Photo-degradation of Monomethyl Mercury in the Sacramento-San Joaquin Delta Estuary and Agricultural and Natural Wetlands in the Yolo Bypass

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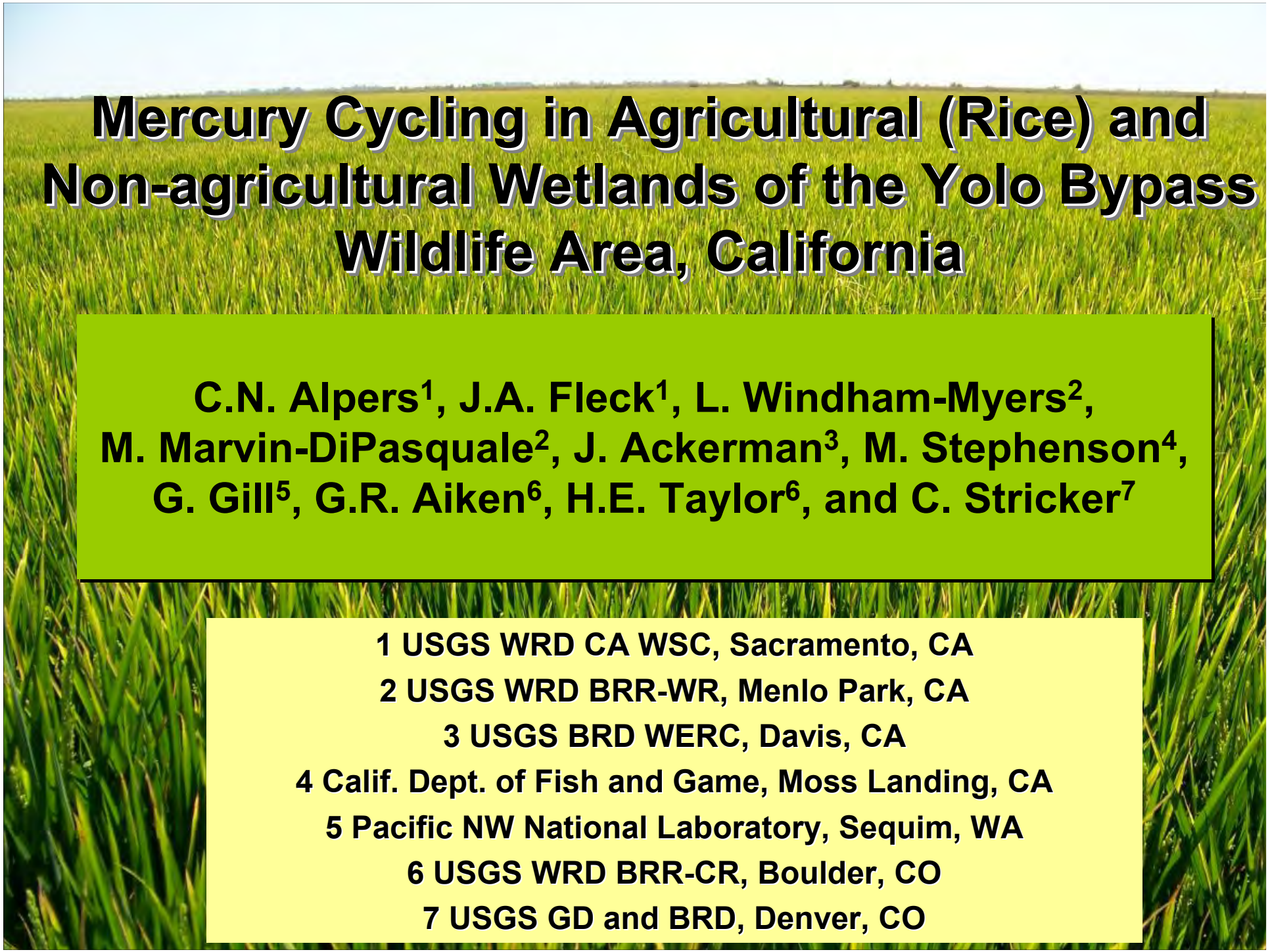
Major Question

How important is photo-degradation of monomethyl mercury in the biogeochemical cycling and transport of mercury in aquatic ecosystems?



Mercury Cycling in Agricultural (Rice) and Non-agricultural Wetlands of the Yolo Bypass Wildlife Area, California

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6 USGS WRD BRR-CR, Boulder, CO

