Planning for Statewide Mercury Program for Reservoirs meeting January 14, 2015

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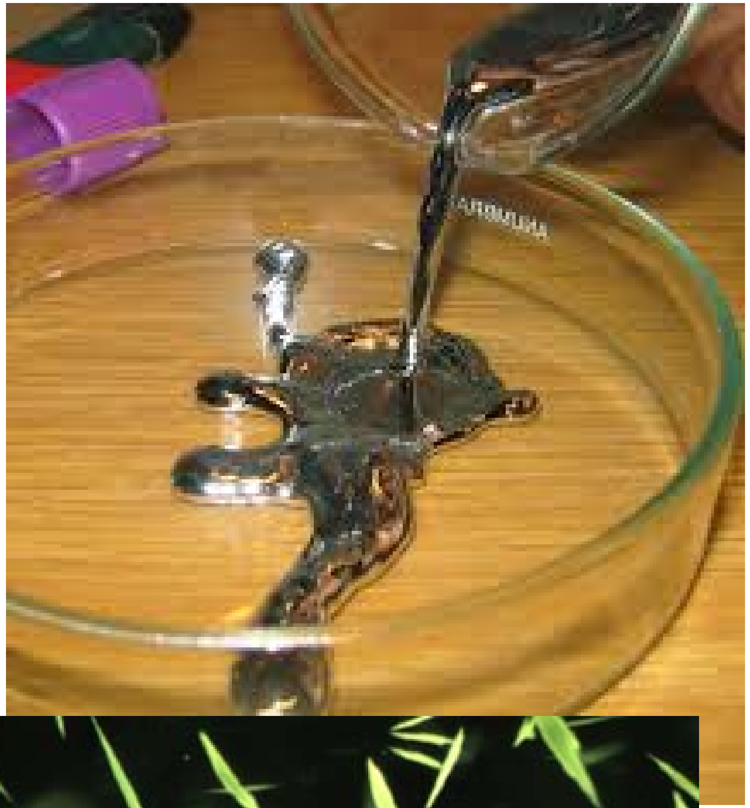
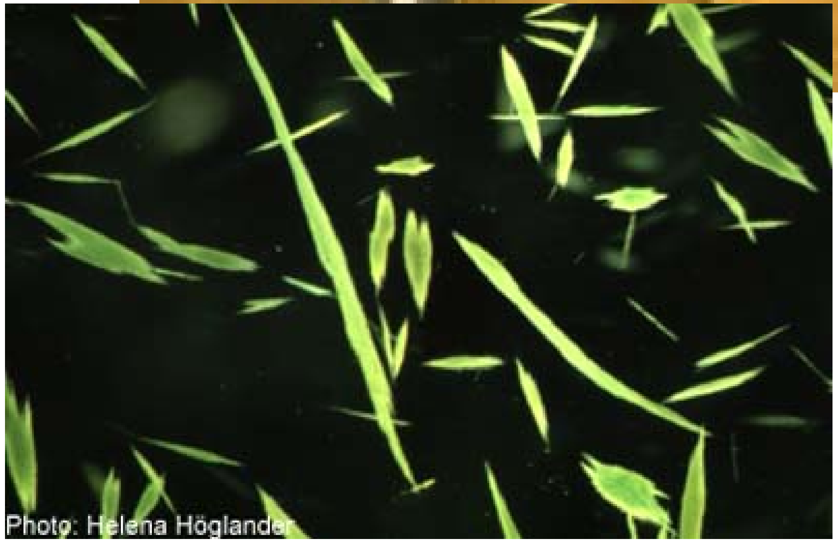
Background

- 160 Californian reservoirs may be affected by proposed/possible new methyl-mercury regulations
- Reservoirs are relatively neglected in terms of using them as part of a treatment train for drinking water supply relative to treatment plants themselves
- Similarly, reservoir fish management is focused on fish biomass not contamination but this could change

Problems

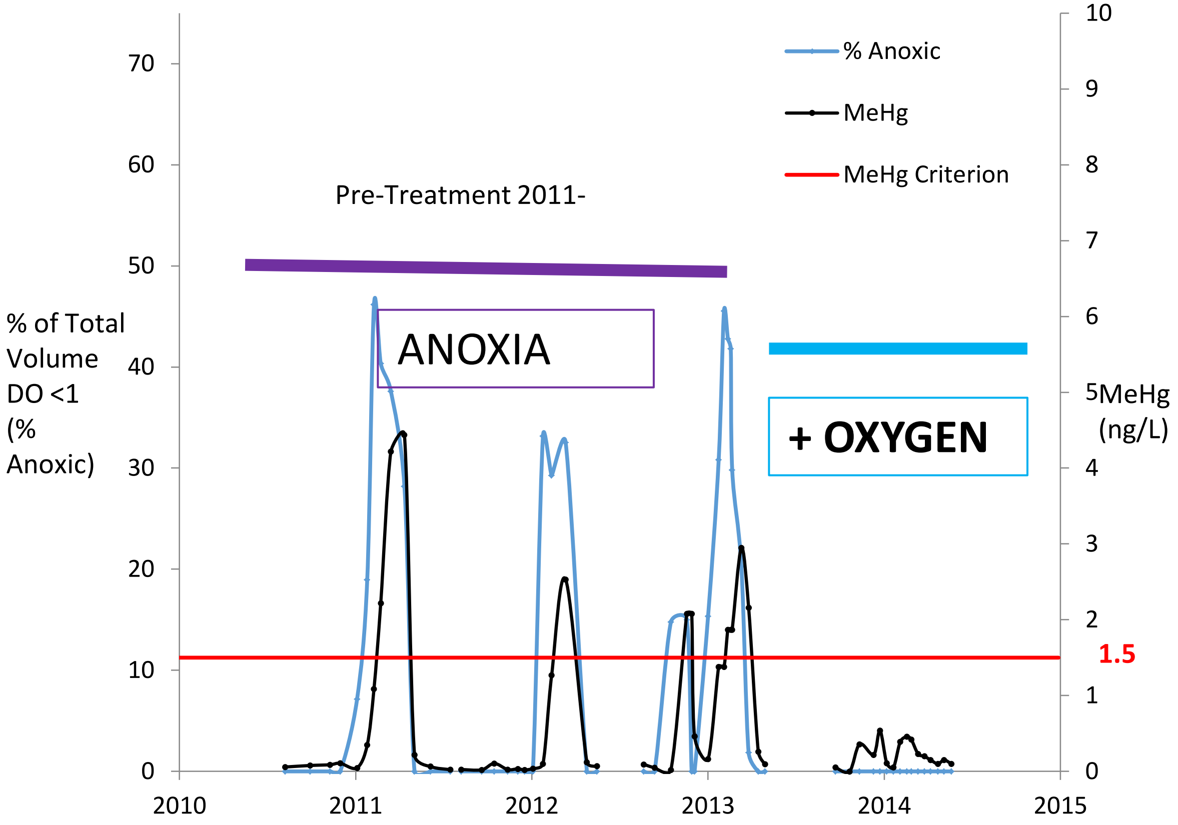
- Methyl-mercury (MeHg) can accumulate in fish via the food web hundreds or thousand fold to reach dangerous levels for humans, animals & birds
- Algae are the main culprit in converting dissolved MeHg from water to cell matter (as with selenium, copper & some organic compounds)
- Mercury loading via the air & runoff is a major factor





Methyl-mercury (MeHg)

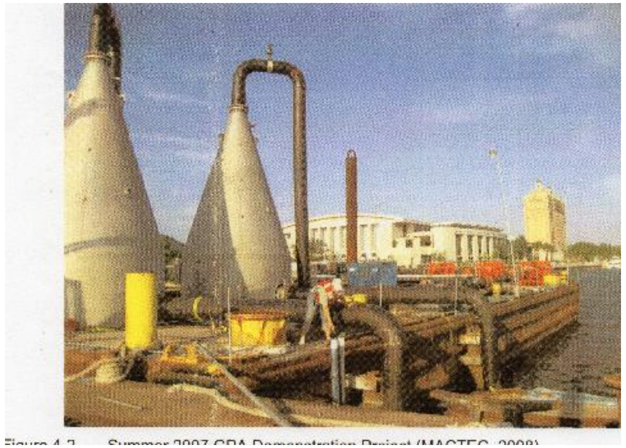
- Produced by bacteria, usually in sediments or close by & under **ANOXIC** (no oxygen) conditions
- *A review of > 100 publications finds almost no mention of anoxia being needed*
- Same bacteria also make hydrogen sulfide (H_2S) under anoxia
- **Getting ride of anoxia removes H_2S so will it get ride of MeHg?**
- More or less true but not been put into practice very often



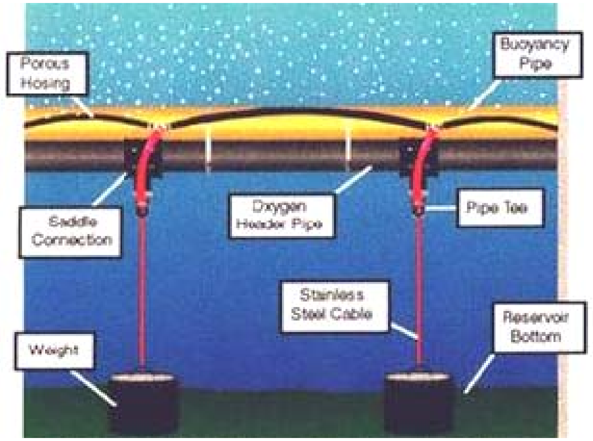
Preliminary fall 2014 data from Dave Drury, Santa Clara Valley WD for Calero Reservoir HOS oxygen treatment

