Wetland Restoration and the Potential for Enhanced Mercury Methylation

By
Mark Marvin-DiPasquale
U.S. Geological Survey, Menlo Park, CA 94025

U.S. Ecosystem Hg Process Studies (1995-2004)

USGS

Wetland Focus for This Presentation
The BIG 3

USGS

Focus on Saltmarsh / Wetlands

- Known to be important zones of MeHg production
- Hg-cycling pathways poorly understood
- Current emphasis on wetland restoration
  (San Francisco Bay, Everglades, Gulf Coast)
- Potential for increased MeHg production
- Critical food web regions
  - high biodiversity
  - link aquatic and terrestrial food webs

USGS

What is a Wetland?

- USFW Definition "Wetlands are lands transitional between terrestrial and aquatic systems where the water table is usually at or near the surface or the land is covered by shallow water."

Huge diversity in:

- vegetation type
- hydrology / inundation periods
- salinity
- organic content
- redox conditions
- food web structure
- mineralogy / grain size
- geomorphic features:
  mudflats, vegetated zones, sloughs, etc…

ALL IMPACT Hg CYCLING!

USGS

What Controls NET MeHg Production?

Net MeHg Prod. = Gross MeHg Prod. - Gross MeHg Degrad.

MICROBIAL ACTIVITY

Hg(II)-Methylating Bacteria & MeHg-Degrading Bacteria

- community composition
- electron donors (org-C)
- electron acceptors

  (e.g. Fe(III), SO_4^{2-})
- pH and redox (Eh)
- temperature

MERCURY AVAILABILITY

Reactive-Hg(II) and MeHg

- amount of total Hg or MeHg
- complexation w/ DOM
- binding to particles
- pH and redox (Eh)
- sulfur chemistry
- salinity (Cl^-)
- chemical form: (HgS, HgS_2^{2-}, $HgCl_2$, $HgCl_4^{2-}$, etc…)

USGS

Hg Radiotracer Studies in Sediment

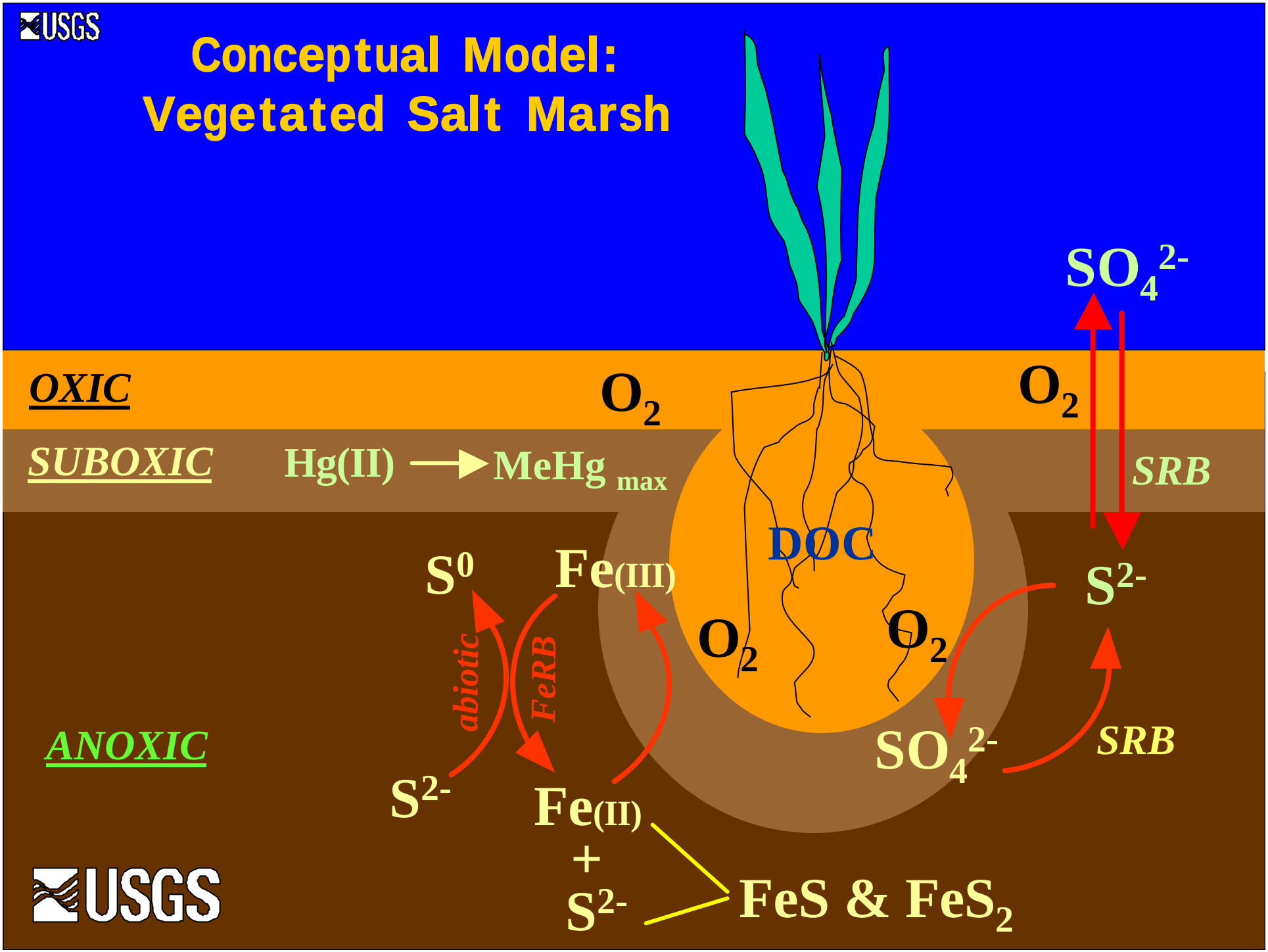
- $^{203}Hg(II)$-Methylation → $CH_3{}^{203}Hg^+$
- $^{14}CH_3Hg^+$ Degradation → $^{14}CO_2$ + $^{14}CH_4$ + Hg(II, 0)
- whole sediment anoxic incubations (4-24 hrs)
- manipulations