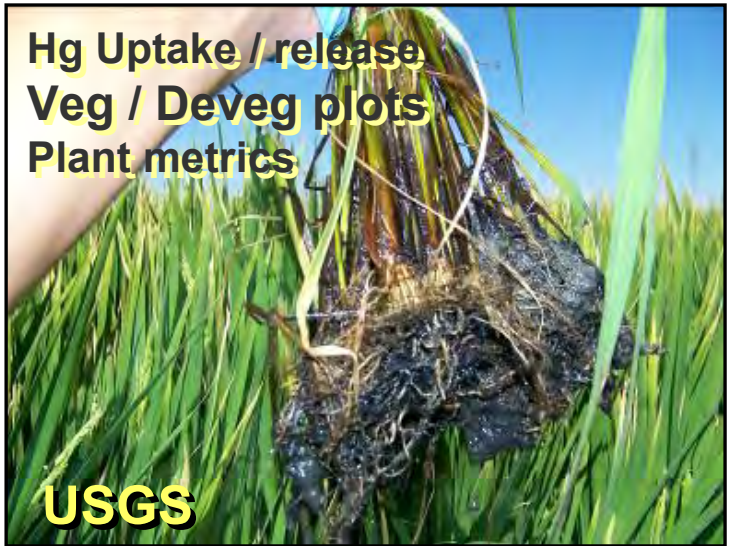
7 USGS GD and BRD, Denver, CO

Study Components

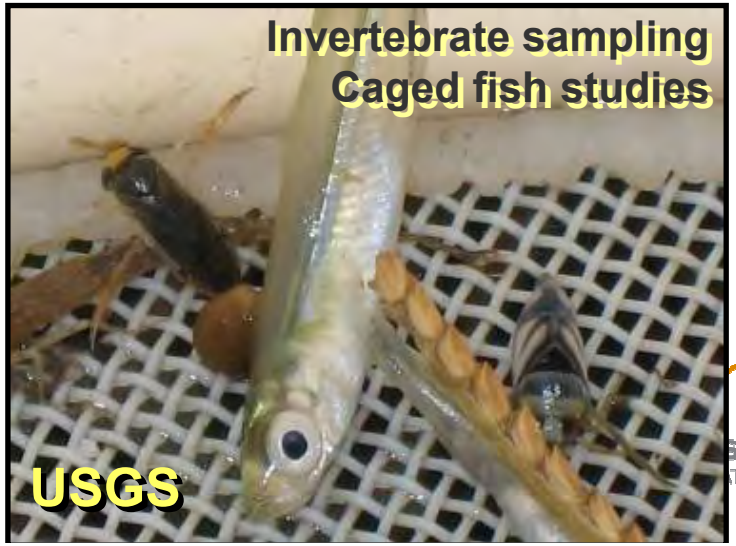
Sediment

Water Column

Plant-Hg Interactions



Bioaccumulation



Overall Project Goals

- Examine MMHg Cycling in Different Agricultural Rice Field Types
