Patterns of Mercury Release from Profundal Sediment of CA Reservoirs

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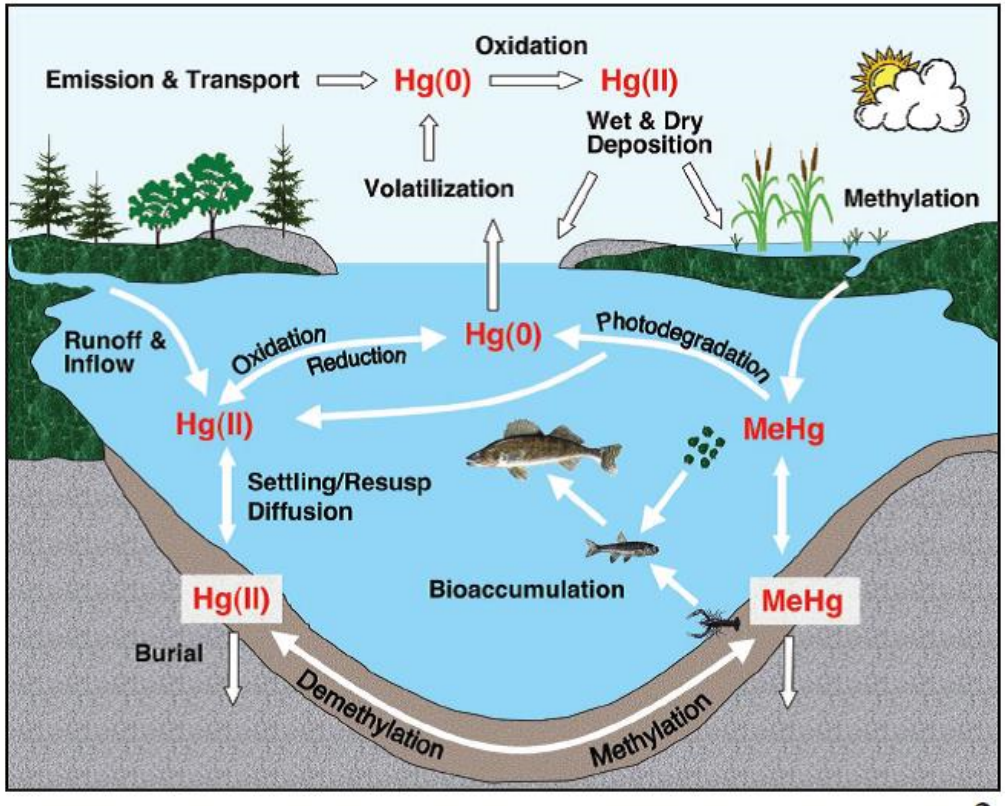
Mercury Cycling: The Basics

Bioaccumulation of Mercury:

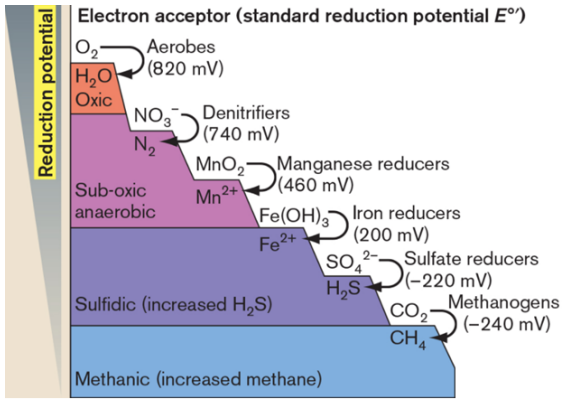
MeHg (aq) -> Bacteria/Algae -> Zooplankton -> Small Fish -> Big Fish -> Humans

