Unexpected Relationships between Methylmercury Enrichment in Fresh Waterbodies and Food-Web Uptake

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Spokane WA

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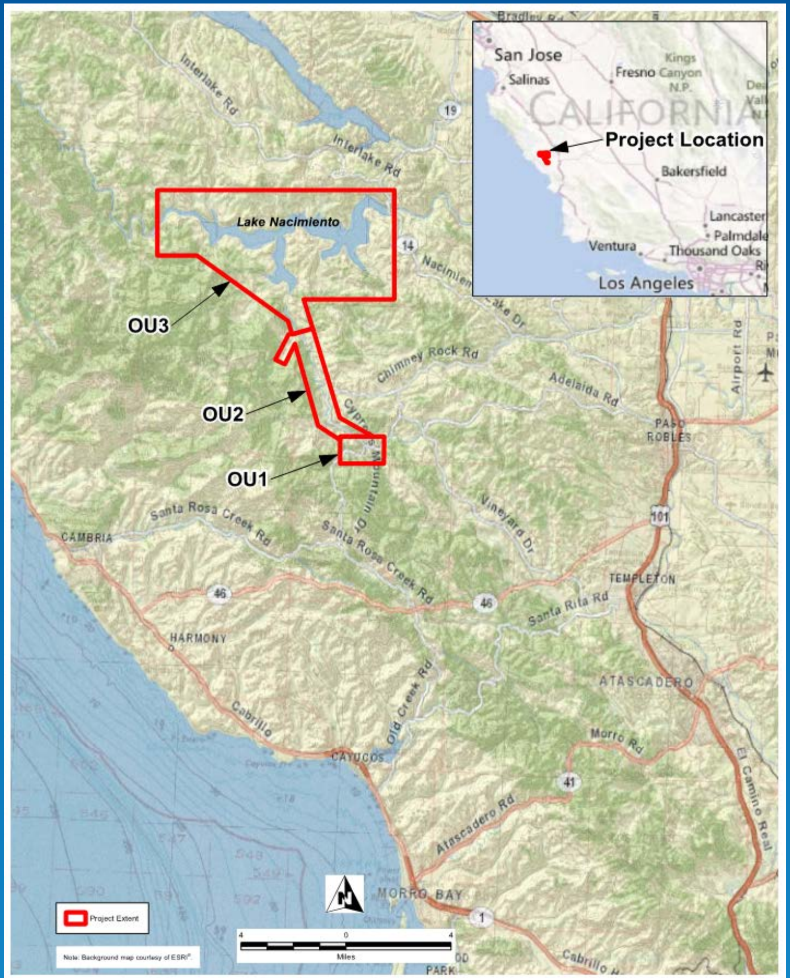
Overview

- Background: Mercury in the Environment
  - Mercury Advisories
  - Food-Web Interactions
  - Trace Mercury Assessments
- Site Introduction
- Small Reservoir Mercury Methylation Assessment
- Summary
- Implications for Future Mercury Assessments
- Potential Remedial Options



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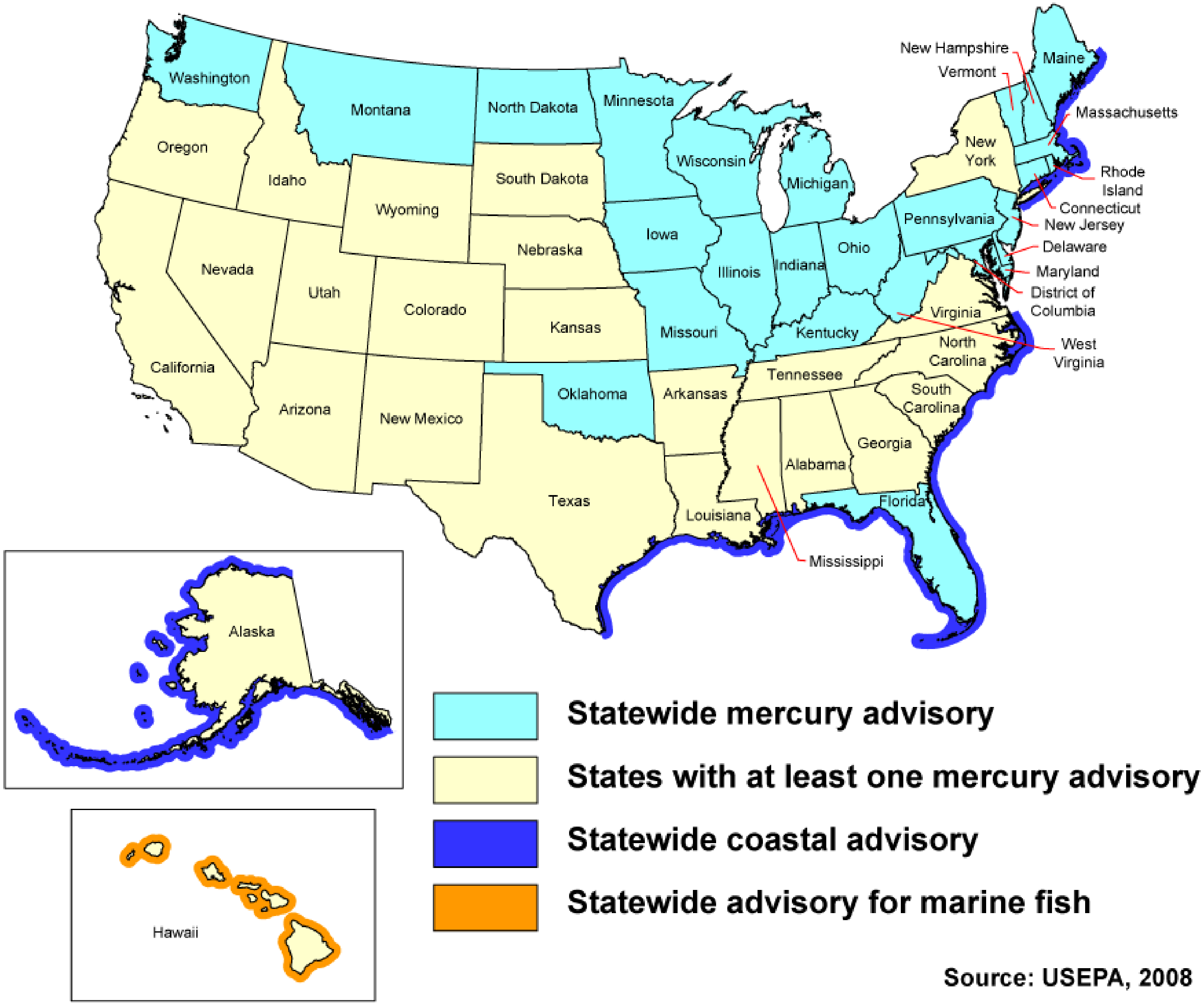
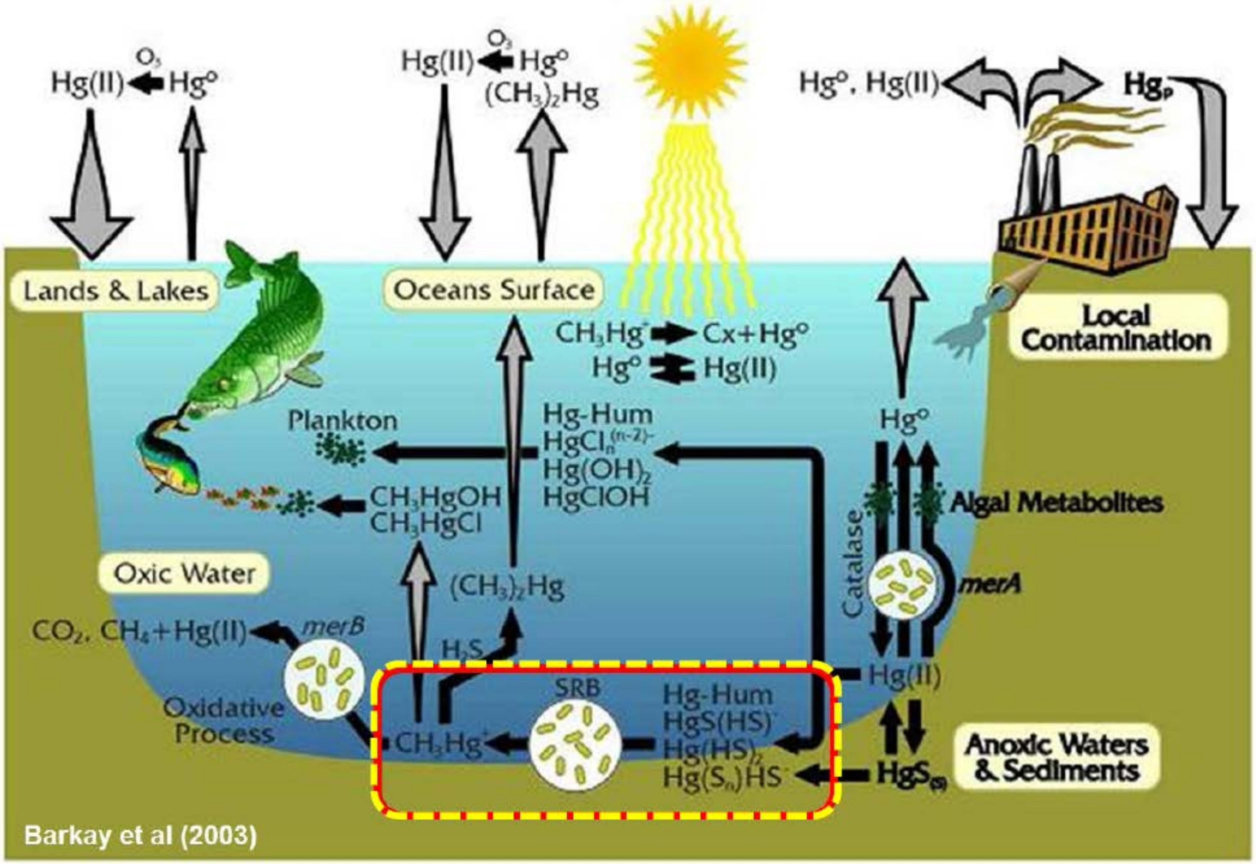
Background: Mercury Advisories in US



