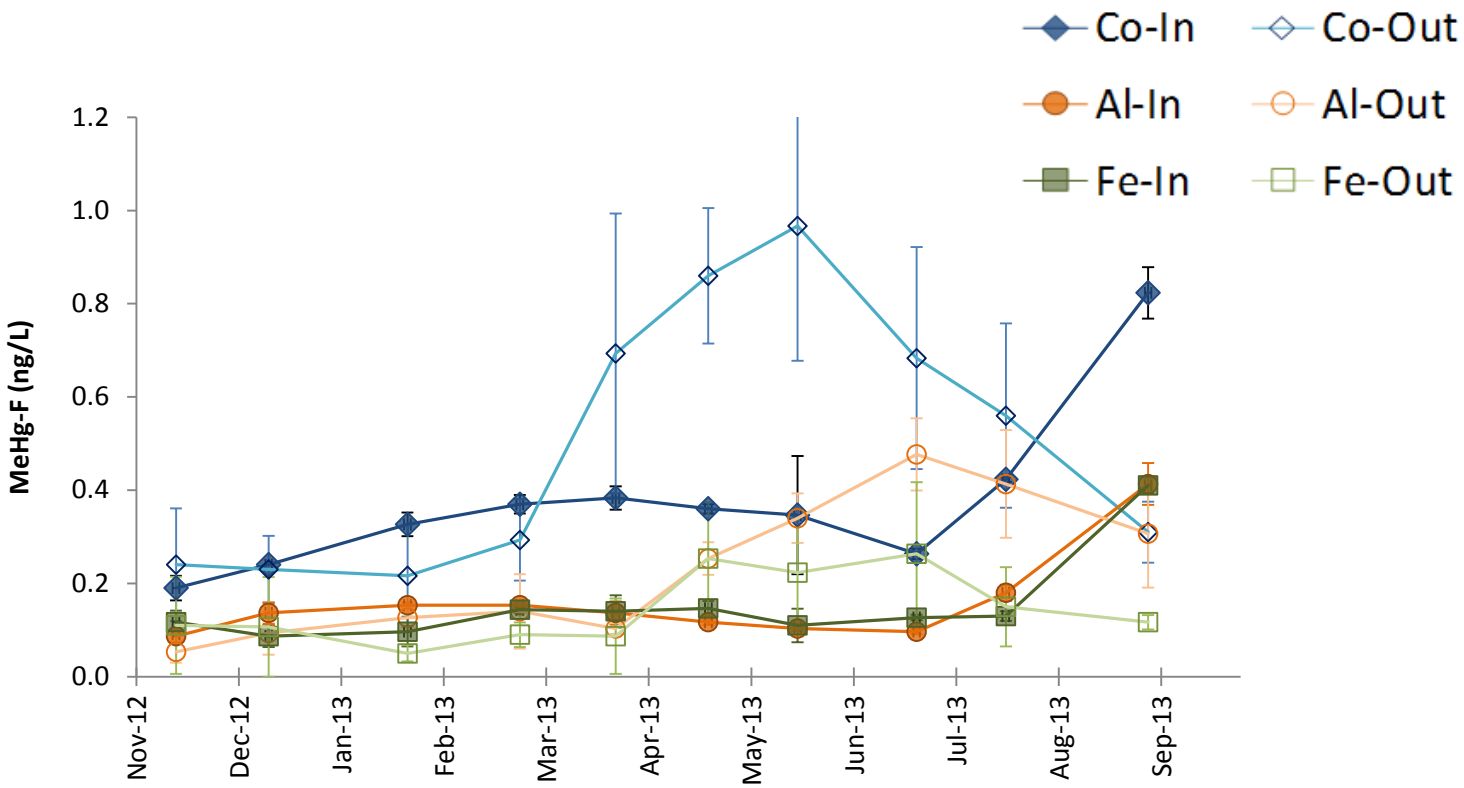
Filtered MeHg



- fMeHg concentrations were reduced by 40-70% due to coagulant addition.