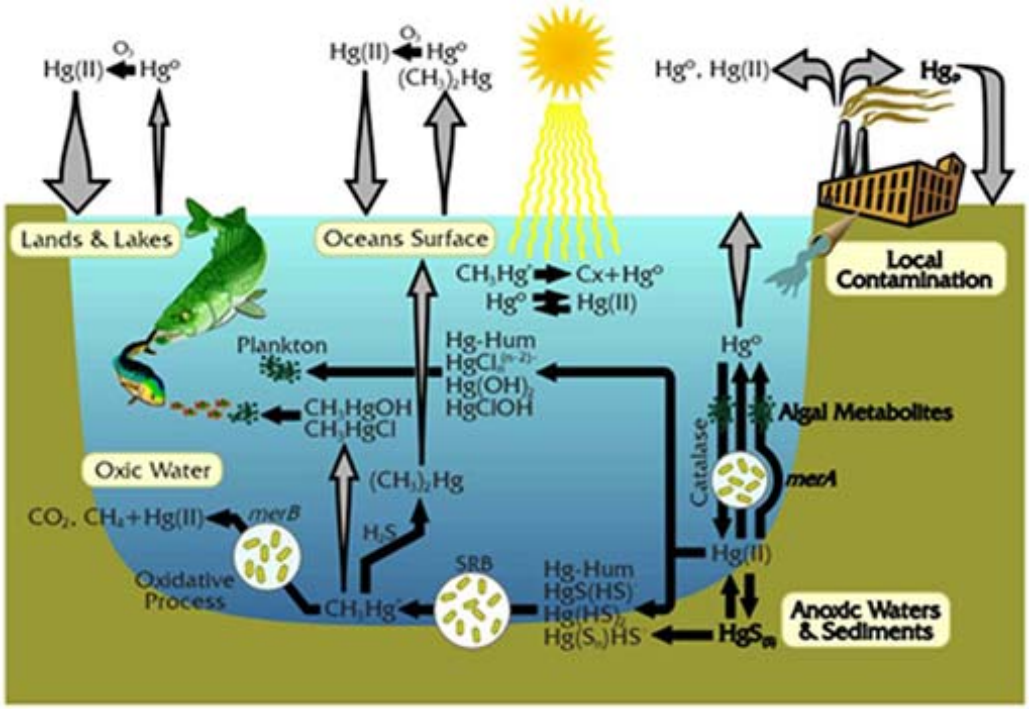


Mercury in Lakes and Reservoirs

- Lakes are full of mercury (Hg)
- Hg2+ = bad, but not terrible
- MeHg = horrible!
- Hg2+ converted to MeHg by anaerobic bacteria

Advanced Mercury Cycling





Accumulation of MeHg is dependent on 2 processes:

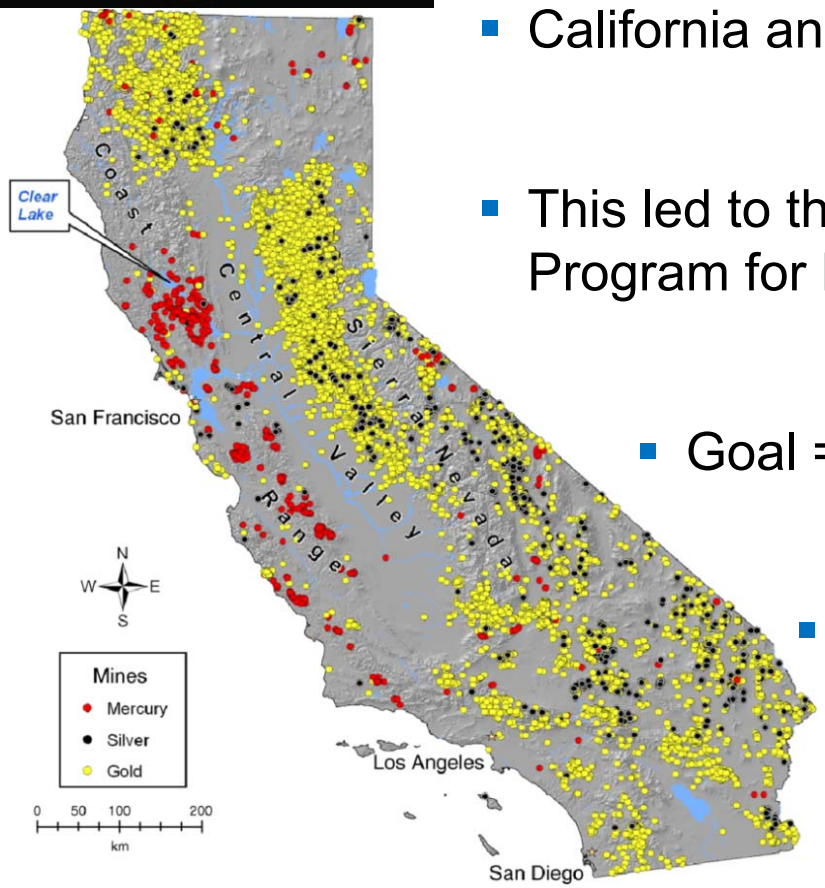
Methylation

- Conversion of Hg2+ to MeHg
- Redox sensitive
- Sweet spot = 200 mV to -200 mV
- Sulfate and iron reducing bacteria

Demethylation

- Conversion of MeHg to Hg2+
- Favorable under high (> 200 mV) or low redox (< -200 mV)
- Aerobic and methanogenic bacteria

Mercury Contamination in CA



- California and Mercury have a history together…
- This led to the conception of the Statewide Mercury Control Program for Reservoirs
  - Goal = reduce MeHg in fish tissue
    - **Reservoir managers: How do we do this??**

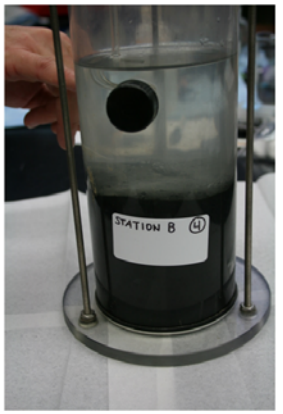
An Extreme Example: Guadalupe Reservoir

- Located in the San Francisco Bay
- 39 million kg of Hg extracted from cinnabar
  - Largest Hg mine in North America
- Sediment THg = 2.8 to 6.3 mg/kg
- Water MeHg = up to 57 ng/L
- Fish tissue = typically 5mg/kg in adults, up to 16.5 mg/kg (EPA limit = 0.3 mg/kg)

Can Oxygen Help?

Chamber Study:
Does DO reduce flux of MeHg?