Hypolimnetic Oxygenation Systems HOS

- HOS covers a range of method that I like to use to get oxygen into the deep waters and sediments of:
- Lakes & reservoirs
- Rivers & streams
- Estuaries (Chesapeake Bay)
- Coastal dead zones (Mississippi River offshore)
- Some areas of the deep ocean (Black Sea or Baltic Sea)



ECO2 Speece cones in estuary



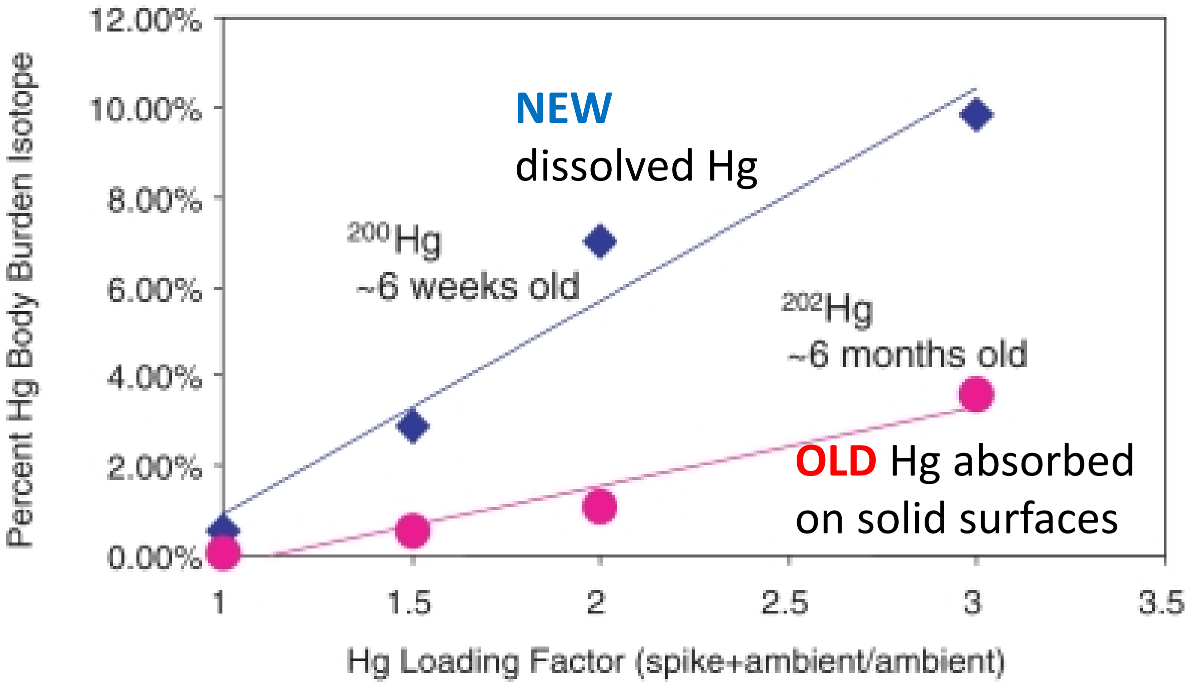
TVA-Mobley HOS diagram

Correlations: good study of 20 reservoirs in Maryland

Chesapeake Bay & Watershed Programs CBWP-MANTA-ASD-03-1

- **No one single factor** controlled MeHg in largemouth bass; most important were MeHg concentrations, SO_4 in water, & lake morphometry ($\hat{z}$ = A/V) = 44% of Σvariance
- **Shallow lakes** that stratify may be worst. Shallow + algae = eutrophication = benthic anoxia
- **Their Solutions**: add forest buffers & reduce acid rain (sulfates high). No use for us.

Hg aging: Supply of New Mercury important:

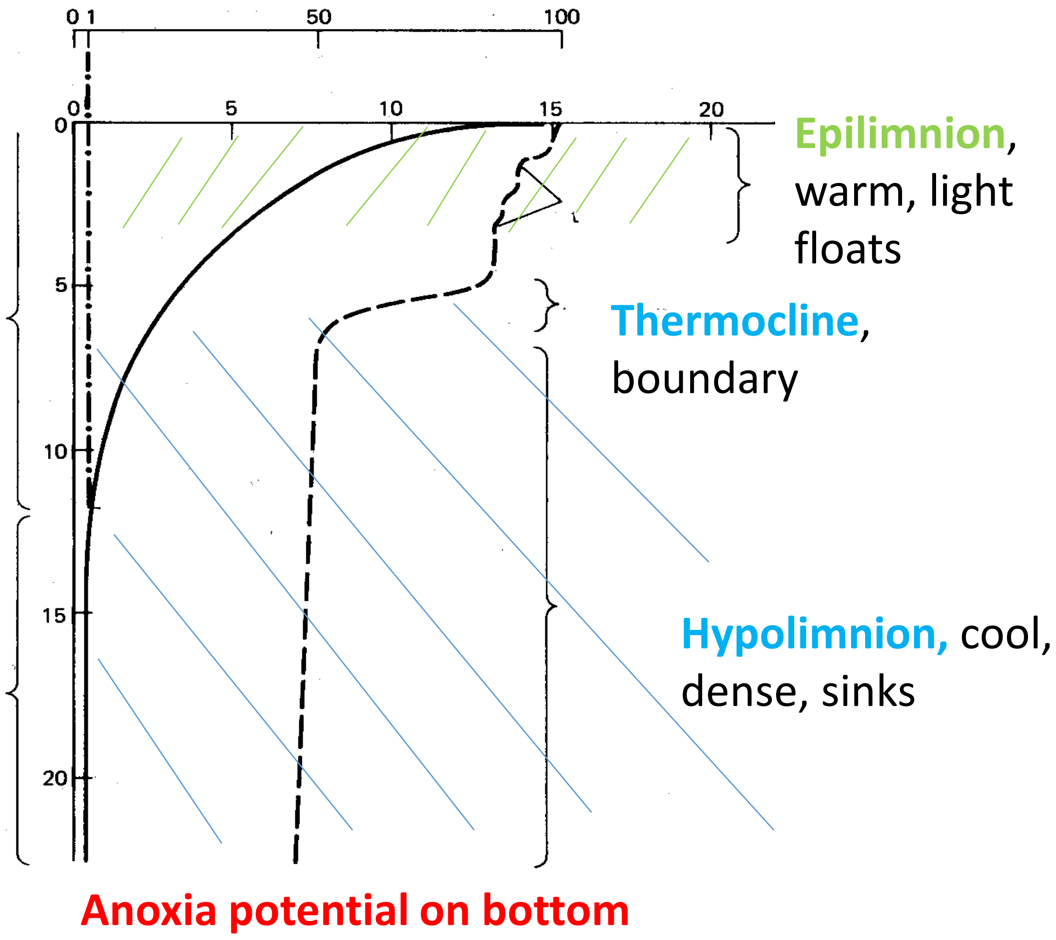


From D. P Krabbenhoft, USGS Wisconsin

- In Florida Everglades new Hg rather than old was most important for MeHg uptake to fish
- Old Hg absorbed onto solid surfaces, new is more dissolved
- So legacy MeHg in sediments may not be too important

How do reservoirs get anoxic water?

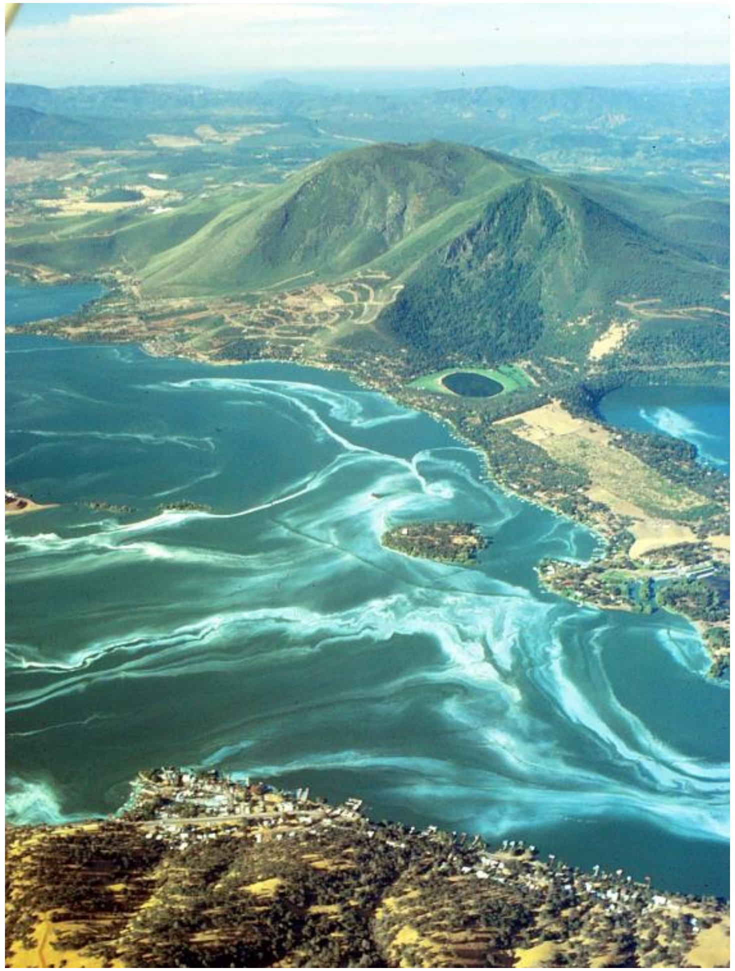
- In spring most waters > 10 feet deep stratify; warm, less dense water on top, cool denser water below.
- The stratification creates a deep block of water is isolated from new supplies of oxygen
- A fixed amount of oxygen in the deep water has to last all summer