- Examine Role of Management Practices on Hg/MMHg Cycling
- Compare Hg Bioaccumulation among wetland habitats

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Types of Agricultural Fields

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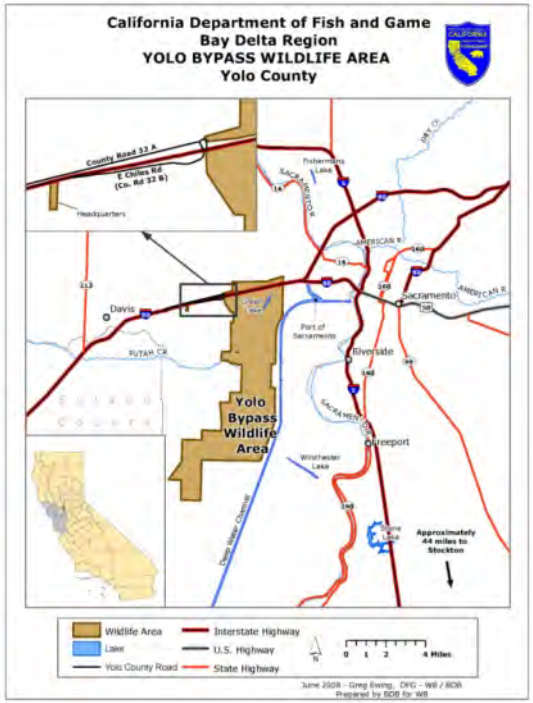
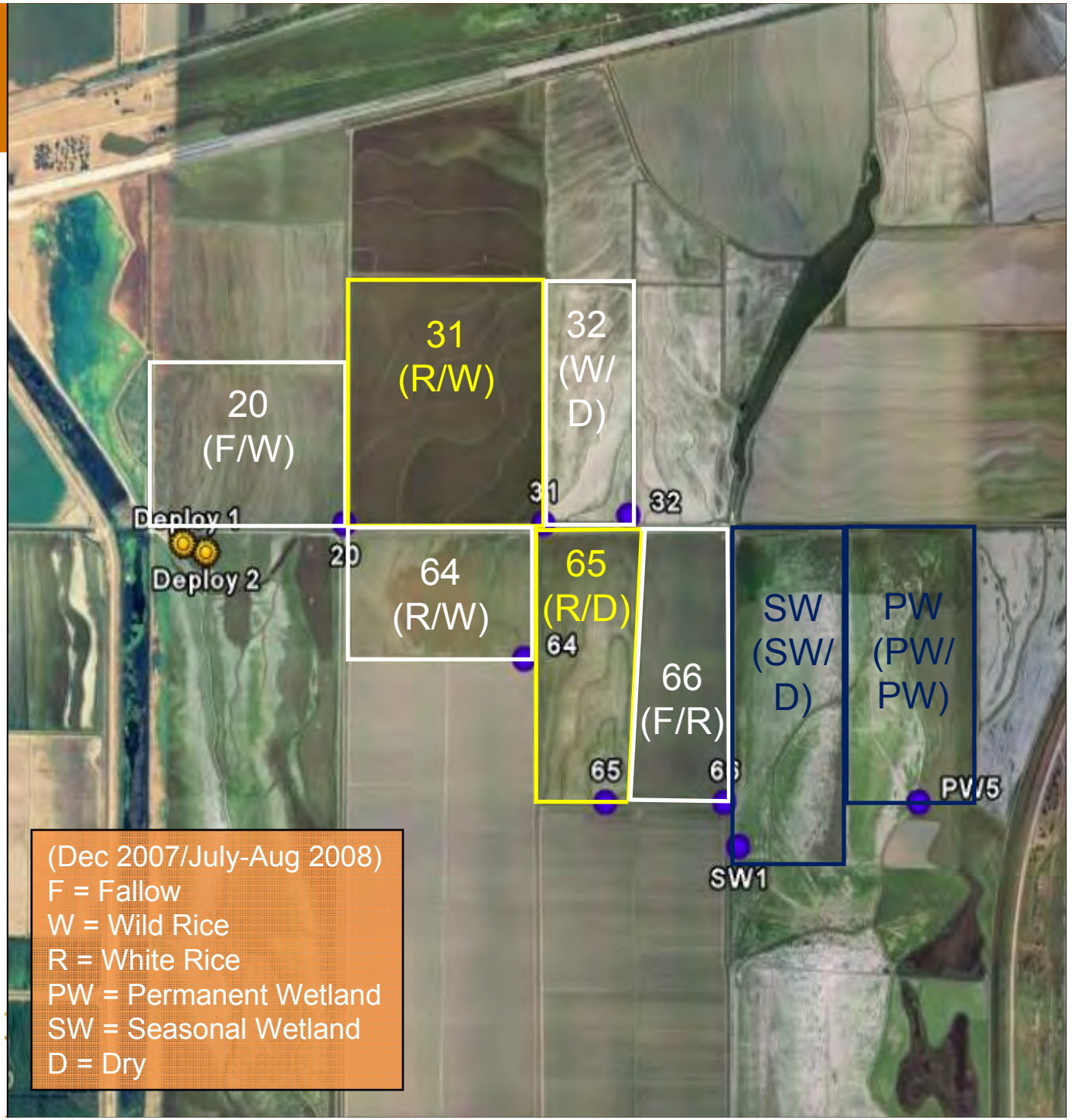
Sampling Sites