Source: USEPA, 2008

Mercury Transformations in the Environment

Hg Biogeochemical Cycle



Key Methylation Ingredients

- Anoxia
- Organic Carbon
- Sulfate/Ferric Iron
- And last, but not least, Labile Inorganic Mercury

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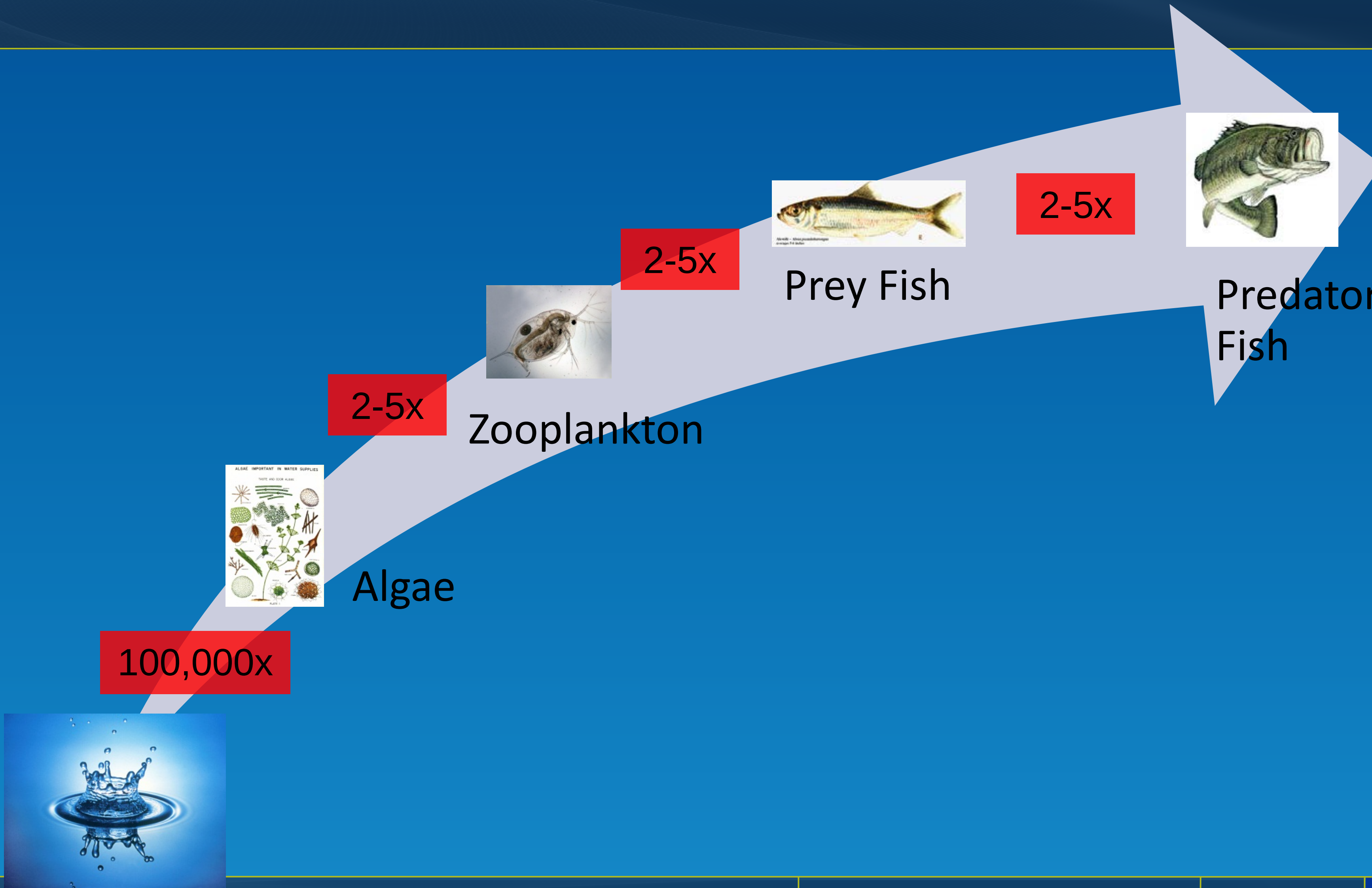
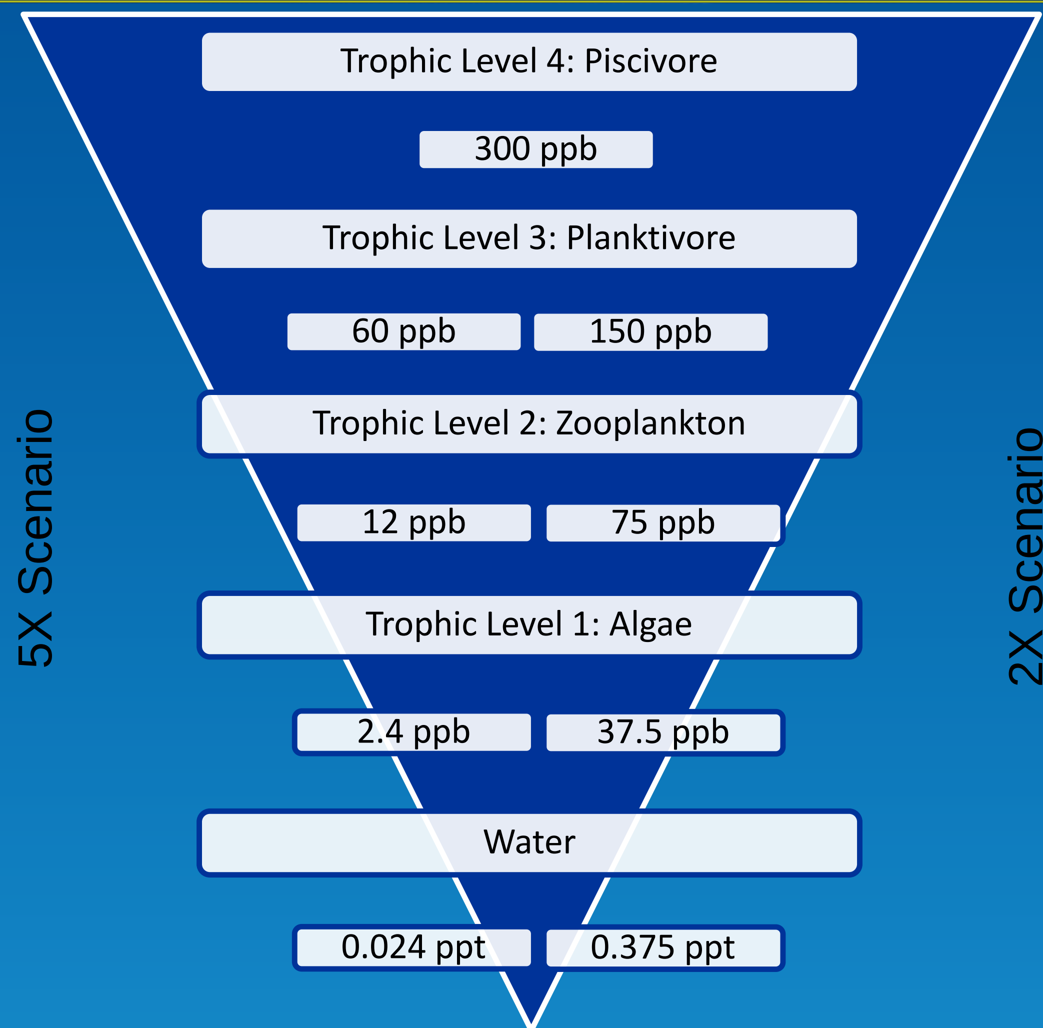
Food-Web Biomagnification