From Horne & Goldman, Limnology textbook 1994

More on anoxic bottom water due to algae

- Algae grow at surface where there is light, die, sink & rot in bottom water & sediments
- Rotting uses up oxygen so too much algae = anoxia
- Algae depend on nutrients
- Hard to reduce nutrients in watershed (unless unit process treatment wetlands used)
- **In-lake treatment** is the only option for most reservoirs

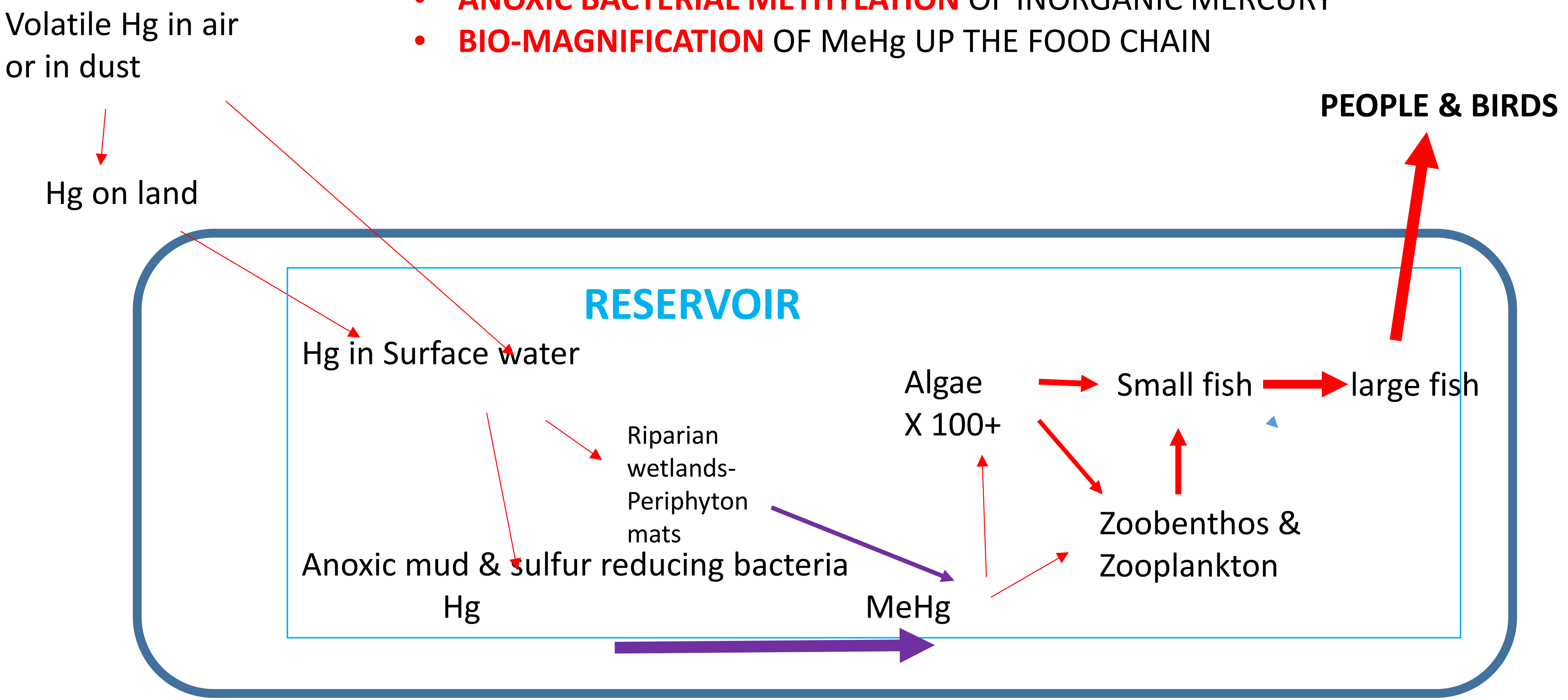


Algae bloom in Clear Lake, Lake Co. CA. ~ 1973
Photo Alex Horne

Critical path for mercury methylation to humans & birds

TWO KEY STEPS

- **ANOXIC BACTERIAL METHYLATION** OF INORGANIC MERCURY
- **BIO-MAGNIFICATION** OF MeHg UP THE FOOD CHAIN



Other possible methylation sites

- Low DO in algae mats –periphyton on rocks. Would need to be thick and anoxic – at least at night
- Low DO possible in decaying layers of the metalimnion (thermocline). Could occur round lumps of decaying matter
- I am not very clear how this could happen very much in California reservoirs
- Riparian wetlands on reservoir edges

Photos: Alex Horne

Questions

- Algae, zoobenthos, zooplankton & fish contain concentrated MeHg
- Uptake by algae is active uptake is from MeHg itself
- Some passive uptake by organic detritus with S-H bonds
- Will more algae & detritus reduce (biodilute) MeHg in reservoir? That is; some oligotrophic lakes fish have less MeHg in fish than green eutrophic ones (2 to 3 times dilution in zooplankton; Pickhard et al, PNAS 2002)
- Will this prevent HOS from working well?

Bio-dilution decreases in MeHg vs HOS

Increased algae = bio-dilution

- Experimental data: with equal concentrations of aqueous Hg, an increase in algae could result in a decrease in Hg uptake—by zooplankton grazers
- Result: increasing algae reduced CH_3Hg^+ concentrations in zooplankton 2–3-fold
- Bloom dilution may provide mechanistic explanation for lower CH_3Hg^+ accumulation by zooplankton & fish in algal-rich relative to algal-poor systems.

HOS = reduced MeHg in water

- Moderate HOS will reduce MeHg by at least 7 times
- This will overwhelm the dilution effect 2:1
- Really effective HOS might reduce MeHg by up to 100 fold but needs to be tested.

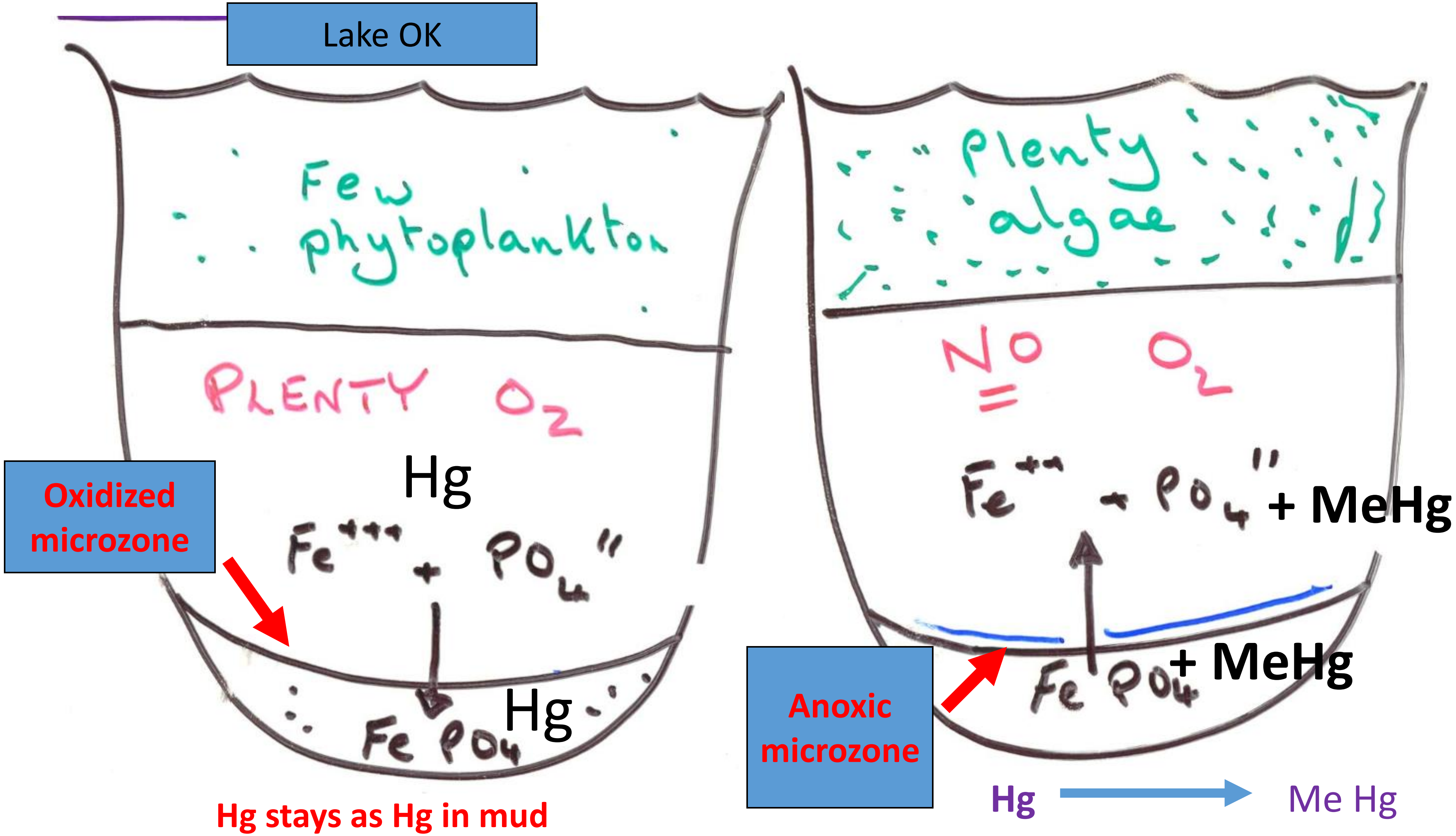
HOS – reservoir oxygenation
ALL YOU NEED TO KNOW ABOUT OXYGEN