- Two Sampling Periods
  - December 2007 – 8 sites
  - July-August 2008 – 5 sites (3 dry sites)
- Samples Collected At Outlets of Field (●)
- Samples Incubated in Open Water Site (○)





Bottle Incubation Experiments

- 10 L of filtered (0.45µm) surface water
- Spiked wintertime samples with MMHg (~ 0.4 ng/L)
- Sample homogenized and aliquoted into clear and opaque FEP Teflon® bottles
- Bottles placed in 13 mm Polypropylene mesh bags
- Bottles incubated horizontally on the surface
- Collected and preserved ~5 time points over 50-70 hour deployments.
- Preserved with acid to stop experiment

A Typical Photo-Degradtion Experiment

- 4-5 time points
- Opaque Bottle - Control
- **Not a Typical Kinetic Experiment**
- Relate decrease in MMHg concentration to total light exposure (rather than time)
  - mol of electrons striking water surface over duration of experiment (mol m^{-2})
  - PAR Measurements
- Slope of Line = photo-degradation rate
- Correct for drop in light intensity through bottle wall

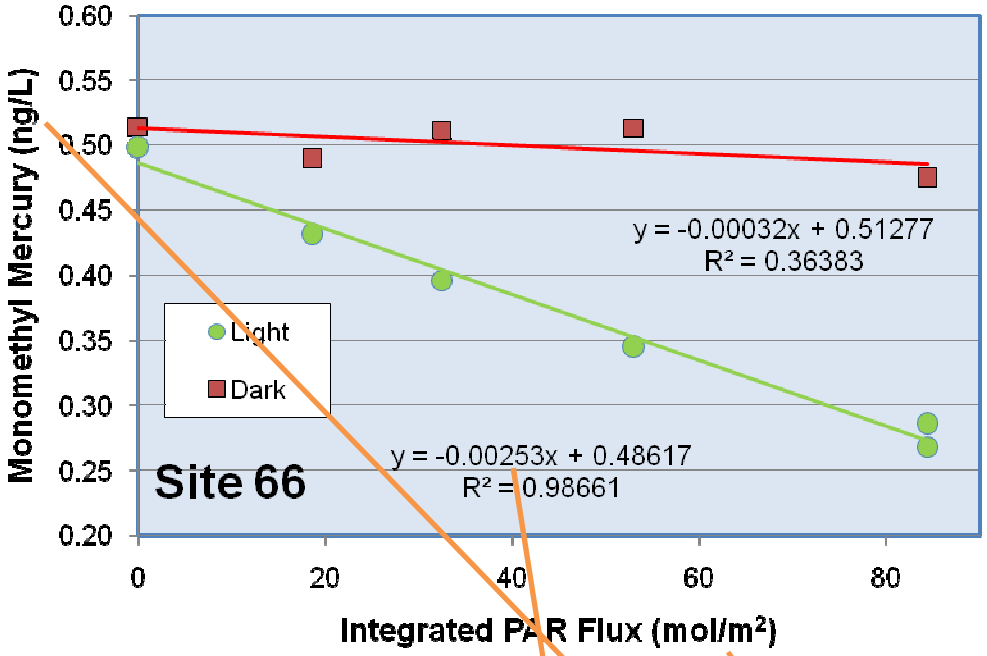
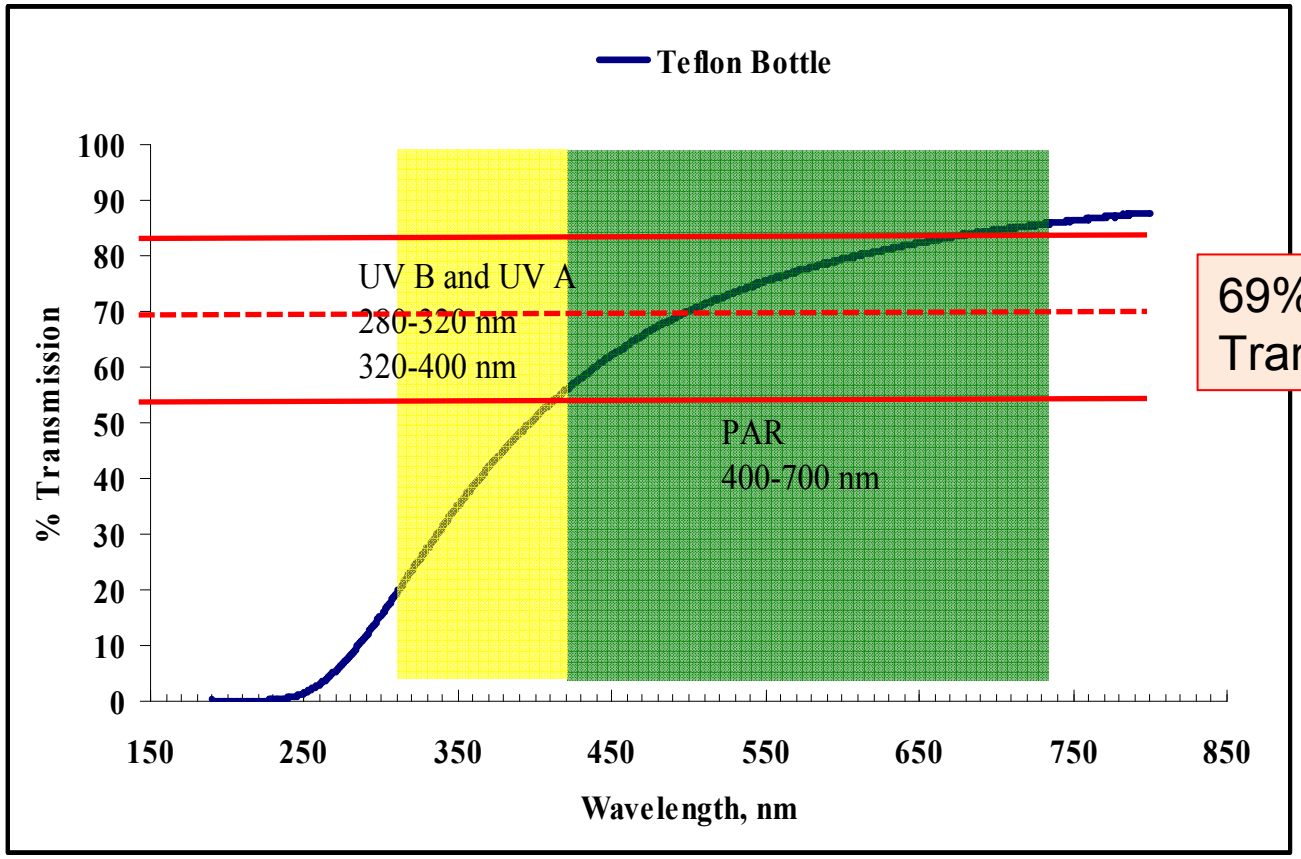


Photo-degradtion Rate = -00253 ng L^{-1} m^2 mol^{-1}

Drop in MMHg Conc.

mol of light striking 1 m^2 of water surface

Light Transmission Through a Teflon bottle



69% Transmission

From: Byington (2007). Photo-degradation of methylmercury in the Sacramento-San Joaquin Delta Estuary. Master Thesis, San Jose State University.