Trace Mercury is Important – And the Numbers are Real



Method 1630 Trace Methylmercury & 1631 Trace Total Mercury

Battelle Marine Science Laboratory

Detection Limits (Brooks Rand Instruments)

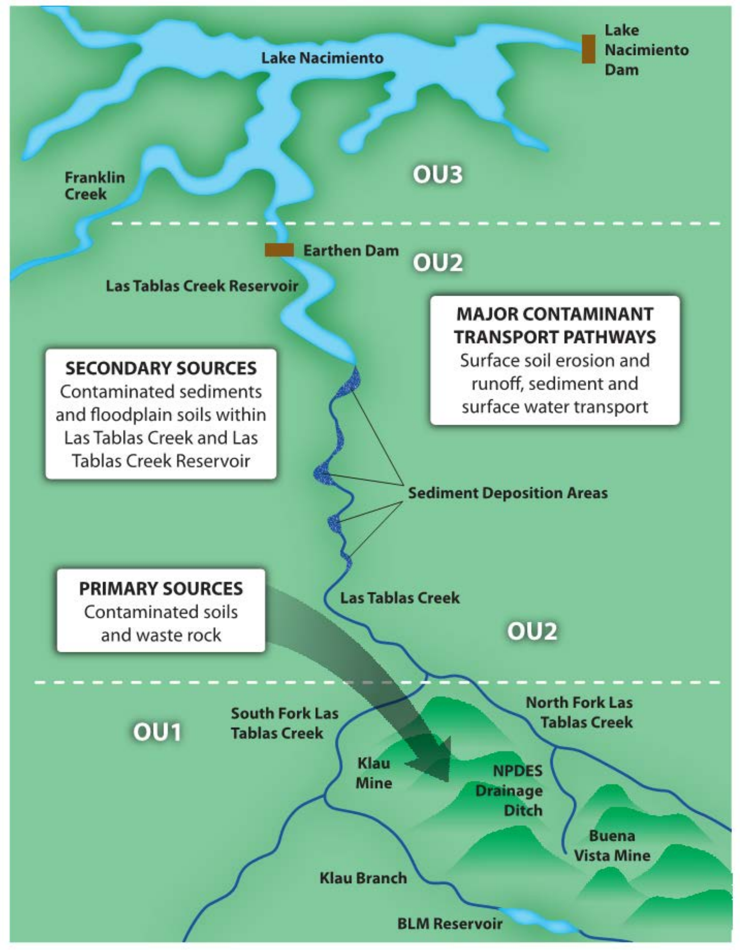
- THg 1631: <0.03 ng/L
- MeHg 1630: <0.002 ng/L

Trace Mercury Sampling

- EPA Method 1669
- Clean Hands/Dirty Hands
- Trace Clean Bottles and Preservative

Site Introduction - Conceptual Site Model

- Mercury mining and processing activities at the Klau and Buena Vista Mines Superfund site has resulted in mercury contamination throughout the watershed
- Contaminant transport is dominated by particulate transport during winter precipitation events
- Mercury is methylated in Las Tablas Creek Ranch Reservoir (LTCRR) sediments and enters food-web
- Loading assessment revealed LTCRR a net source to Lake Nacimiento