- **DISSOLVED OXYGEN (DO) IN WATER BECOMES DEPLETED MUCH MORE EASILY THAN GASEOUS OXYGEN IN AIR. LOW DO IN THE HYPOLIMNION IS POSSIBLY THE MOST IMPORTANT PROBLEM IN LAKES & RESERVOIRS**

- **DO CAN EASILY BE ADDED TO WATER ARTIFICIALLY AS COMPRESSED AIR OR PURE OXYGEN & IS THE MOST COMMON LAKE MANAGEMENT TECHNIQUE**

- **DO IS PRODUCED BY PHYTOPLANKTON PHOTOSYNTHESIS & USED BY THEM & ALL OTHER AQUATIC ORGANISMS, GIVING DAILY, SEASONAL & ANNUAL CYCLES OF DO.**

Effect of oxygen on lakes

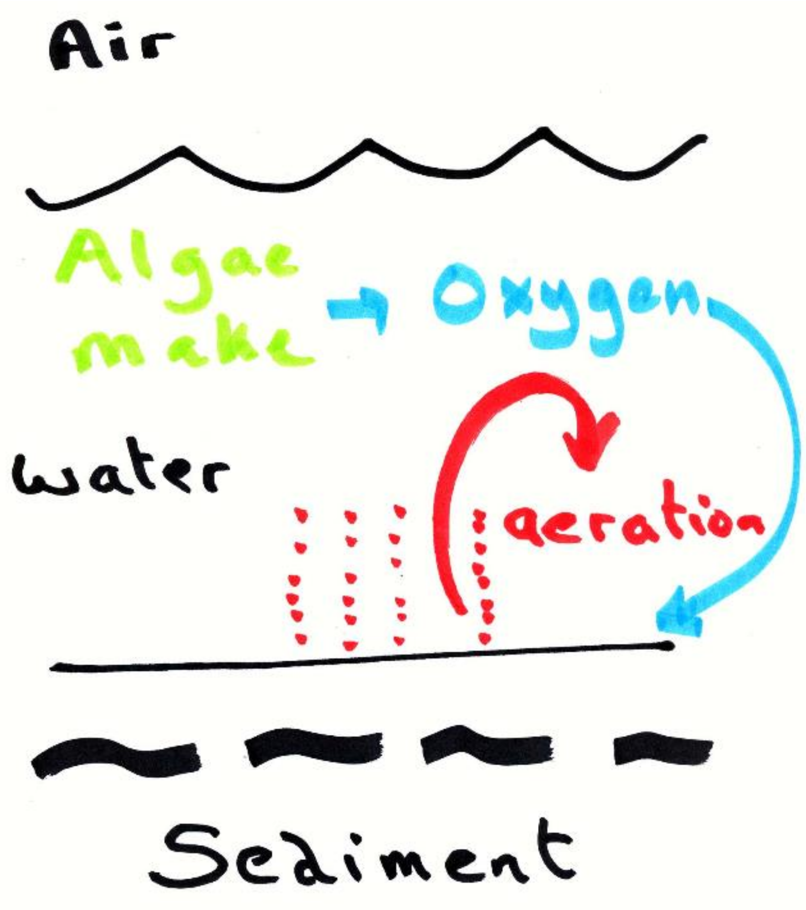


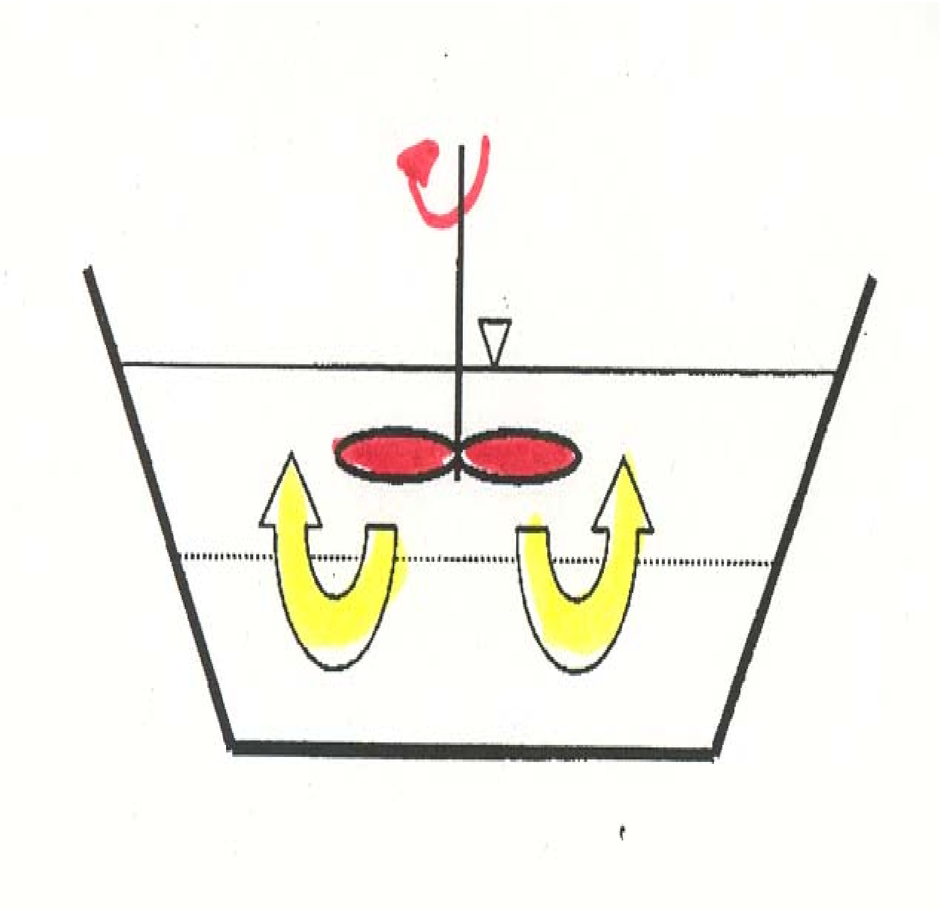
What oxygenation/aeration/mixing choices are there?

- Destratification: mixes oxygen-rich surface water with anoxic deep water
- Compressed air lift pumps as unconstrained free bubbles or inside double tubes
- Pure oxygen as unconstrained free bubbles or inside a cone
  - Choice depends on reservoir & local folk