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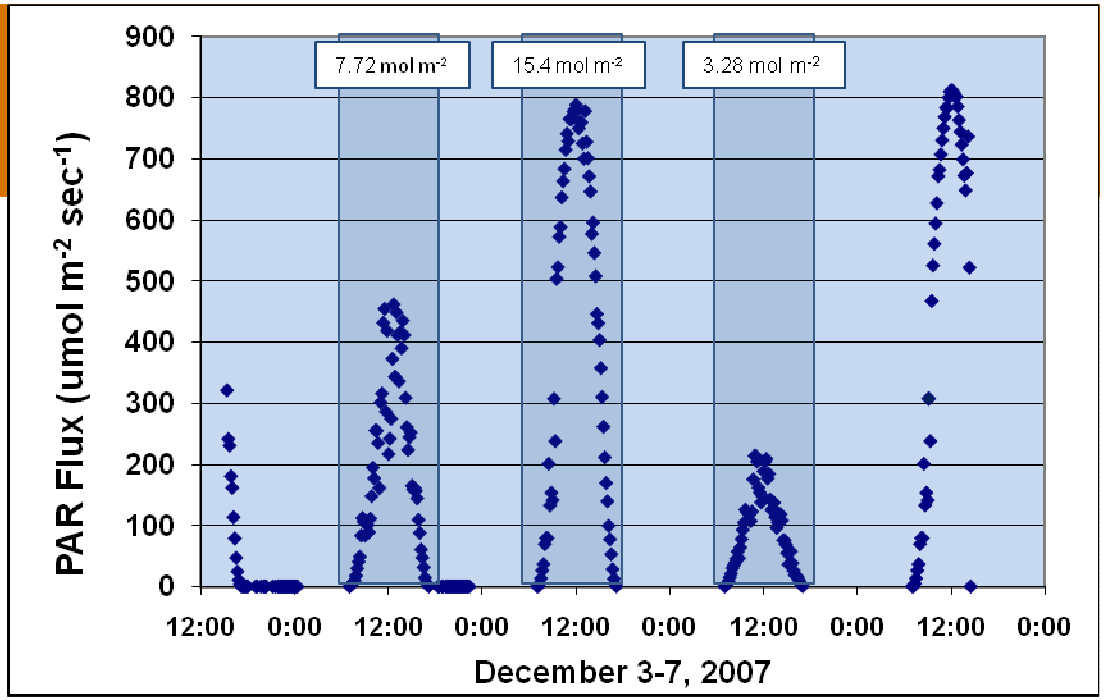
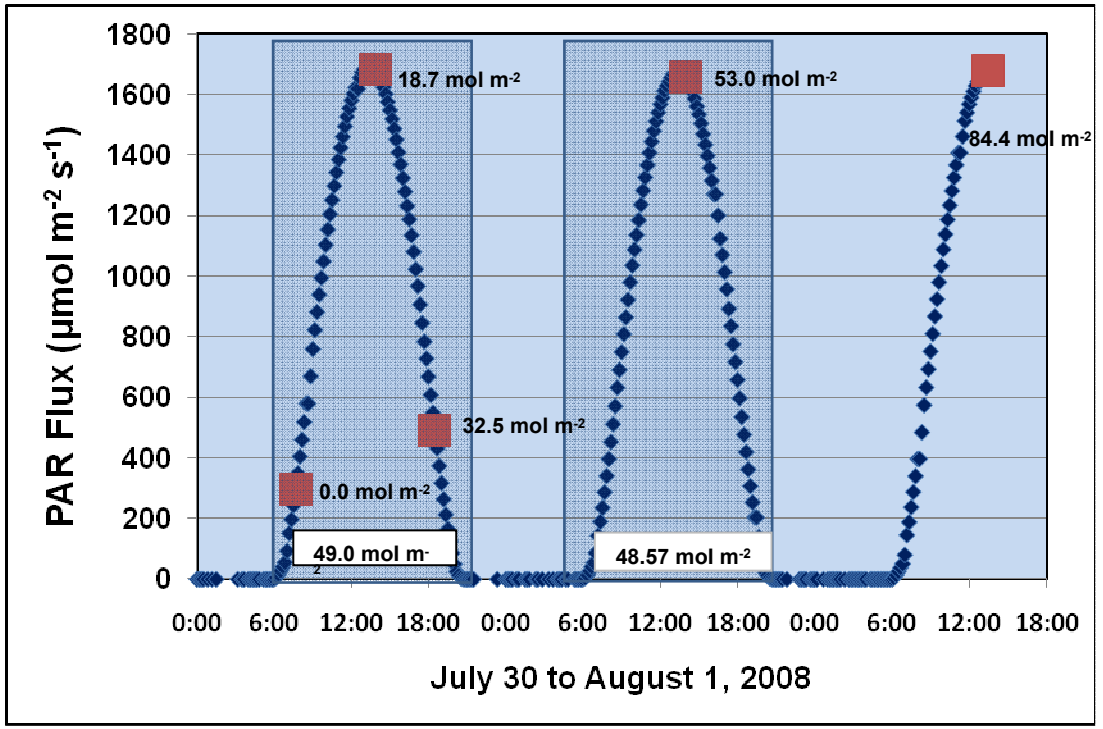
Light Intensity

- Photosynthetic Available Radiation (PAR)
- Ultraviolet Radiation (UV-a plus UV-b)
- 10 minute intervals (µmol/m^2/s)
- Integrated PAR (mol/m^2)
- Discrete Profiles (attenuation with depth)