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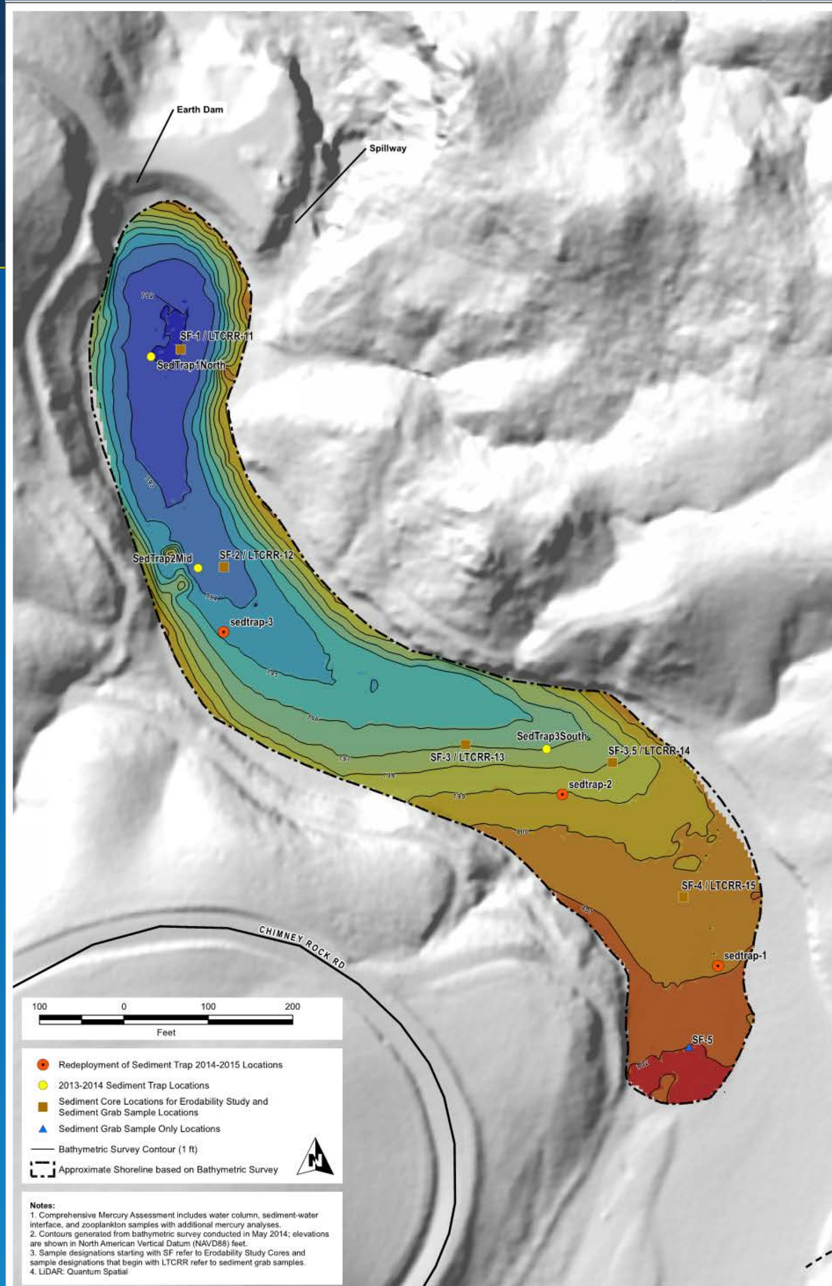
Las Tablas Creek Ranch Reservoir

- Small Reservoir
  - ~52 acre feet
- Fed by Intermittent Stream
  - Storm Flows >10X Reservoir Volume Observed
- Shallow and Warm
  - 8 to 13 ft @ 50 to 70 °F
- Net Mercury Source
  - Annual THg Loading Increased 3x to 4x
  - Fish Body Burden: **2.3 PPM**



Methylation and Food-Web Connectivity Evaluation

Sediment Oxygen Demand

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Sediment MeHg Production

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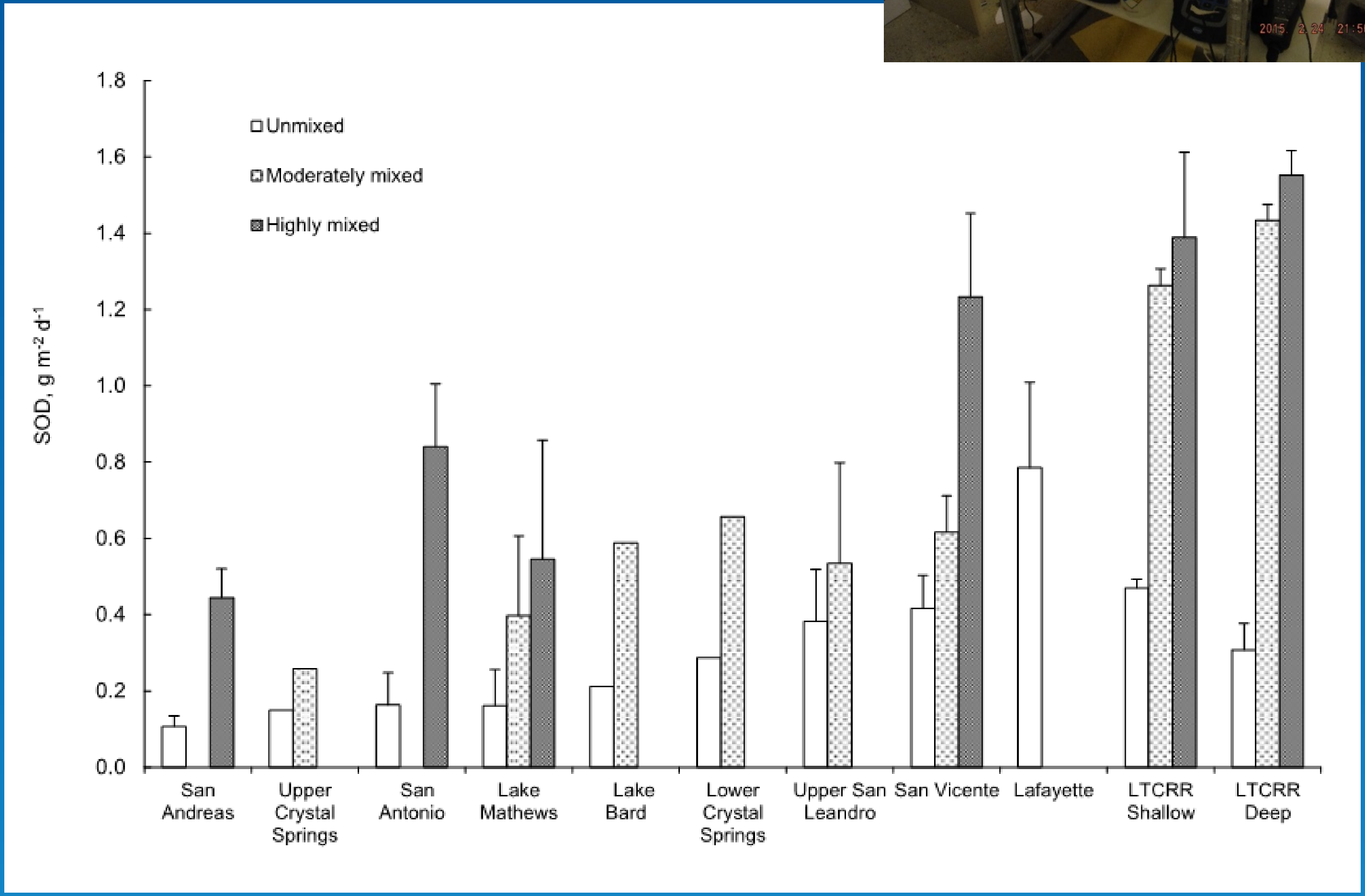
Mercury in Water and Large Body Zooplankton