Oxic



Anoxic

Findings:

- Anaerobic MeHg flux = 22.3 ng/m2 per day
- Aerobic MeHg flux = 5.5 ng/m2 per day

Impact:

- Implemented oxygen line diffuser to reduce summer anoxia

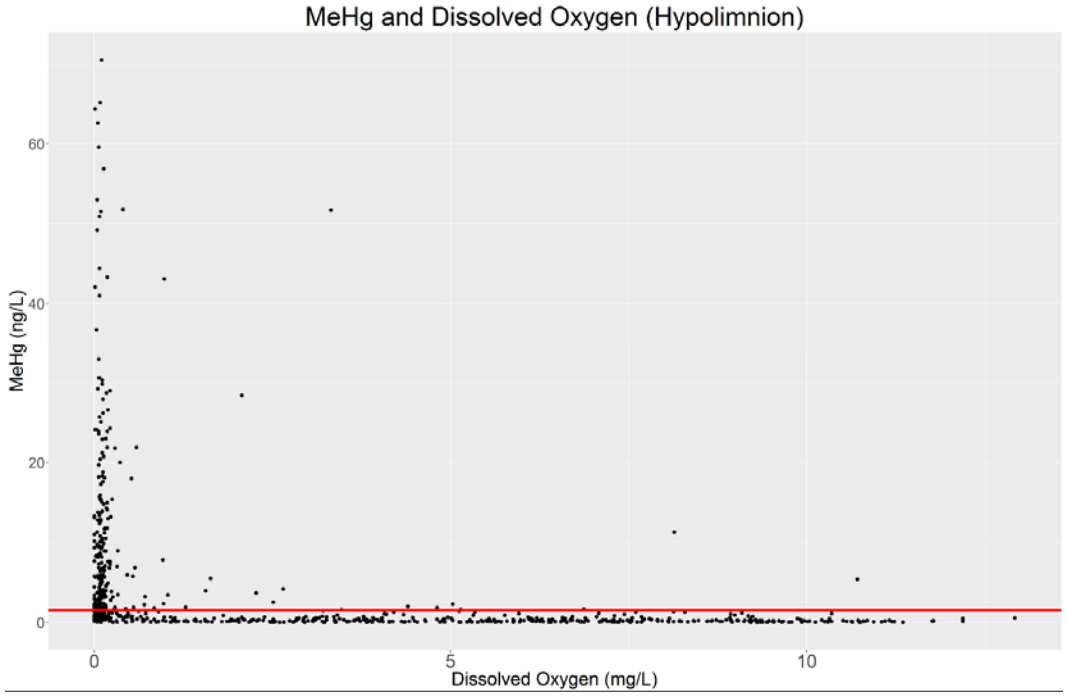
Oxygenation Results

<u>Pre-Oxygenation</u>

- Bottom Water MeHg Avg = 17 ng/L

<u>Post-Oxygenation</u>

- Bottom Water MeHg Avg < 1 ng/L
- Slow decline in fish tissue MeHg



What's the Catch?

- $600,000 construction cost
- $25,000/year in electricity
- Fish tissue will still be elevated decades from now at current rate

Why?

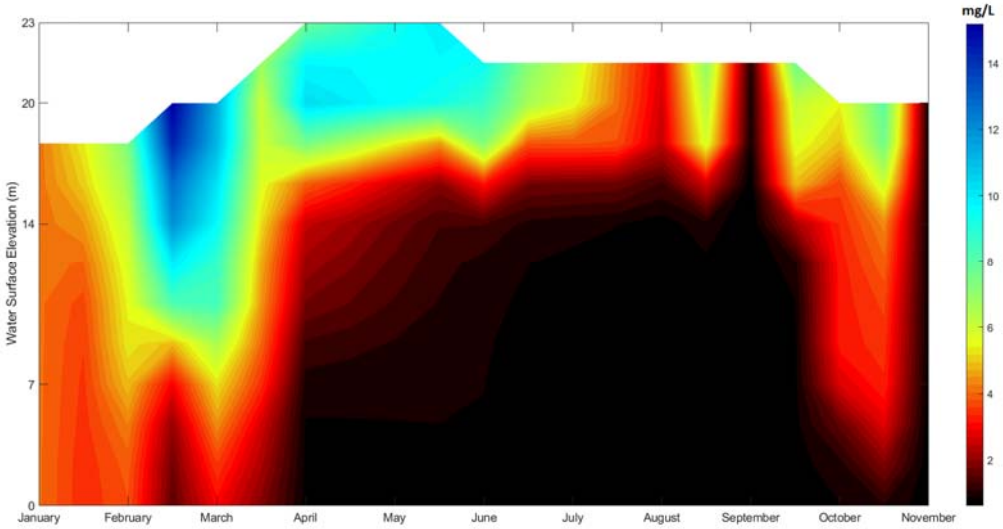
- Total mass of MeHg in water column < than 10 mg
- < MeHg in 10 lbs of Large Mouth Bass

Recycling!?