Stumpner et al. 2015
USGS Data Series Report
http://dx.doi.org/10.3133/ds950

Filtered MeHg

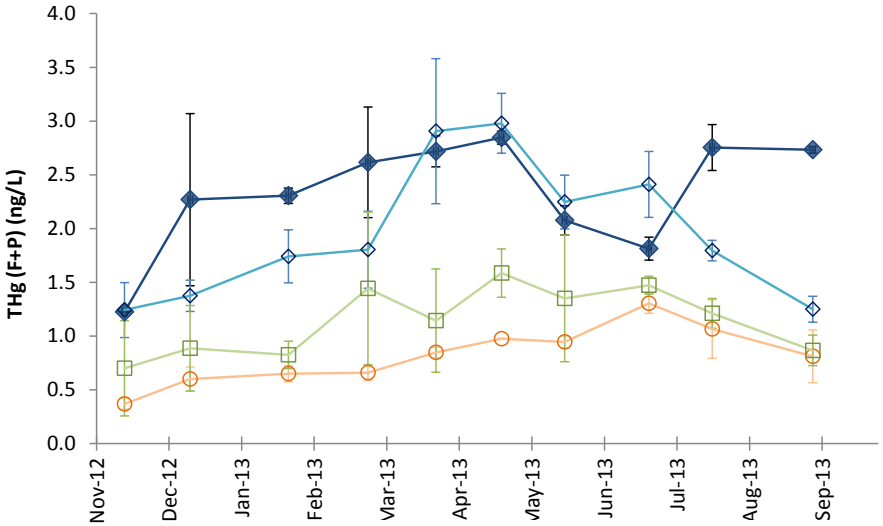


- MeHg was produced within the control wetlands, as well as in the treatment wetlands, but mainly in the warmer months (April-Aug)

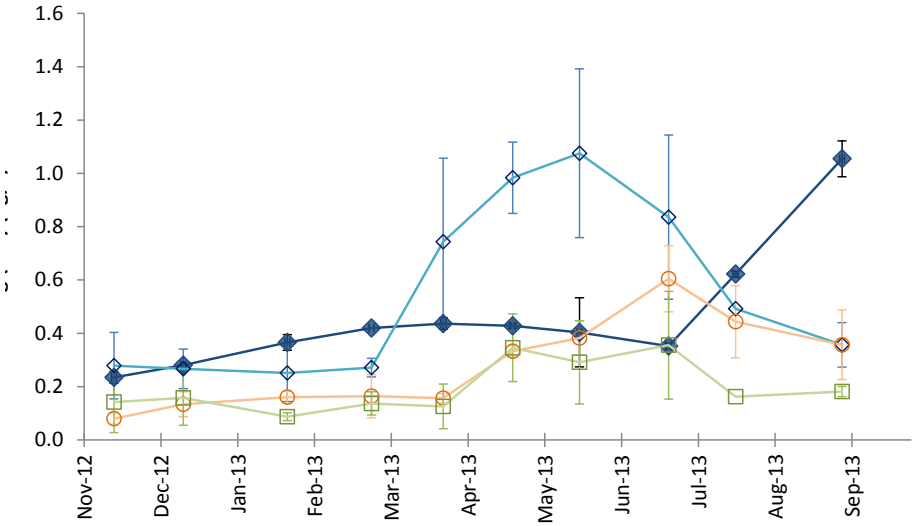
Stumpner et al. 2015
USGS Data Series Report
http://dx.doi.org/10.3133/ds950