  (O_2, SO_4^{2-}, S^{2-}, acetate,

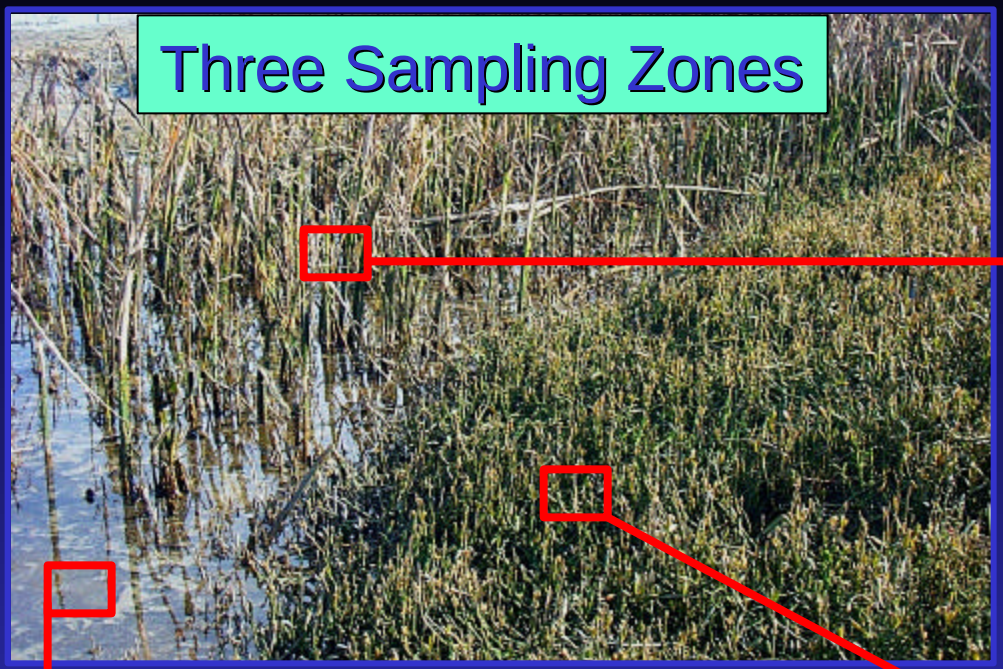
  DOC, Fe, temp., …)
- POTENTIAL RATES!