Modeling MMHg Photo-degradation

- Mass Balance Assessment Must Account for:
  - Temporal Changes in Solar Irradiation (Daily and Seasonally)
  - MMHg Concentration Dependence on Degradation Rate
  - Light Attenuation with Depth in Water Column (TSS dependent)
  - Shading by Emergent Grass
- Output
  - Mass of MMHg lost in a square meter of the water column per day (ng MMHg/m^2/day)
  - Percent loss per day

Concentration Dependance

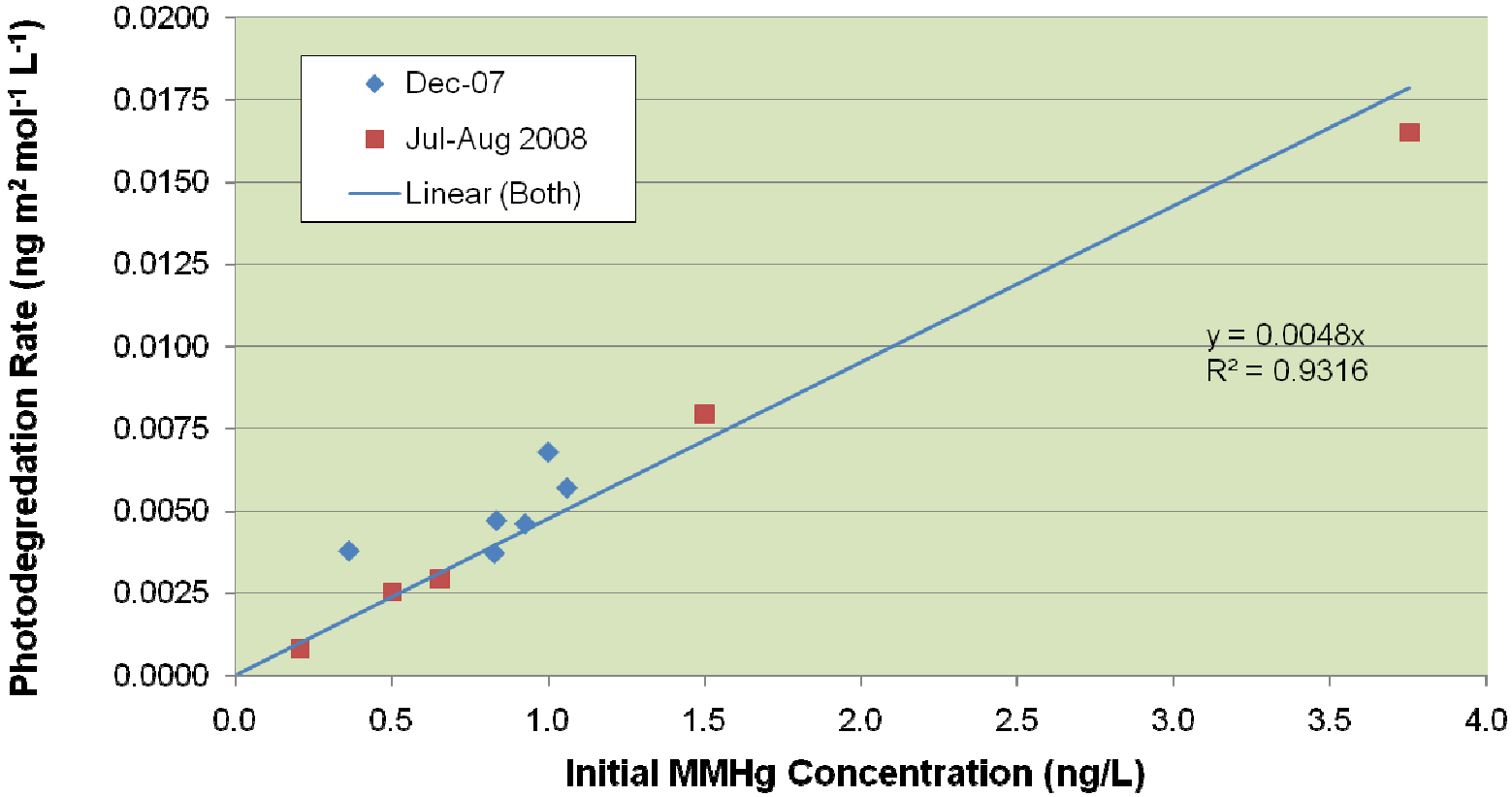


Photo-degradation Rate (ng m^2 L^{-1} mol^{-1}) = 0.0048 $[MMHg, ng\ L^{-1}]_{dissolved}$

Rate Constant = 0.0048 m^2 mol^{-1}

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PAR Depth Dependence

PAR at depth (z)