Aeration: destratification with compressed air or propeller

Oxygen comes from algal photosynthesis NOT from air

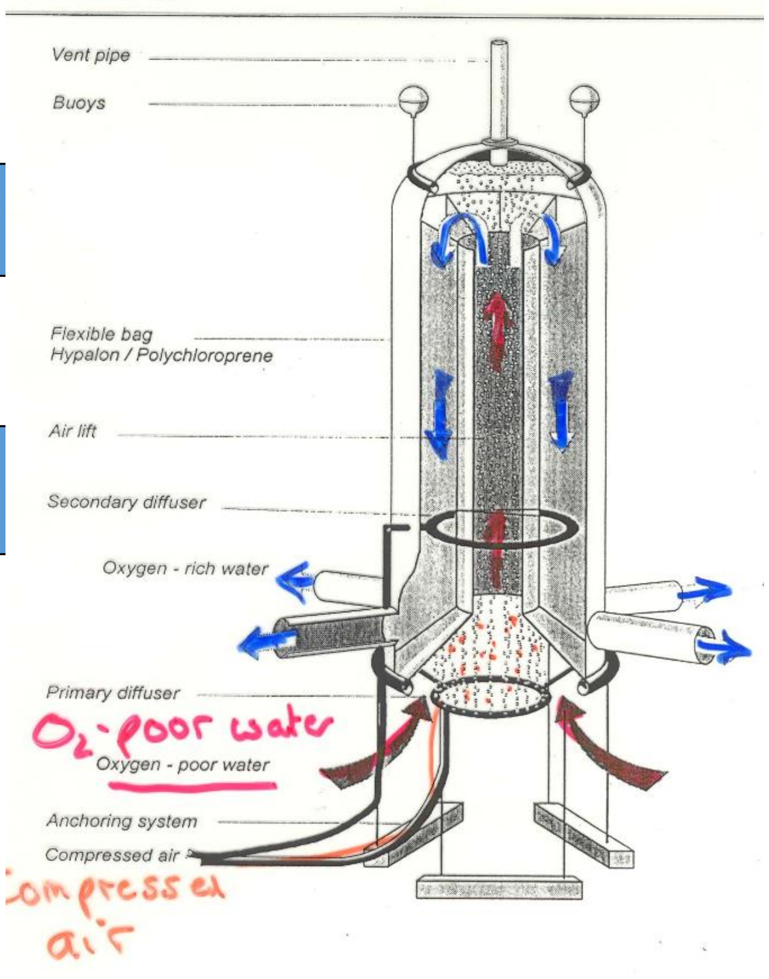




Hypolimnetic Aeration: Partial air lift pump - Limnos unit

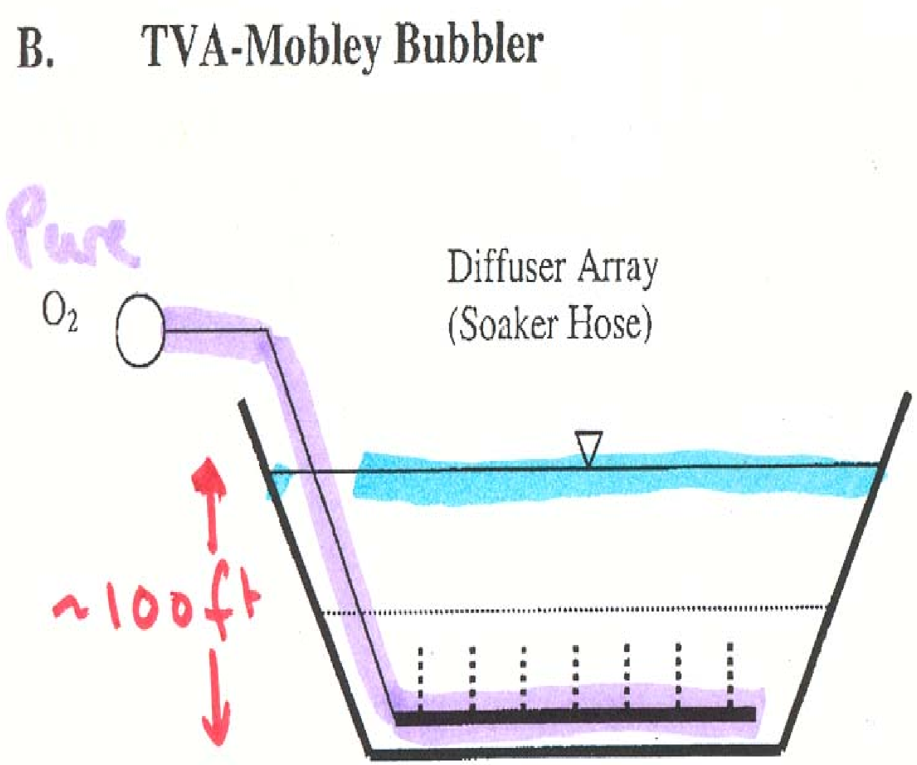
Epilimnion

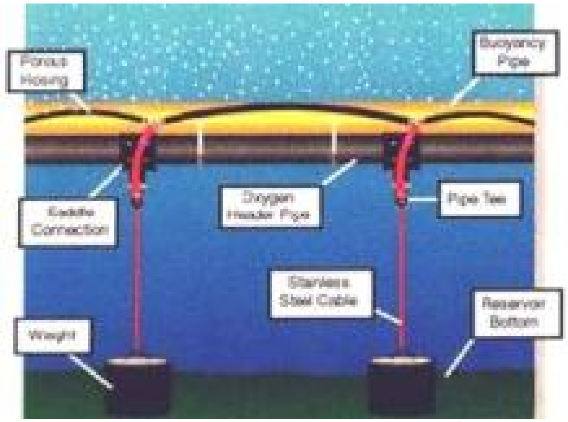
Hypolimnion

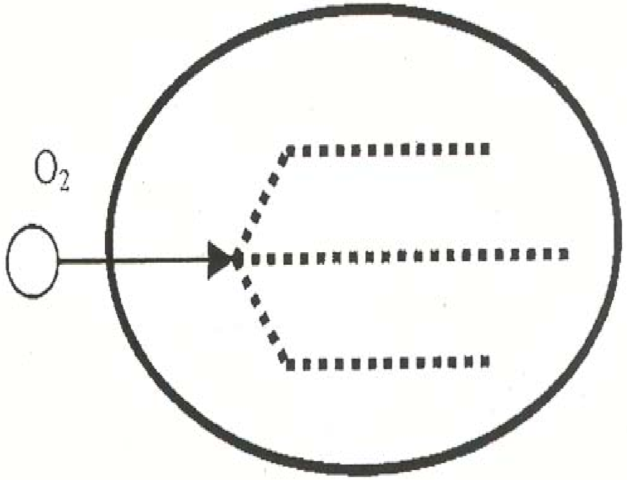


- Double tube
- Adds air, transfer efficiency 5-35% probably ~ 10%
- Oxygenated water can be passed out at any level including over sediments
- Outlet plume less dense than bottom water