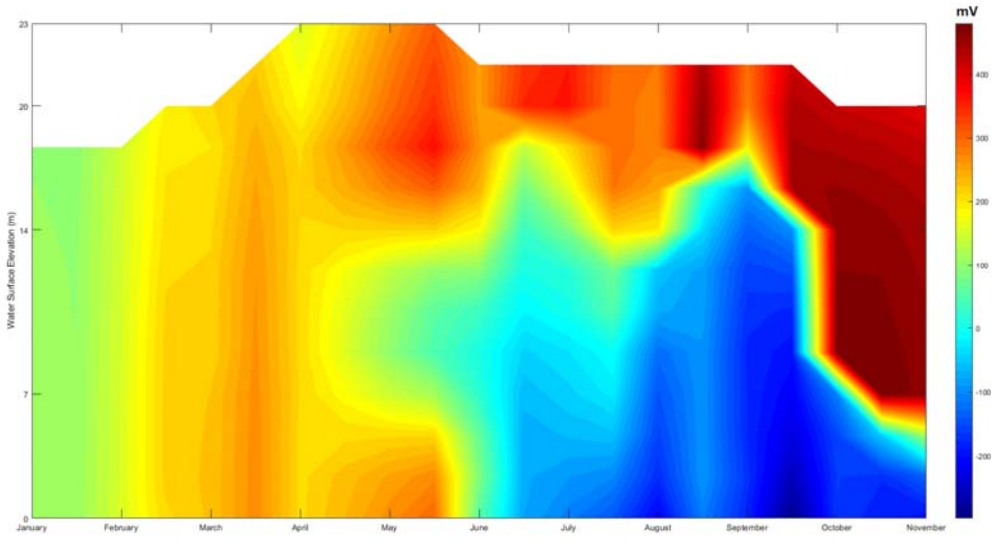
Hodges Reservoir

- Backup water supply
- 37 million m^3 volume
- 25 m maximum depth
- 64,000 hectare watershed
- Urban and agriculture
- Degraded water quality
- Recreational Fishing: Trophic Level 4
- 303(d) listed for mercury in fish tissue