Filtered + Particulate

TOTAL THg



TOTAL MeHg



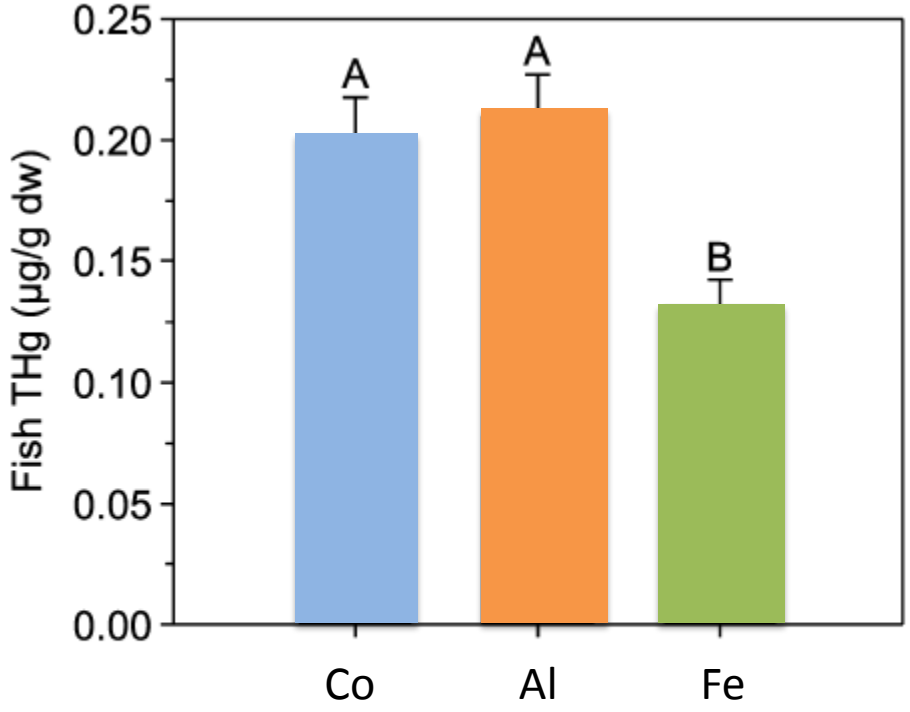
Co-In Co-Out Al-In Al-Out Fe-In Fe-Out

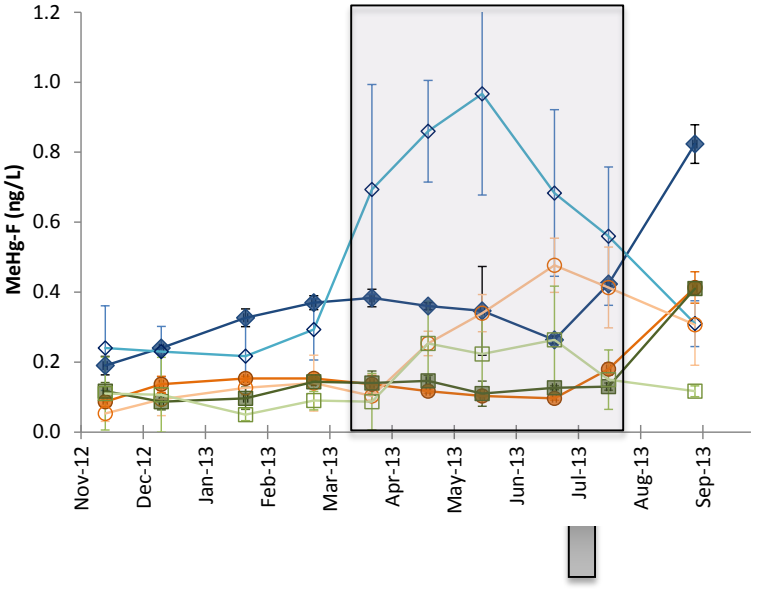
- The coagulation-wetland systems generally lowered both Total and Methyl Mercury concentrations relative to untreated water.
- The untreated wetlands contributed MeHg during the summer months.

Stumpner et al. 2015
USGS Data Series Report
http://dx.doi.org/10.3133/ds950

Bioaccumulation – mosquitofish from Twitchell Island

- **Fish Hg data indicate lower bioaccumulation (35%) of Hg occurred in the Fe treatment vs. the control wetland**