Las Tablas Creek Ranch Reservoir Sediment Oxygen Demand



Beutel, 2003

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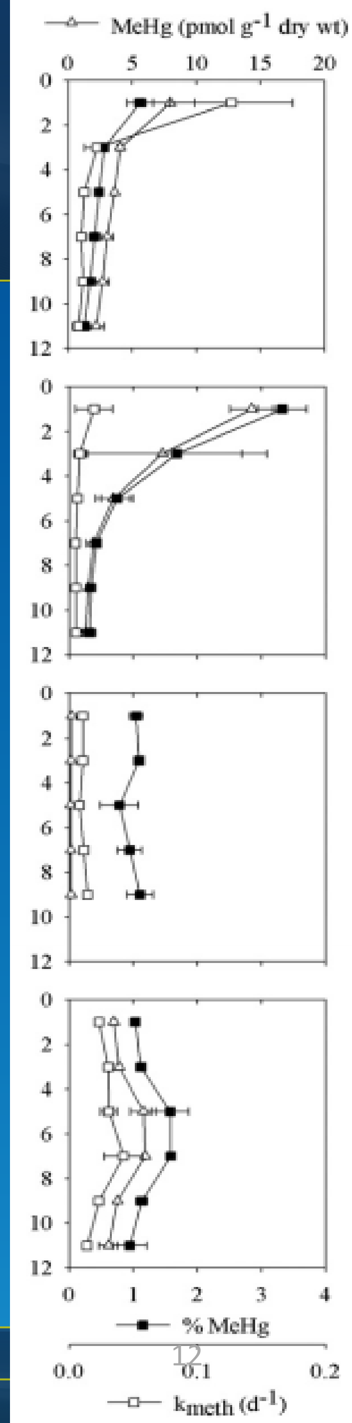
Methylmercury Production

- Surrogate for MeHg production
  Windham-Myers et al., 2009
  - %MeHg of THg in sediment
- Sites with highest *surface* methylation also have highest fish concentrations
  Benoit et al., 2003
- Growing database in literature to use for comparison



Hollweg, et al., 2009

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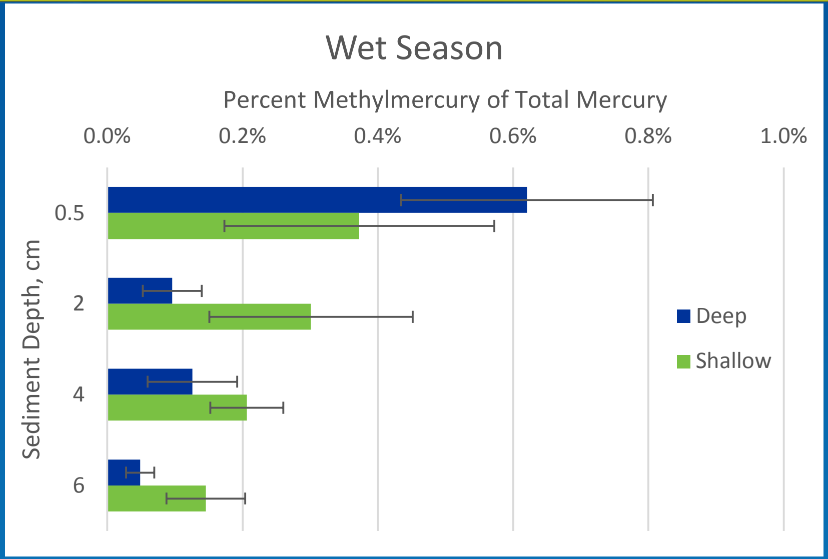
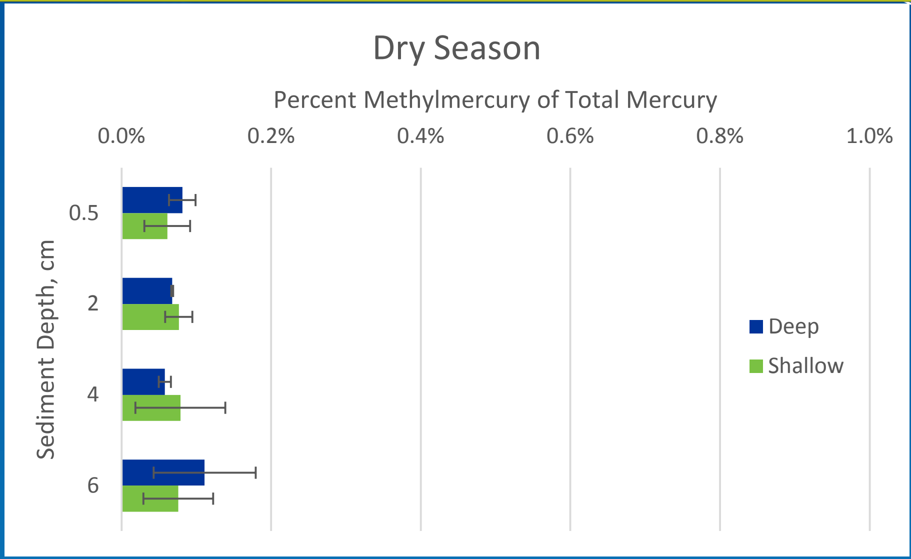
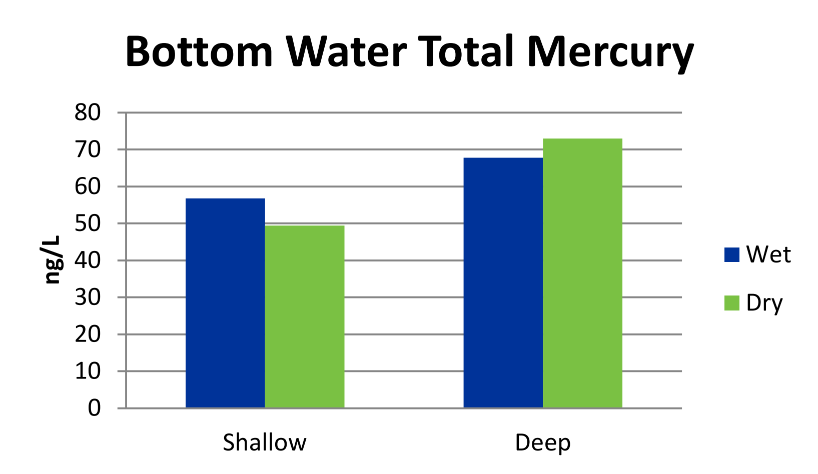
Sediment Methylation and Bottom Water Enrichment

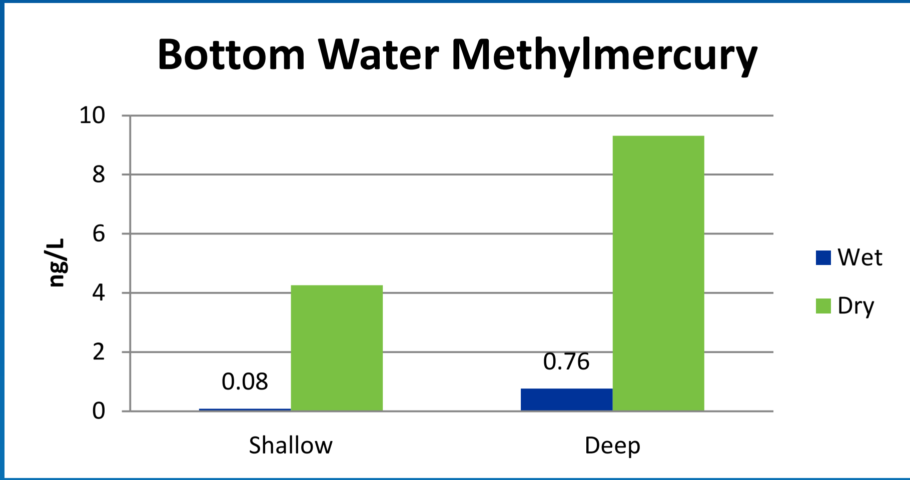




- Highest Surface Methylation in Deep Site in Wet Season
- Highest Sub-Surface Methylation in Shallow Site in Wet Season
- Methylmercury Essentially Shut Down in Sediments During Dry Season