Hodges 2017

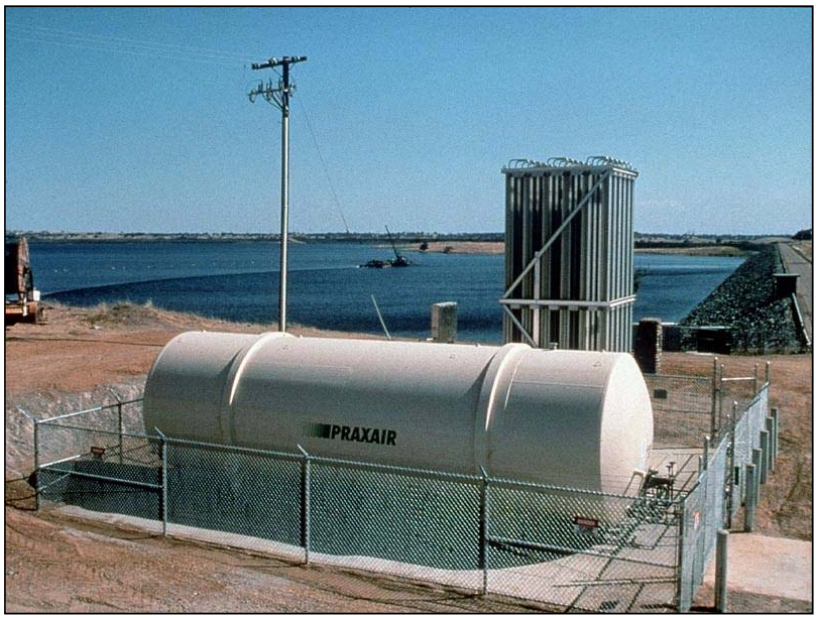


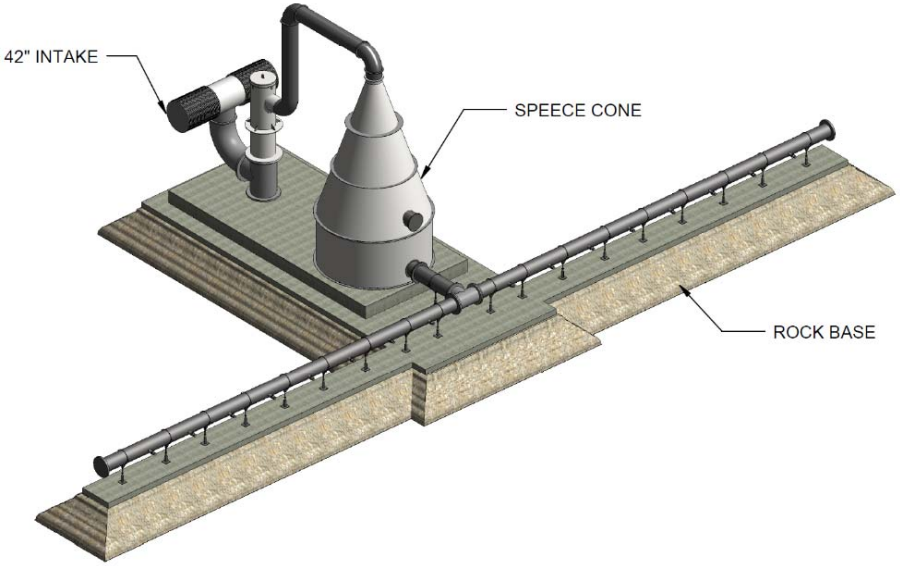
Dissolved Oxygen



Redox Potential

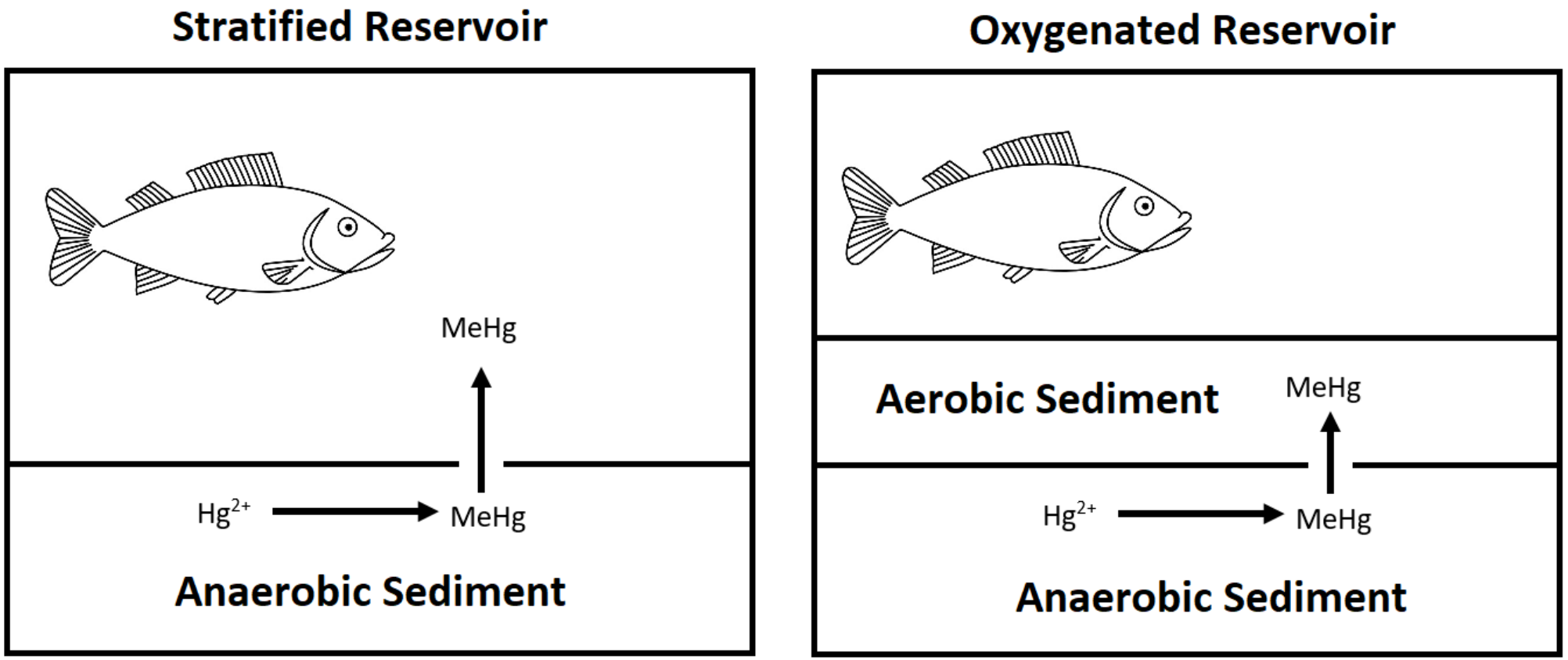
Speece Cone Oxygenation





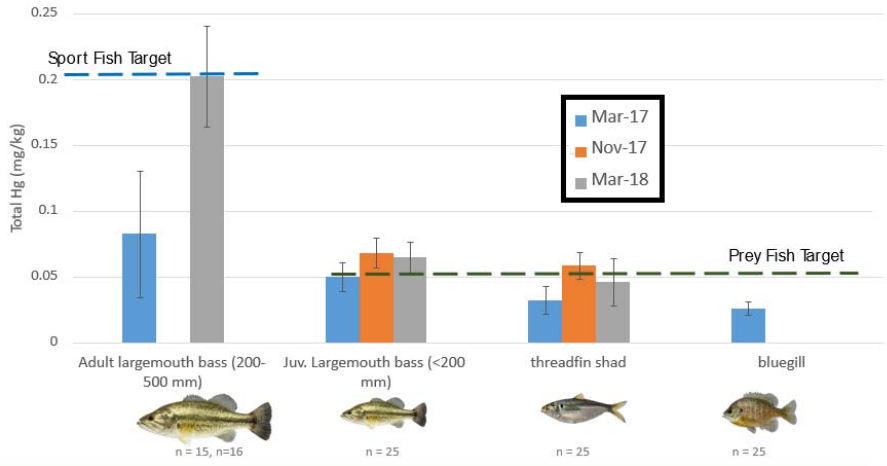
- On-shore Liquid Oxygen storage
- Submerged cone at Site A
- 8 tons of oxygen per day
- $4 million construction cost