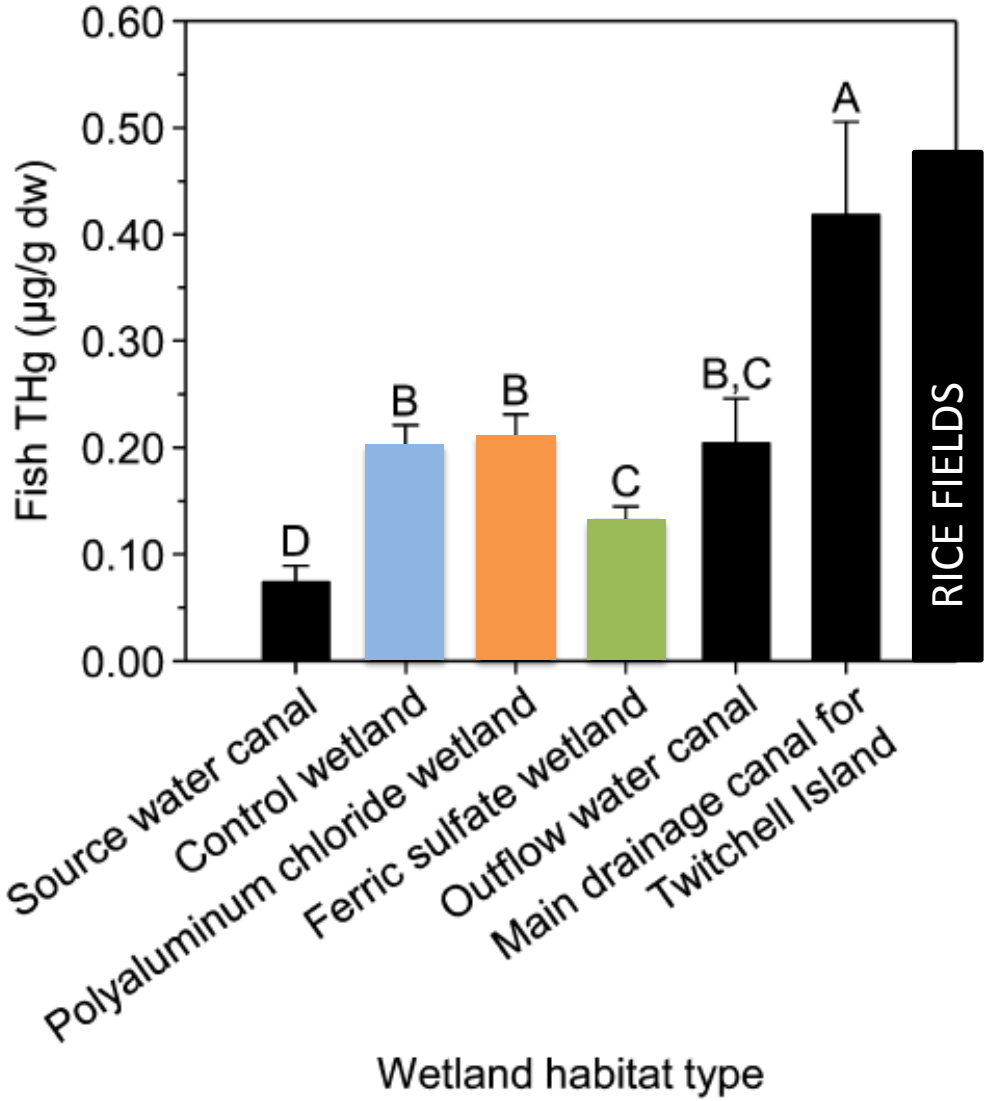




- **Why wasn't there lower bioaccumulation in the Al treatment?**

Ackerman et al. 2015
Environmental Science and Technology
DOI: 10.1021/acs.est.5b00655

Bioaccumulation – mosquitofish from Twitchell Island



Ackerman et al. 2015
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DOI: 10.1021/acs.est.5b00655