Unconstrained oxygen bubble plume

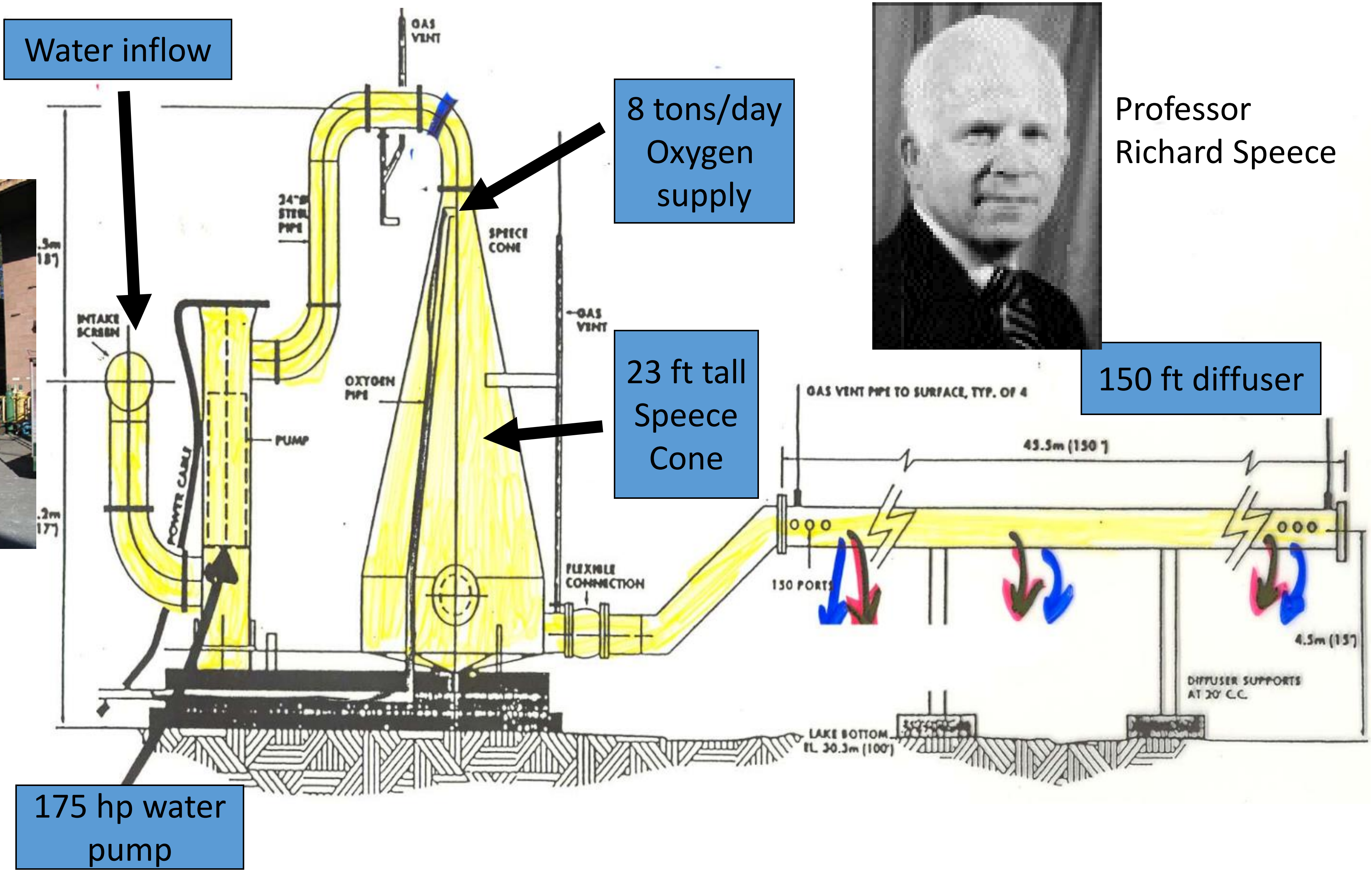






Mark Mobley

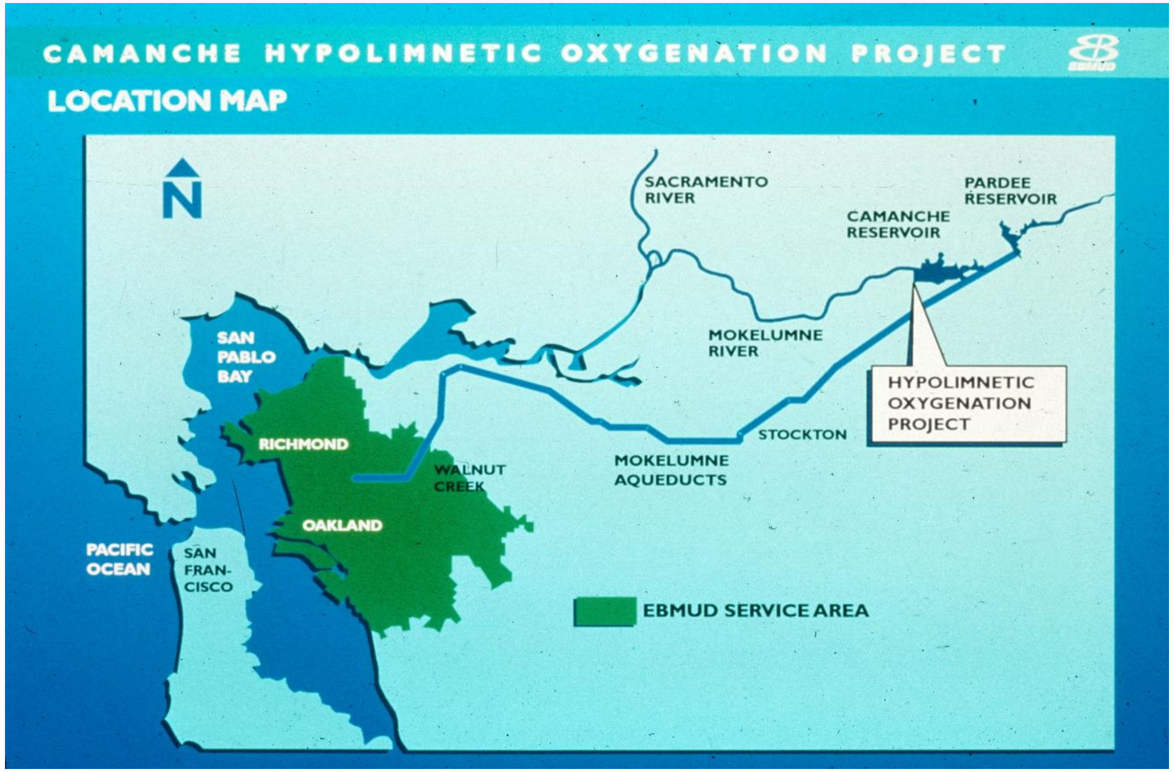
Bubble-free plume: Speece Cone



Professor Richard Speece

Camanche Reservoir
EBMUD

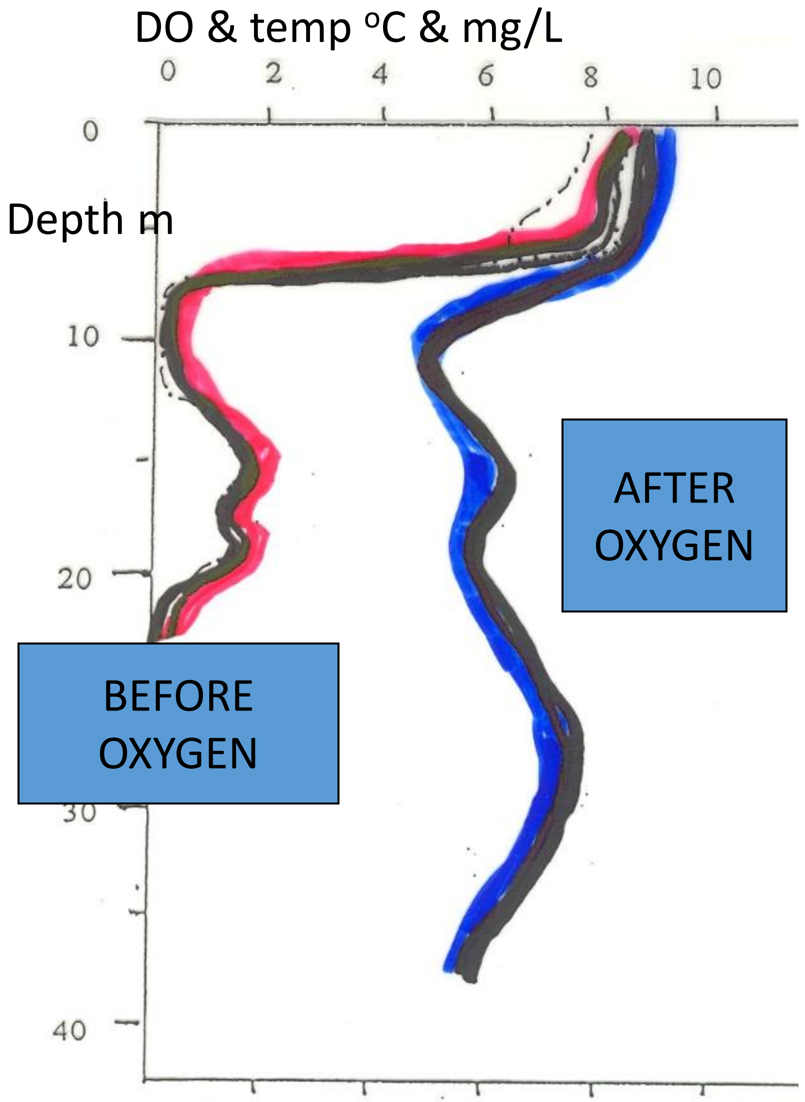
- In 1986-90 over 300,000 salmonids died in fish hatchery below Camanche & many more may have died in Mokelumne River
- Cause of death was ascribed by Prof. Horne to hydrogen sulfide
- Hydrogen sulfide is generated in anoxic muds
- So oxygenation of water above muds needed



Camanche Reservoir Summary

- Oxygenation installed in 1992 **– no fish kills since**
- Can also now use hydropower at dam
- Natural Chinook spawning increased from 3,000 to 8,000+
- Capital cost $1.3 m ($1992)
- O&M $90,000/y (electricity for water pump + liquid oxygen supply)
- **Cost benefit ratio: ~ 1:30**

Results of Camanche Reservoir HOS oxygenation

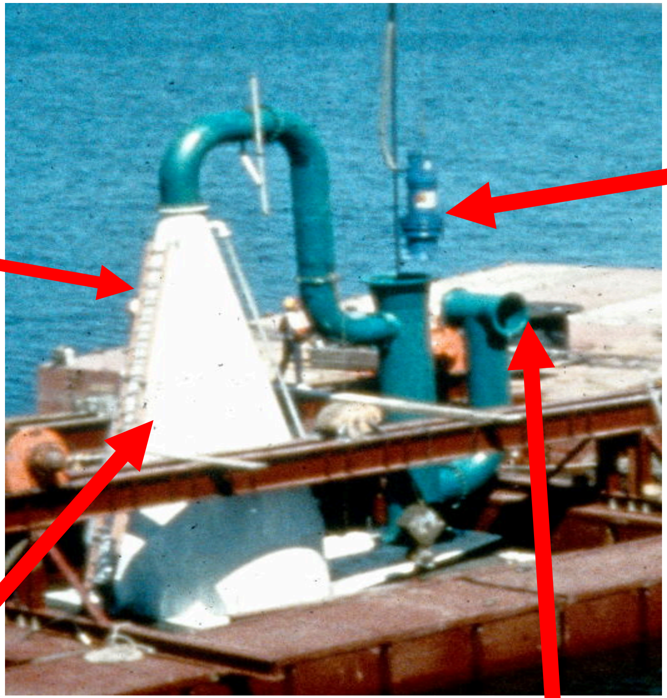


- Before hypolimnetic oxygenation DO below thermocline was absent
- After oxygenation DO minimum in hypolimnion was ~ 5 mg/L

Speece Cone close up (8 tons/day)

Oxygen Supply line

Water pump being lowered into place



Speece Cone 23 ft high

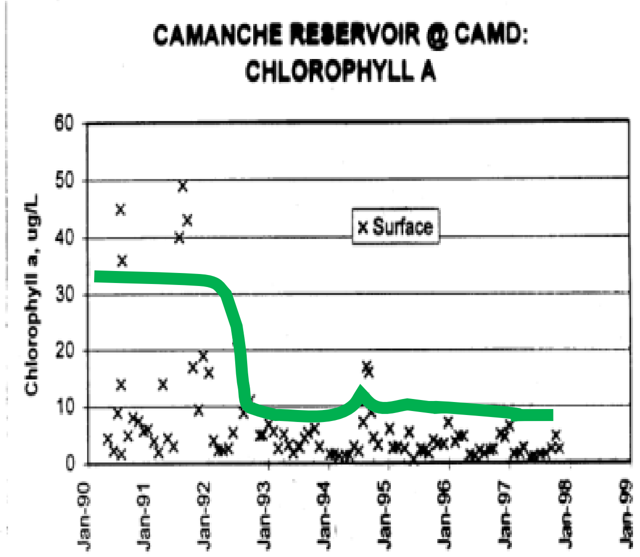
Deep Water inlet

- Evaporator + oxygen tank
- Camanche Reservoir EBMUD

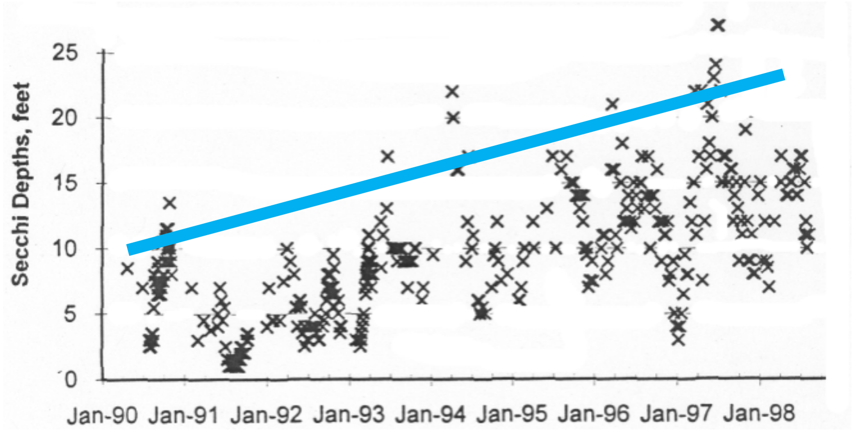
What other benefits are there with HOS?