The Oxygen Barrier

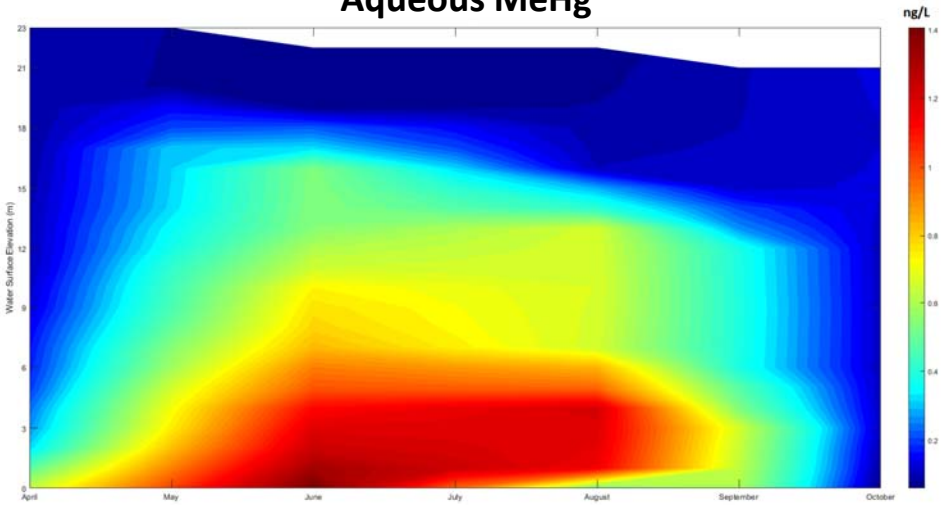


Bioaccumulation

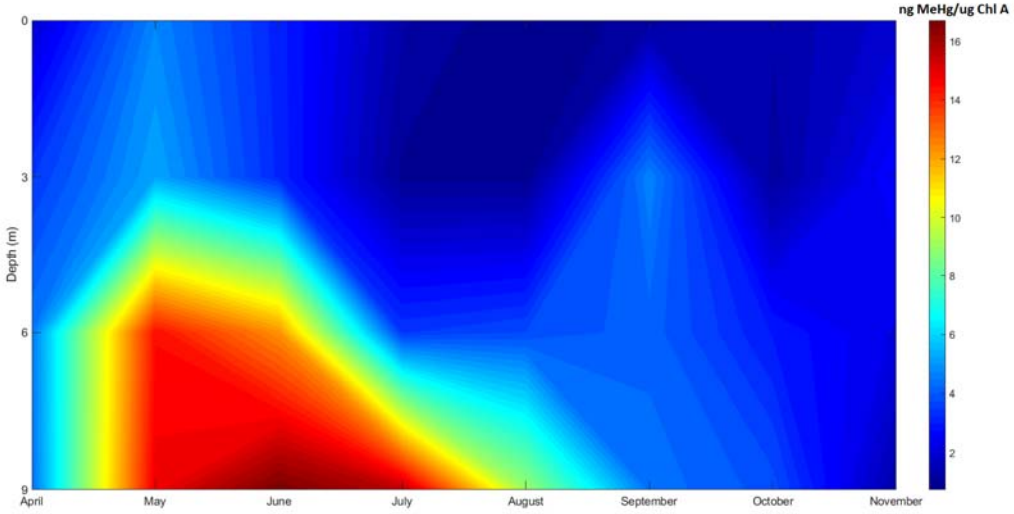
- MeHg peak production/release = May to August
- Algae = “hot” fish food in May to July
- Zooplankton MeHg increases during stratification
- Little fish = no significant change
- Big fish = dramatically increasing Hg content



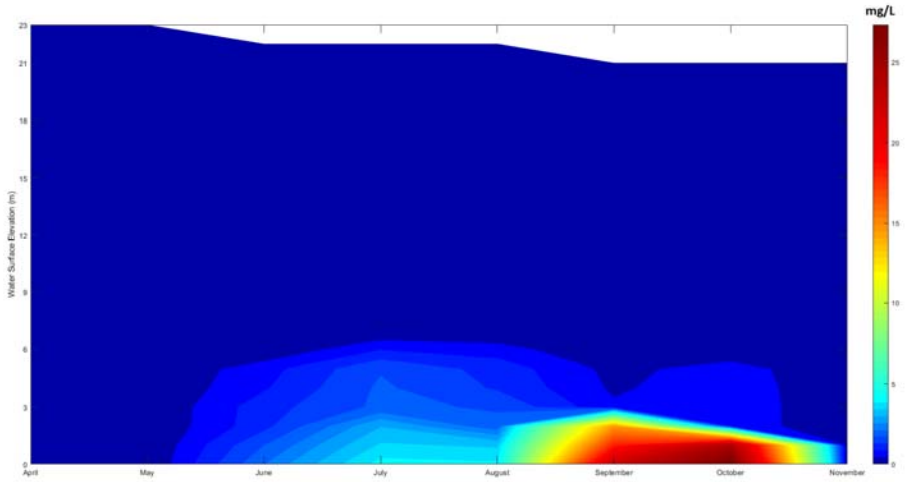
Aqueous MeHg



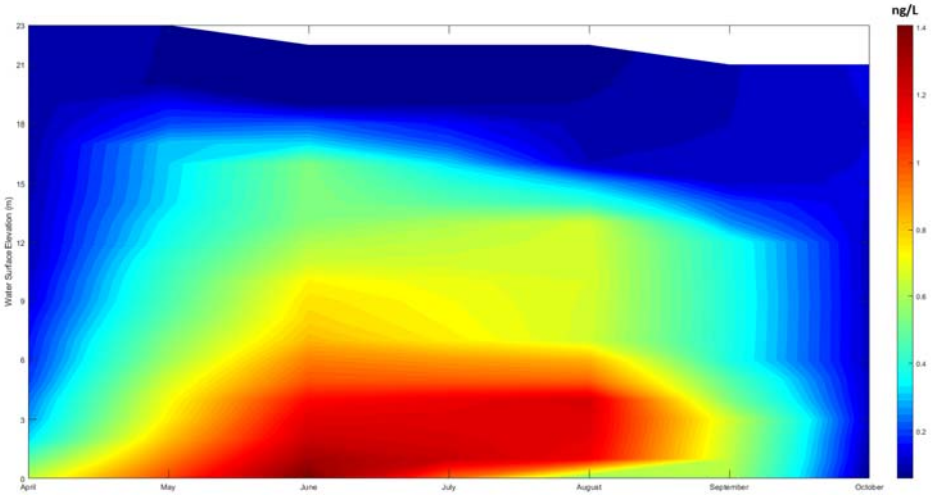
Surface Algae: MeHg to Chlorophyll A Ratio