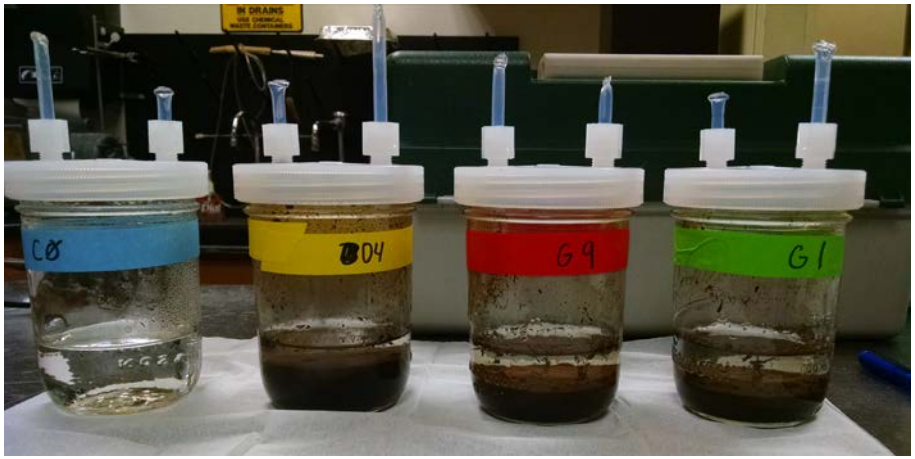
Accreted Material

Control

Iron Sulfate

Poly Aluminum Chloride

Mercury release from accreted material – in progress

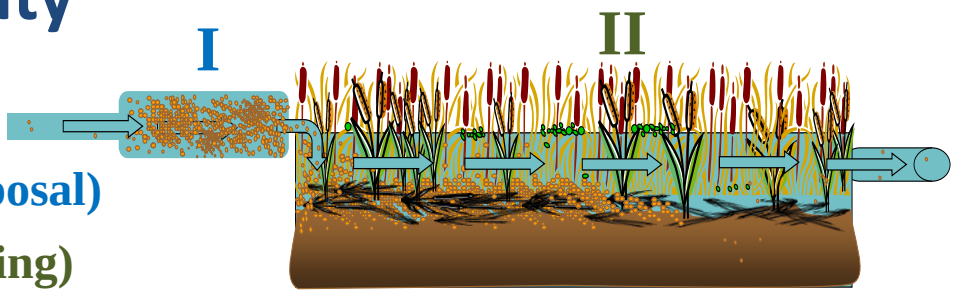


Expose to different REDOX and WET/DRY conditions

Assessment of methyl mercury release from sediment formed in the wetland treatment cells

Jacob Fleck, Lead PI
with Erica Schmidt, Mark Marvin DiPasquale, Dave Krabbenhoft, Tamara Kraus
Funded by EPA

Considerations – Applicability



TWO APPROACHES:

I. Coagulation Alone (floc removal/disposal)

II. Treatment Wetland (on site floc settling)

- **Immediate Concerns**
  - **pH** – can control, avoid overdosing
  - **Al toxicity** – no evidence to date
  - **Stimulate methylation** – no evidence to date
  - **Adding Hg** – as part of coagulants
  - **Cost/Feasibility** –site specific, TBD

Define Objective

Total or MeHg Export

Bioaccumulation in wetlands

- **Longer Term Effects**
  - Multi-year treatment system – floc accumulation
  - Hg sequestration / release from sediments
  - Physical stability of accreted material
  - P limitation?

- **Transferability**

  other sites with different
  - DOC concentration & quality
  - THg:DOC, MeHg:DOC ratios
  - clay particles
  - dredge materials
  - wetland properties
  - tidal systems

USGS science for a changing world

- Mesocosm studies using isotopically labeled Hg – to look at Hg cycling within the treatment wetlands.

Primary Questions:

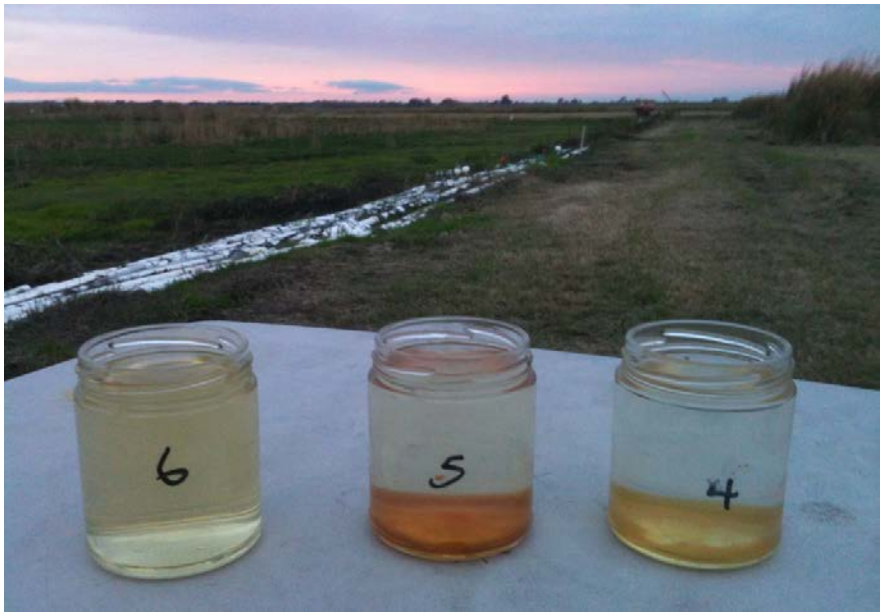
- What are the sources of Hg that primarily contribute to MeHg concentrations?
  - **particulate bound**
  - **dissolved riverine**
  - **atmospheric**

- How do the coagulation treatments impact Hg cycling?

See for example, Jonsson et al. 2014

Questions?

Tamara Kraus
tkraus@usgs.gov



Co Fe PAC