- HOS & similar methods have been used for decades for other water quality advantages for drinking & recreational lakes & reservoirs
- While reducing MeHg you could get a lot of other benefits – lower algae, pH, particulates, toxicity, taste & odor
- Cost/benefit ratio can be very favorable $$$ saved?

HOS Oxygenation in Camanche Reservoir: first decade of eutrophication reversal

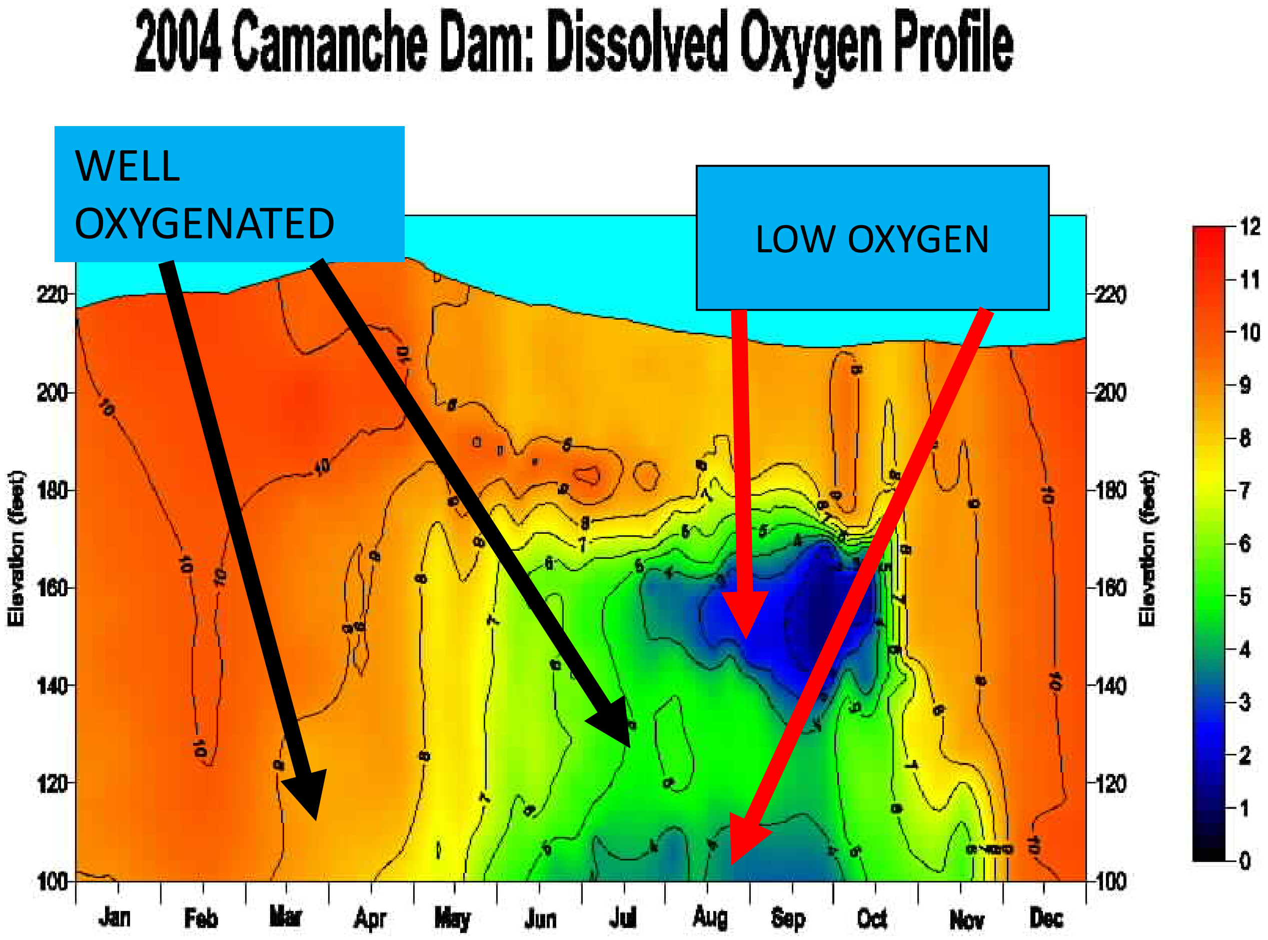


Secchi Depth



Important similarities & differences between HOS for removal of H_2S & MeHg

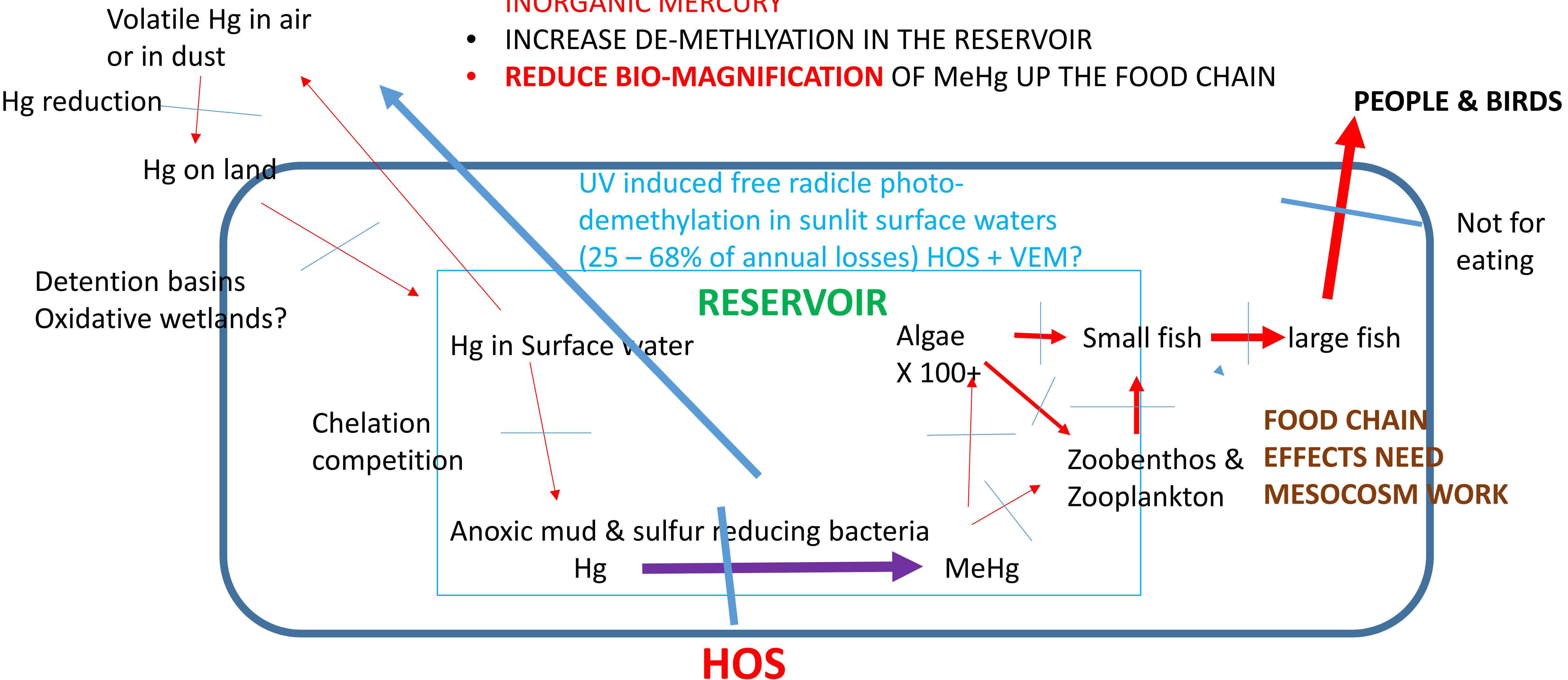
- Oxygen will easily & rapidly suppress production of H_2S or MeHg
- Any H_2S that is in the reservoir will be converted to harmless SO_4 or S within a day after mixing with oxygenated water
- Any MeHg in the reservoir will not easily or quickly be converted to Hg



MeHg removal: Critical path for mercury de-methylation & other losses from reservoirs (to be completed)

TWO KEY STEPS

- **REDUCE OR ELIMINATE ANOXIC BACTERIAL METHYLATION** OF INORGANIC MERCURY
- INCREASE DE-METHLYATION IN THE RESERVOIR
- **REDUCE BIO-MAGNIFICATION** OF MeHg UP THE FOOD CHAIN



More questions about MeHg

CHELATION

- Can we use methods used to decrease harmful effects of other metals for mercury? E.g. use of EDTA CHELATION for 6 heavy metals in the Los Angeles ACTA project.
- Method transports metal in an unavailable form to dilution & eventual breakup in the ocean
- Will it work for Hg & prevent methylation?