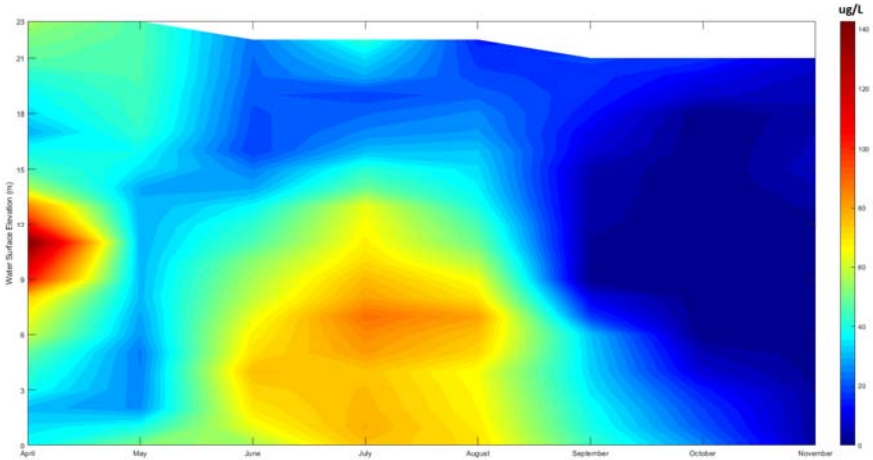
Sulfide



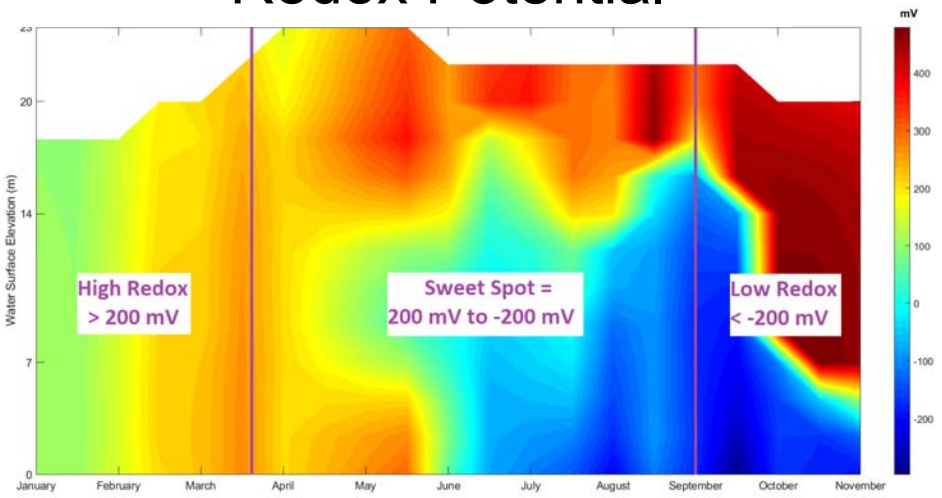
MeHg



Dissolved Iron



Redox Potential



2018 Water Quality Monitoring

1. Standard profile
2. Aqueous nutrients and metals
3. Carbon quality
4. Sediment ORP and pH
5. Sediment sulfur and iron speciation

2018 Mercury Analysis

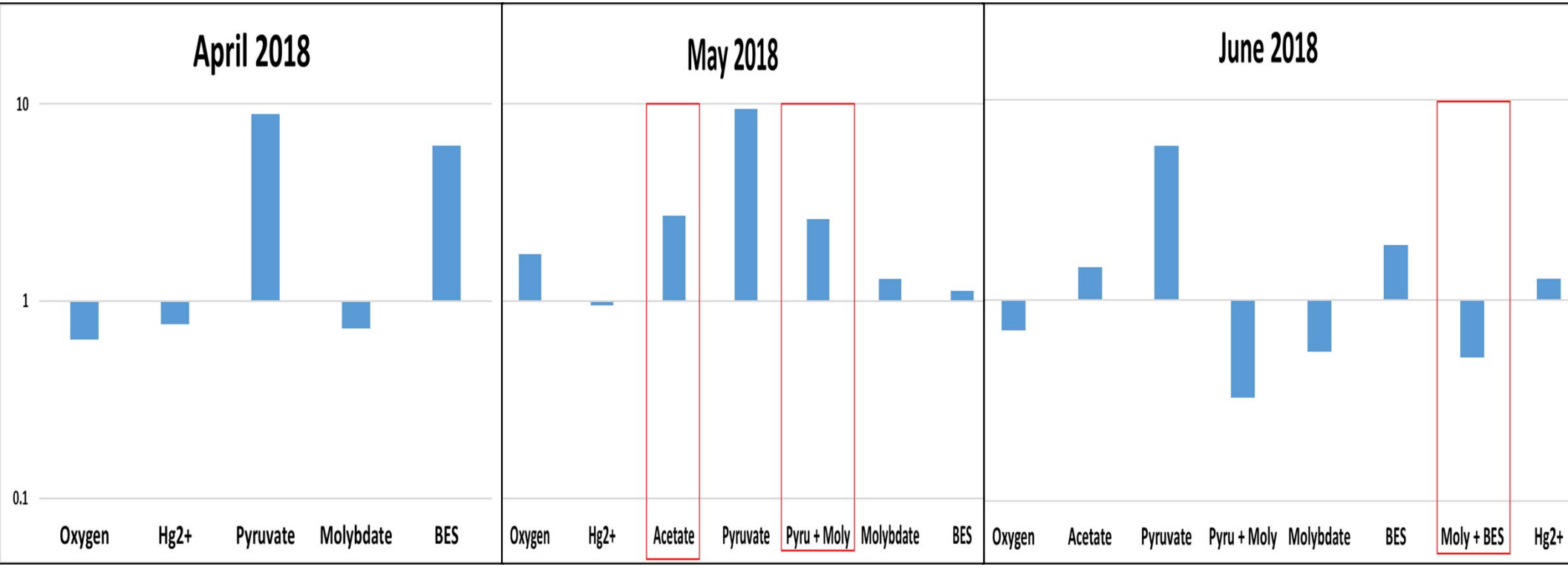
1. **Water Column:**
   - Total and Dissolved MeHg/THg