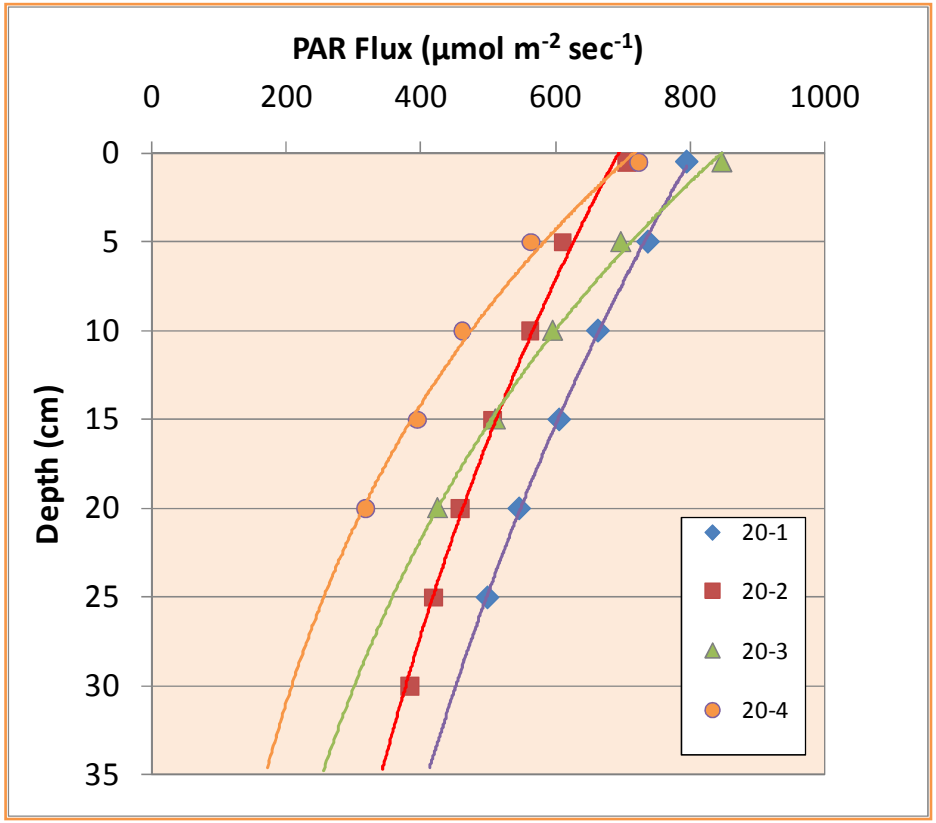
$$PAR_{(z)} = PAR_{(0)}\, e^{\mu(z)}$$

Where:

μ = extinction coefficient or attenuation coefficient (units = cm^{-1})

(z) = depth in centimeters

- Highly Variable Extinction Coefficient
- Range = -0.019 to -0.041 cm^{-1}
- Average = -0.029 ± 0.011 cm^{-1}
- 38-82% of surface light at 20 cm
- Integrate over water depth



PAR Measurements From Four Open Water Locations in Domestic Rice Field 20 (June 26, 2008)

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Shading By Emergent Grass

Mass Loss of MMHg as Function of Light Intensity and MMHg Concentration

Average Water Column Loss ($ng/m^2/day$)

MMHg Conc. (ng/L)	Daily Integrated PAR (mol/m^2)							
	3	5	10	15	20	30	40	50
0.5	0.048	0.080	0.16	0.24	0.32	0.48	0.64	0.80
1.0	0.096	0.16	0.32	0.48	0.64	0.96	1.3	1.6
1.5	0.14	0.24	0.48	0.72	0.96	1.4	1.9	2.4
2.0	0.19	0.32	0.64	0.96	1.3	1.9	2.6	3.2
2.5	0.24	0.40	0.80	1.2	1.6	2.4	3.2	4.0
3.0	0.29	0.48	0.96	1.4	1.9	2.9	3.8	4.8
4.0	0.39	0.64	1.3	1.9	2.6	3.8	5.1	6.4
5.0	0.48	0.80	1.6	2.4	3.2	4.8	6.4	8.0
6.0	0.58	0.96	1.9	2.9	3.8	5.8	7.7	9.6
8.0	0.77	1.3	2.6	3.8	5.1	7.7	10	13
10.0	0.96	1.6	3.2	4.8	6.4	9.6	13	16

Extinction Coefficient = -0.029

Water Depth = 30 cm

Open Water Winter

Open Water Summer

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Percent Loss of MMHg as a Function of Water Column Light Attenuation And Daily Light Intensity

Average Water Column Loss (%/day)

Extinction Coefficient	Daily Integrated PAR (mol/m^2)							
	3	5	10	15	20	30	40	50
-0.01	1.2	2.1	4.2	6.2	8.29	12	17	21
-0.02	1.1	1.8	3.6	5.4	7.22	11	14	18
-0.03	0.95	1.6	3.2	4.8	6.33	9.5	13	16
-0.04	0.84	1.4	2.8	4.2	5.59	8.4	11	14
-0.05	0.75	1.2	2.5	3.7	4.97	7.5	9.9	12
-0.06	0.67	1.1	2.2	3.3	4.45	6.7	8.9	11
-0.07	0.60	1.0	2.0	3.0	4.01	6.0	8.0	10
-0.08	0.55	0.91	1.8	2.7	3.64	5.5	7.3	9.1
-0.09	0.50	0.83	1.7	2.5	3.32	5.0	6.6	8.3
-0.10	0.46	0.76	1.5	2.3	3.04	4.6	6.1	7.6