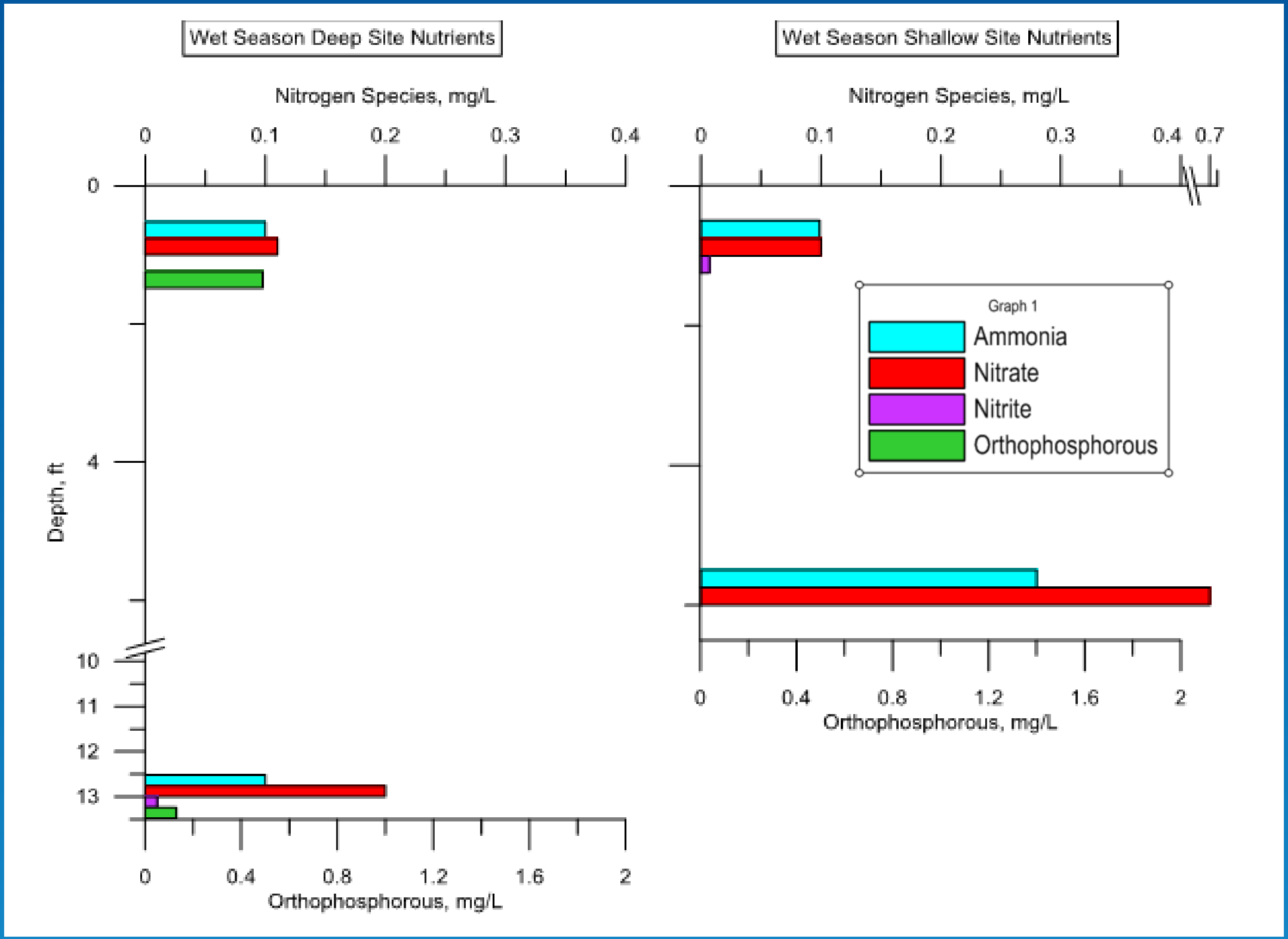
Bottom Water Enrichment



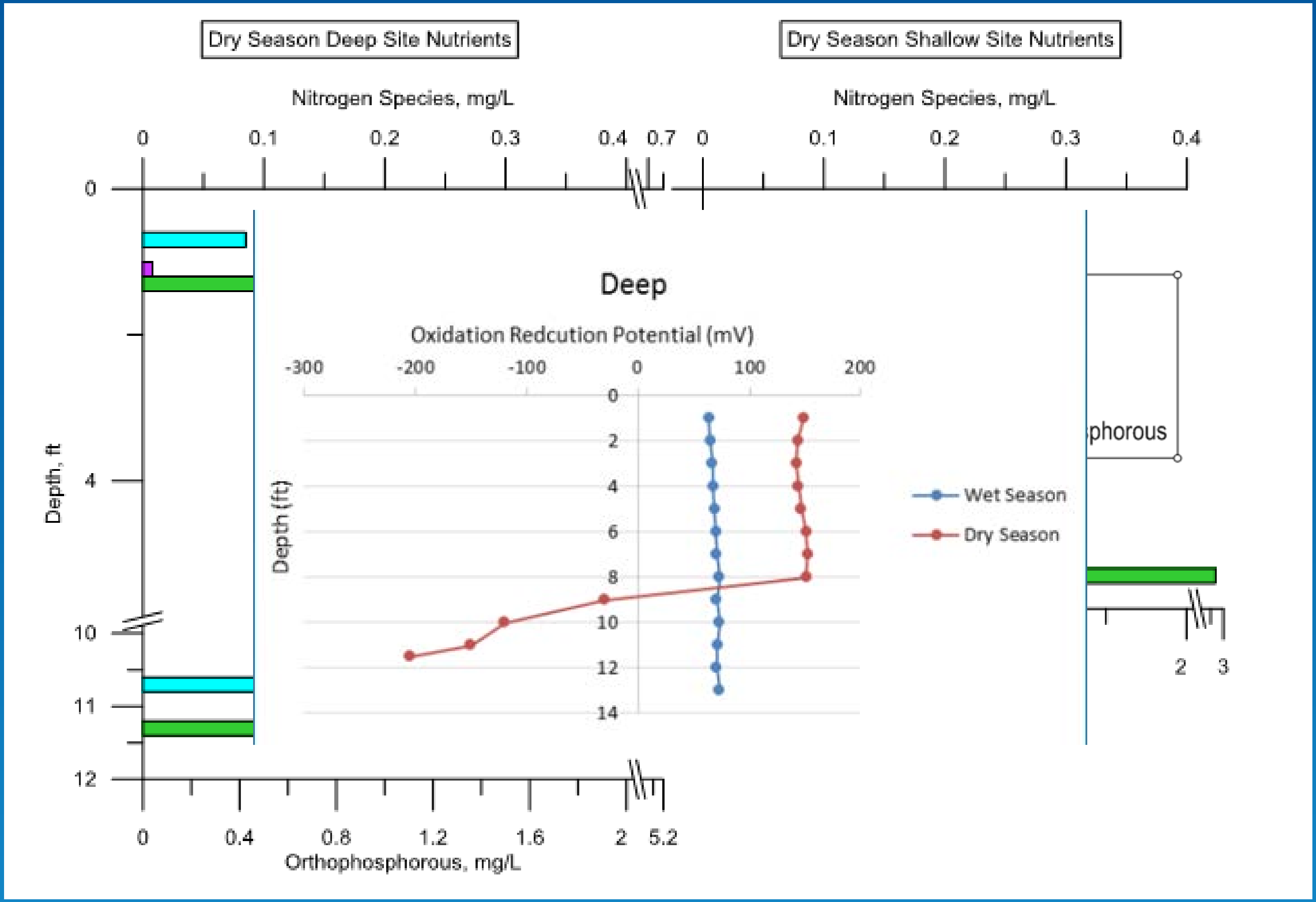


- Small Variability in Total Mercury Between Seasons
- Methylmercury Highest in Dry Season
  - Inverse to surface methylation observation
- Contributing Factors: In Water Methylation, No Flow Through, Incomplete Picture of Wet Season Dynamics

Reservoir Nutrient Dynamics – Wet Season



Reservoir Nutrient Dynamics – Dry Season

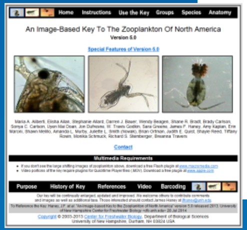


Zooplankton Body Burden/Enumeration

Large body > 243 um

DI Rinse

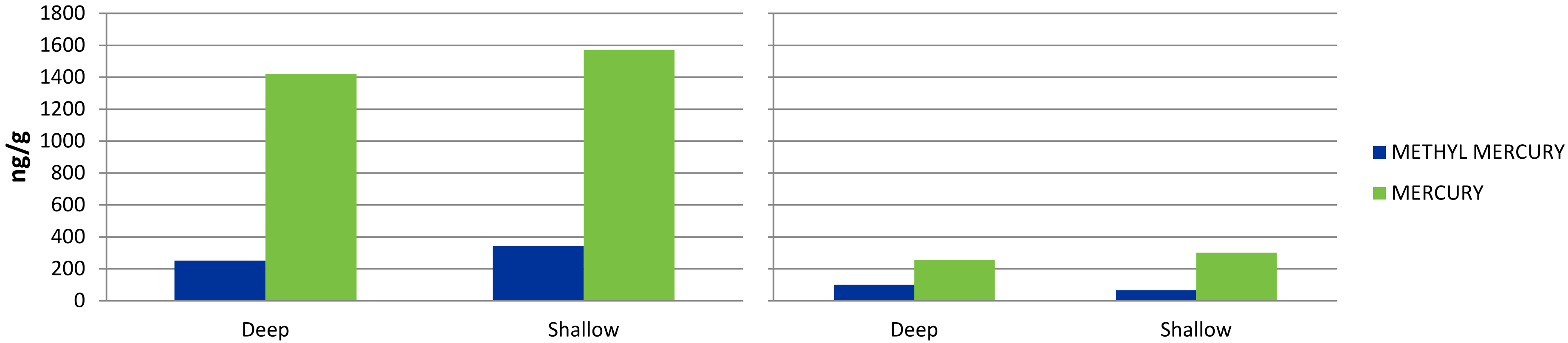