2. **Hg Bioavailability**
   - Sediment Sequential Extraction
   - Sediment Tin-reducible Hg
   - Porewater Thiol Extractable Hg

3. **Trophic Transfer**
   - Seston MeHg/THg and Stable Isotopes
   - Zooplankton identification and MeHg/THg
   - Fish Tissue THg

4. **Genetic Analysis (16-S RNA)**
   - HgcA - methylation gene
   - MerB - demethylation gene
   - Bacteria genes: dsrA, cymA, mcrA

Incubation Experiment Response Rates



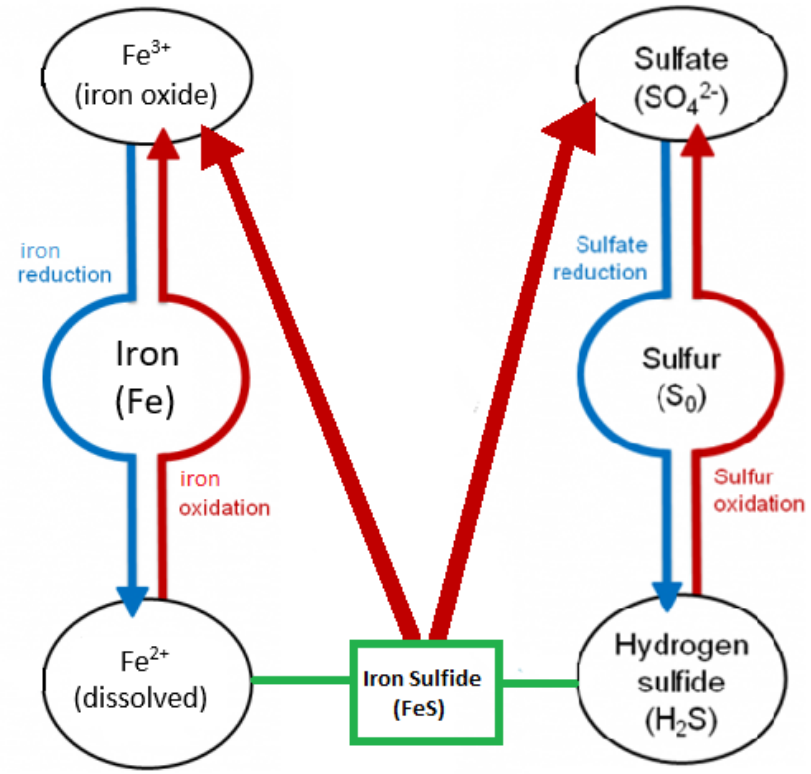
Is MeHg production linked to Oxygen??

- No known aerobic methylators -> can't blame it on the bacteria!

However

- Iron reduction requires oxidized iron
- Sulfate reduction requires oxidized sulfur compounds

Short answer – it depends!



Takeaways

- Reducing Bioaccumulation is tough
  - Food webs are complex!
- 200 mV to -200 mV Redox = MeHg production
- Iron and sulfur cycling heavily involved
- Oxygen can serve as redox barrier
- However, Oxygen can also replenish oxidized sulfur/iron compounds

Mercury Levels in Fish

HIGH	MODERATE		LOW	
• Bluefish	• Bass (Striped, Black)	• Perch (Freshwater)	• Anchovies	• Perch (Ocean)
• Grouper	• Carp	• Sablefish	• Butterfish	• Plaice
• Mackerel (King, Spanish, Gulf)	• Cod (Alaskan)	• Skate	• Catfish	• Pollock
• Marlin	• Croaker (White Pacific)	• Snapper	• Clam	• Salmon* (Canned, Fresh)
• Orange Roughy	• Halibut (Atlantic, Pacific)	• Tuna (Canned Chunk Light, Skipjack)	• Crab (Domestic)	• Sardine
• Sea Bass (Chilean)	• Jacksmelt (Silverside)	• Weakfish (Sea Trout)	• Crawfish/Crayfish	• Scallop
• Shark	• Lobster		• Croaker (Atlantic)	• Shad (American)
• Swordfish	• Mahi Mahi		• Flounder	• Shrimp
• Tilefish	• Monkfish		• Haddock (Atlantic)	• Sole (Pacific)
• Tuna (Bigeye, Ahi, Canned Albacore, Yellowfin)	*Farmed salmon may contain PCBs & chemicals that have serious long-term health effects.		• Hake	• Squid (Calamari)
			• Herring	• Tilapia
www.nrdc.org			• Mackerel (Chub, N. Atlantic)	• Trout (Freshwater)
			• Mullet	• Whitefish
			• Oyster	• Whiting