FOOD WEB MeHg REDUCTION

- Seems to be some contradictions in results. Could be due to test details
- Need to sort these out with MESOCOSM experiments in reservoirs along with pilot project work (a la Orange County Water Districts wetlands projects)

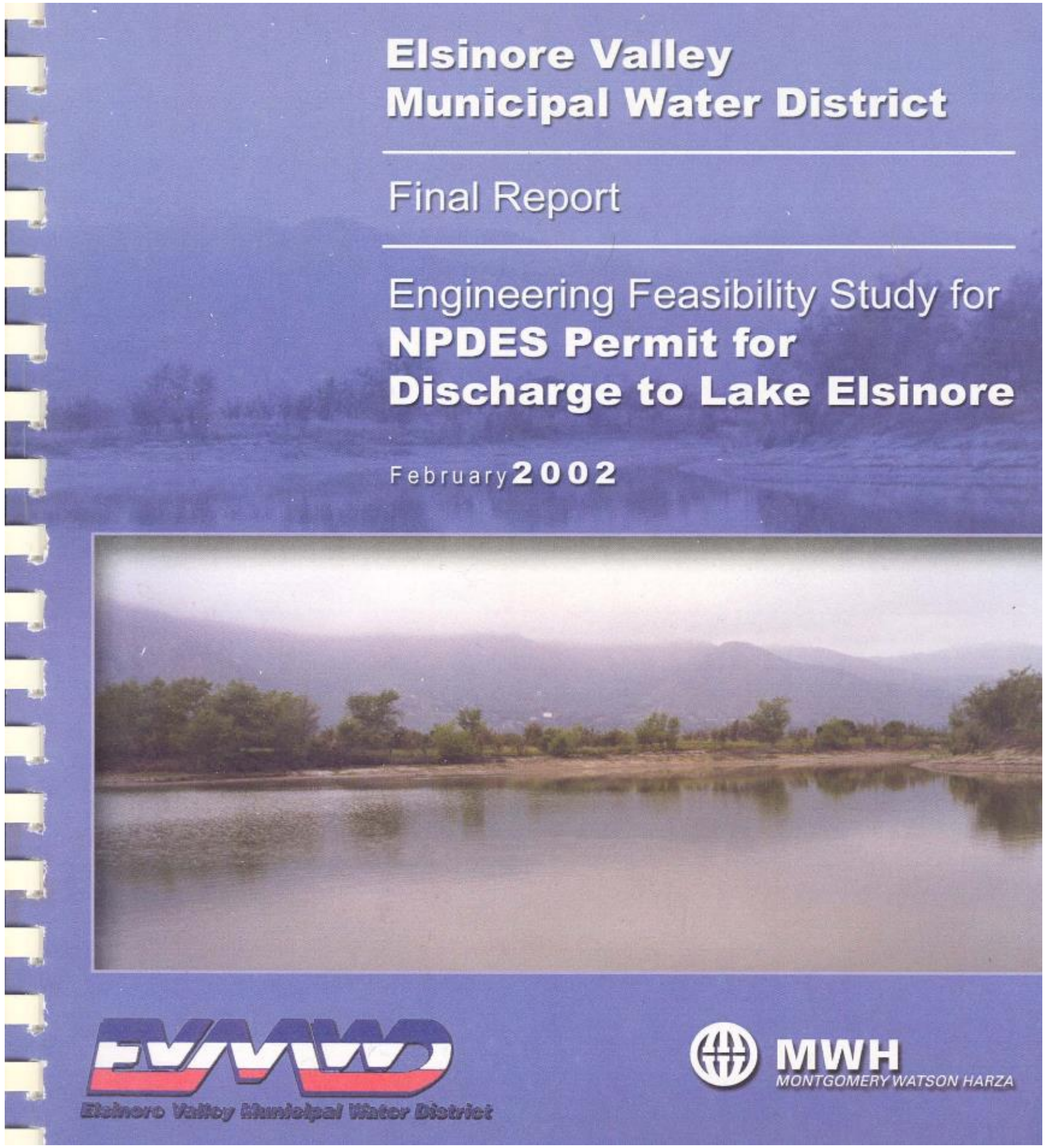
Cosms

- Microcosms are test tubes or small flasks in laboratories (~ 1 - 100 liters) that can be replicated (triplicate samples) easily
- Mesocosms are lager containers (1-10 m3) that can be replicated with some logistic problems
- Macrocosms are large, hard to replicate (acres or land or hundreds of m3)

THE 17 IN-LAKE & LAKE BED METHODS

- Physical controls: **Change** lake bathymetry, water/nutrient residence times, sediment chemistry, or light regime. Harvest weeds, algae, trash & fish.
- Chemical controls: **Poison** the undesirables or **restrict** anoxia, light or nutrient recycling.
- Biological controls: **Eat** or **harvest** the undesirables
- Biomanipulation: **Change** the food web and trophic pyramid

Lake Elsinore improvement



The 17 methods in action!

Table 5-2
Applicability Review of In-Lake Methods for Lake Elsinore

No.	Method	Applicability for Lake Elsinore	Use
1	**Dredging**	Too costly for a large lake where over 20 feet must be removed	No
2	**Water level fluctuation**	Stable lake level will improve shoreline for humans and riparian & submerged vegetation. Addition of recycled water is feasible from local sources. Nutrients added can be offset with oxygenation, wetlands and at-plant treatment. Is needed for bio-manipulation.	Yes
3	**Destratification and lake mixing**	Possible method using air mixing to move oxygenated surface water to anoxic sediments. Will require most energy when problems are worse. Not shown to work in warm climates	No
4	**Macrophyte (water weed) harvesting**	No weeds at present, mechanical harvesting may be needed along with herbicides in enhanced lake for inshore swimming/boating areas. Combine with bio-manipulation	Maybe
5	**Wetland algae filters (off-line wetlands)**	Good method for direct removal of algae using redesigned 350 acres of current lakebed "wetlands". High pumping cost, successful in tests in Florida. Discontinue after bio-manipulation	Yes
6	**Algae (phytoplankton) harvesting**	Cost is high unless algae are harvested and sold as high priced health food or food dye. Possible use with Oregon firms.	No
7	**Selective withdrawal of hypolimnion water**	No spare water to lose, would require a large siphon from the deeper lake to outlet	No
8	**Dilution/flushing**	No spare or clean water available in large amounts	No
9	**Sediment sealing (fabric liners, barriers)**	Lake too large for these methods. Could be used for weed control alongside docks, swim areas	Limited
10	**Herbicides (for algae or macrophytes)**	Will be needed to shape the expected vegetation growth following bio-manipulation. Combine with harvesting?	Yes
11	**Oxygenation or aeration**	Main method to prevent fish kill, odors, internal nutrient loading. Oxygenation only feasible method in Elsinore due to huge pipe runs needed for aeration in very shallow water. Reduce after bio-manip.	Yes
12	**Shading (dyes)**	Lake too large, dye lasts only a few months.	No
13	**Sediment sealing (alum, Phosloc or calcium carbonate)**	Lake very large for these methods, high cost, reserve for limited use if aeration/oxygenation is not fully effective for PO_4. Not recommended for Elsinore; increases toxicity and pH. Recent experiments show alum can be replaced with oxygenation.	No
14	**Pathogens of algae or macrophytes**	Ineffective for blue-green algae due to resistance buildup. None known for macrophytes	No
15	**Fish grazers on algae or macrophytes**	Not applicable, lake needs more submerged macrophytes, not less	No
16	**Nutrient harvesting from fish or other biota**	Many small fish and large carp will be harvested as part of the bio-manipulation process. N and P removal expected to be small relative to inflows. Combine with bio-manipulation	Yes
17	**Bio-manipulation**	Main sustainable method to remove nuisance algae, tie up nutrients, reduce sediment re-suspension	Yes

Limnological metrics for anoxia

- MeHg bacteria are inhibited by even a whiff of dissolved oxygen (~ 0.1 mg/L)
- This is easy with many methods of aeration-oxygenation-mixing
- However, getting oxygen deeper into the mud depends on method used
- So DO > 2 mg/L in bottom water essential, really need > 5 mg/L

Climate change & MeHg

- Assume an increase over next 50 years of 0.5-3.0 ºC (0.01 to 0.06ºC/y - current rate of increase is – 0.006ºC/y, NASA)
- Reservoirs will stratify earlier in year and de-stratify later = longer anoxia
- Hypolimnion deep water will be warmer = faster MgHg production