Water Depth = 30 cm

Open Water Winter

Open Water Summer

Typical Hydraulic Residence Times = 12-25 days
Bachand et al. (2010)

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Mass Loading Comparison

	Mass Loading of Unfiltered MMHg ($ng/m^2/day$)		
Field	**In**	**Out**	**Difference**
F20	0	2.1	-2.1
F66	9.6	3.5	6.1
R31	6.1	4.9	1.2
R64	9.3	44	-34.7
W32	0.5	0	0.5
W65	3.9	3.8	0.2
Median	5.0	3.6	0.3
Avg.	4.9	9.7	-4.8

Typical Summer Photo-demethylation Rate = 1-4 $ng/m^2/day$

Mass Loading Taken From: Bachand et al. (2009)

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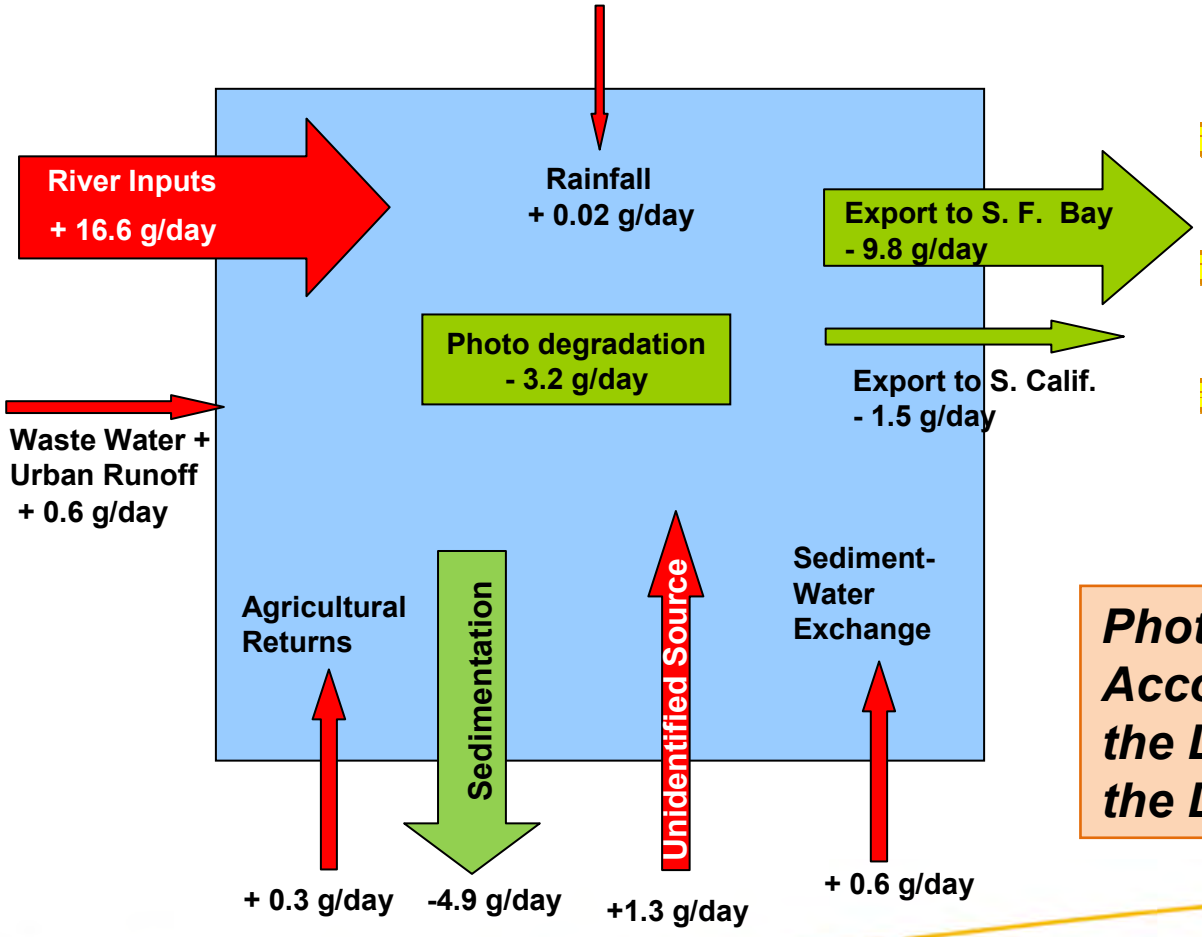
MMHg Mass Balance in the Delta



Major Assumptions

- Average River Flow Conditions
- Total Delta Surface area is 1906 km^2
- Open Water Surface Area is 238 km^2

Photodegradation Accounts for 17% of the Loss of MMHg in the Delta

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Conclusions

- Photo-degradation is abiotic and mediated by sunlight.
- Mass balance assessments suggest that photo-degradation is an import process in the cycling of mercury in aquatic ecosystems
- Knowledge of environmental factors that influence photo-degradation will clearly be useful in developing management strategies to mitigate MMHg problems and for controlling high MMHg inputs into the Delta
  - Water clarity (TSS)
  - Emergent Aquatic Vegetation (shading)
  - Water Residence Time
  - Water Depth

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