Enumeration/
Speciation



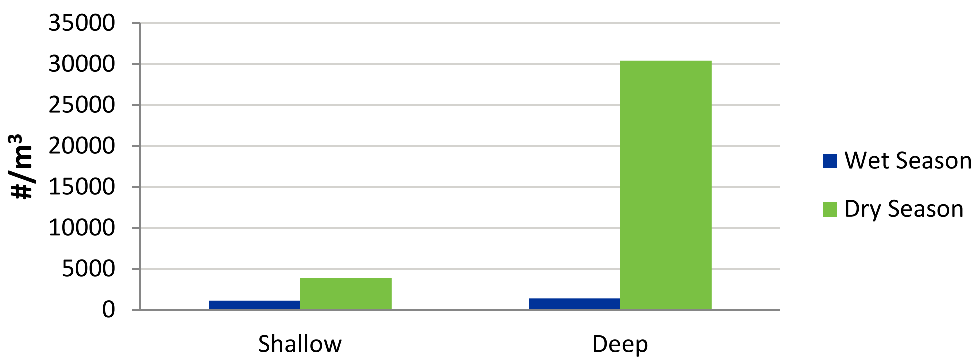
THg Analysis: EPA Method 7473
MeHg Analysis: EPA Method 1630

Zooplankton Body Burden: Unexpected Patterns

Wet Season Body Burden: MeHg ~20% | **Dry Season Body Burden: 30%**



Total Zooplankton Counts



Potential Factors

- Dissolved Organic Carbon Competition
- Algea Density
  - Secchi Wet: ~4 feet
  - Secchi Dry: ~3.5 feet

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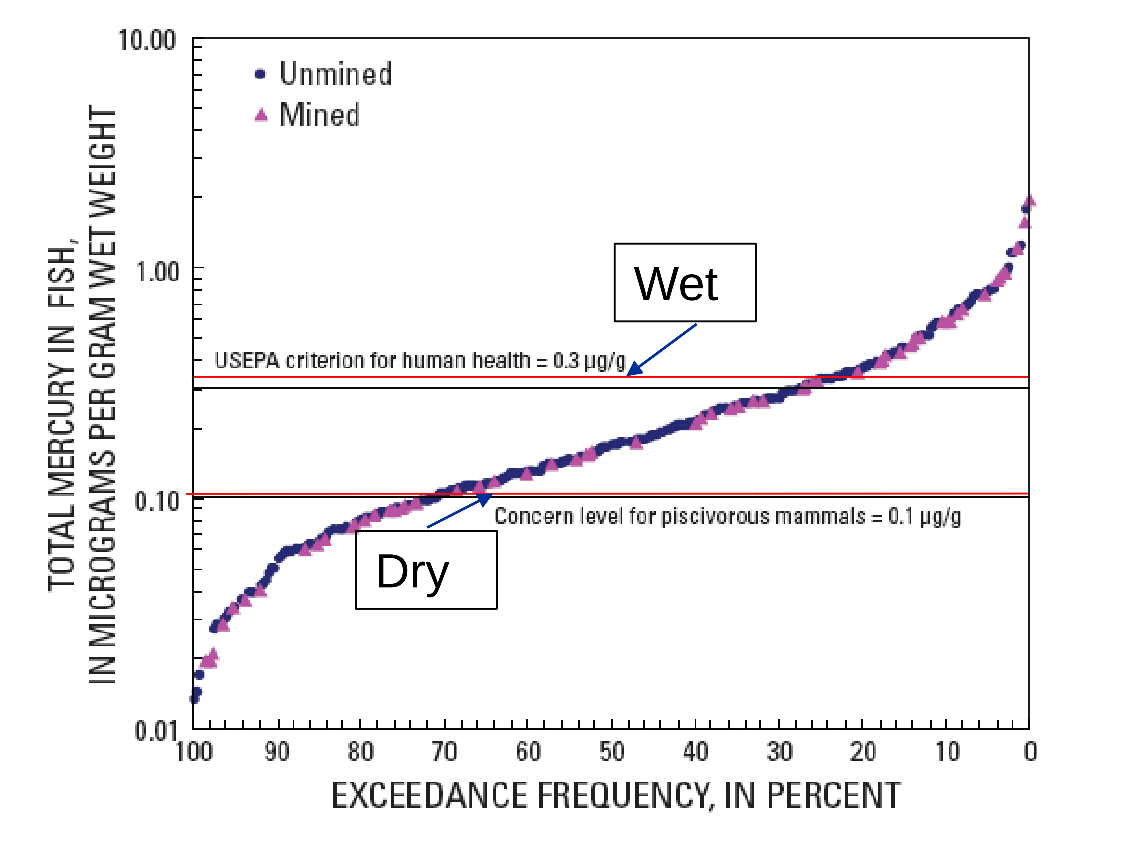
How Does Our Site Compare to Others: Fish Body Burden in US Basins

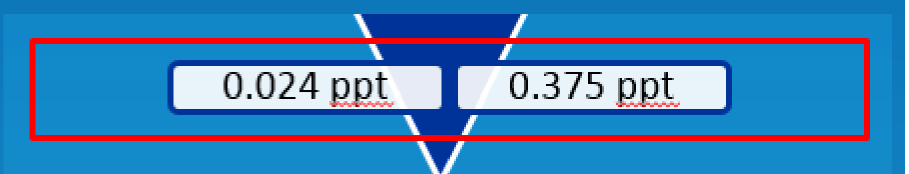
- 367 stream sites sampled across United States
- Sites with fish greater than 0.3 µg/g
  - 25% Exceed Target
- Sites with fish greater than 0.6 µg/g
  - 10% Exceed Target

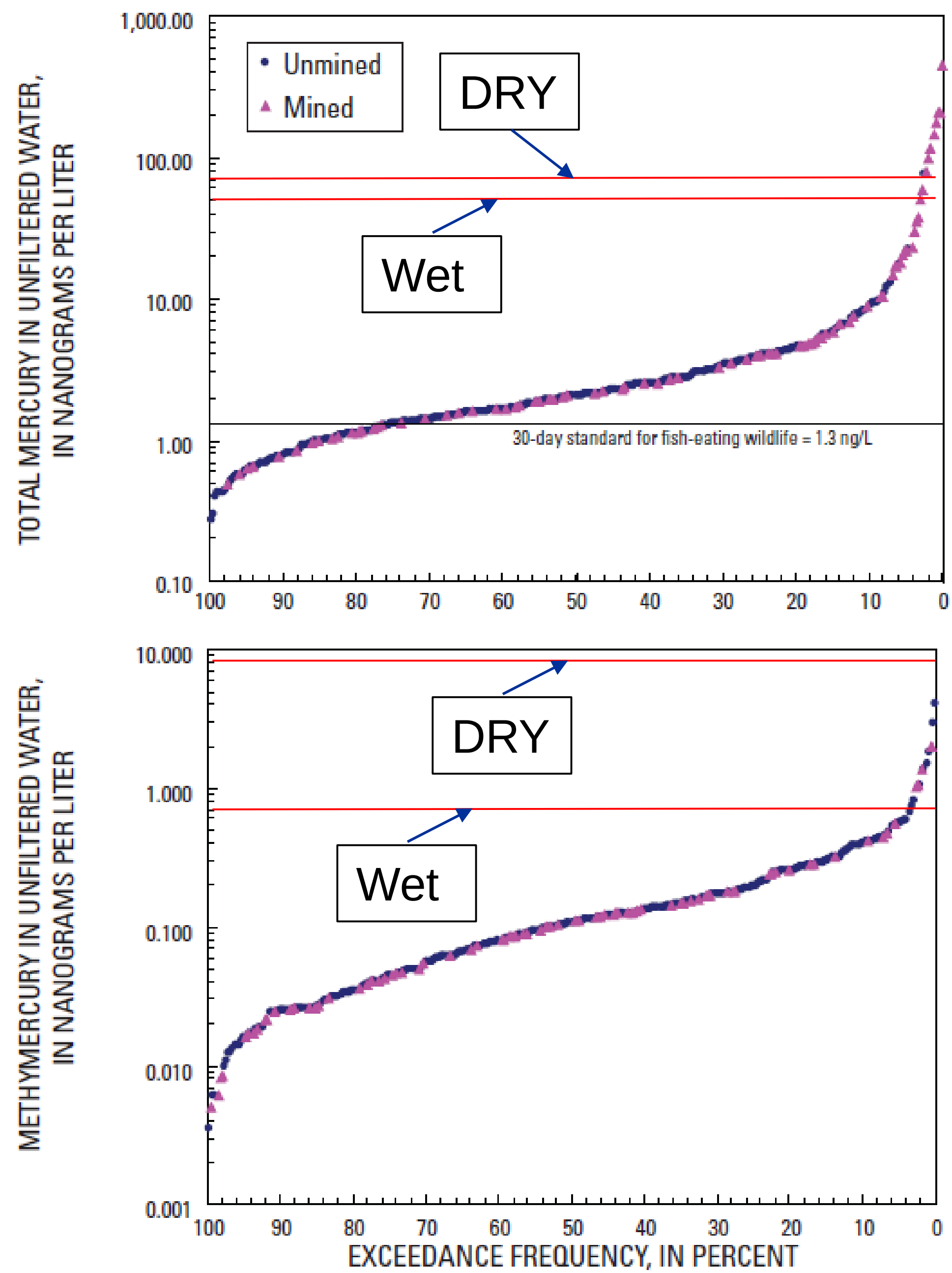


USGS, 2009

Total Mercury and Methylmercury Surface Water In US Basins

- LTCRR on High End of Mercury Impacted Systems in US
- Variability Between Seasons
  - Small THg Change
  - Large MeHg Change
- Remember This???





Summary and Conclusions – Reservoir Assessment Summary

- LTCRR sediments consume oxygen rapidly and maintains conditions conducive to reduction in both wet and dry seasons
  - Elevated external nitrate loading in wet season
  - Elevated internal phosphorous and ammonia loading in dry season
- Inverse relationship between mercury methylation in sediment and methylmercury bottom water enrichment
- Inverse relationship between methylmercury enrichment water column relative to food-web uptake

Future Assessments and Technology Screening

Recommended Additions to Future LTCRR Assessments

- DOC Analysis
  - UV 254: Aromatic Fraction of DOC
- Algae Enumeration
- Wet Season Sample Timing
  - Target a post storm event with longer antecedent dry condition ~mininum 2 to 4 weeks
- Dry Season Sample Timing
  - Target a sampling event at the end of the dry season prior to the first flush of the wet season.

Potential Remedial Options

- Source Control:
  - Reduce load of mercury from both the mine site and watershed.
  - Reduce load of nutrients from watershed.
- Select In-Situ Remedial Options:
  - Dredging
  - Capping
  - Redox Controls
    - Aeration/Oxygenation
    - Nitrate Addition
  - Coagulation/Precipitation
  - Biomanipulation

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Questions?

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