  MP = K x $^{203}Hg(II)$

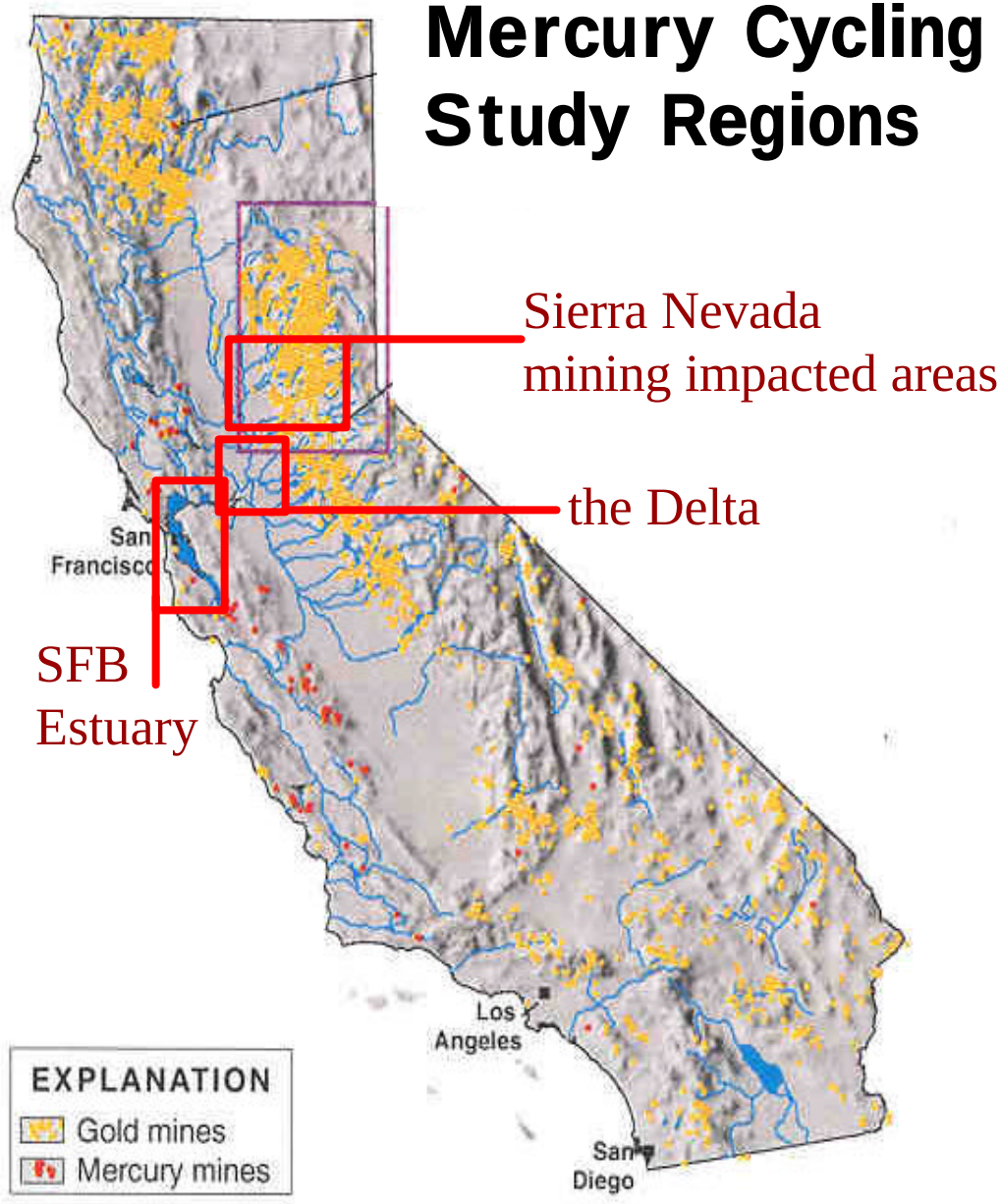
  MD = K x $^{14}CH_3Hg^+$


USGS
Conceptual Model:
Vegetated Salt Marsh
OXIC
SUBOXIC
ANOXIC
Hg(II) → MeHg max
O2
O2
O2
O2
SO4 2-
SRB
SRB
DOC
S0
Fe(III)
S2-
abiotic
FeRB
SO4 2-
S2-
Fe(II)
+
S2-
FeS & FeS2
USGS

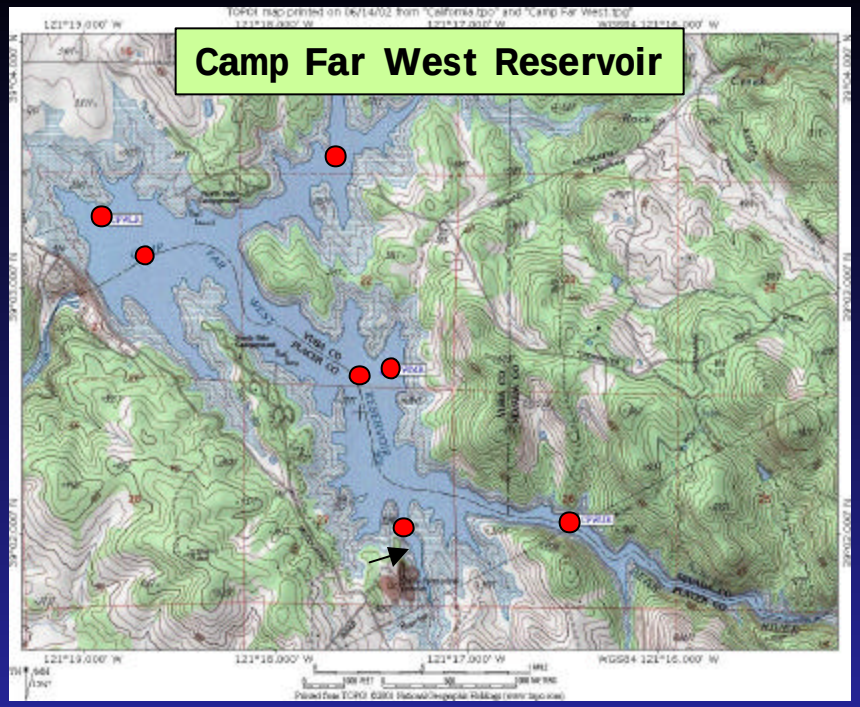
Steven's Creek Marsh- South SFB

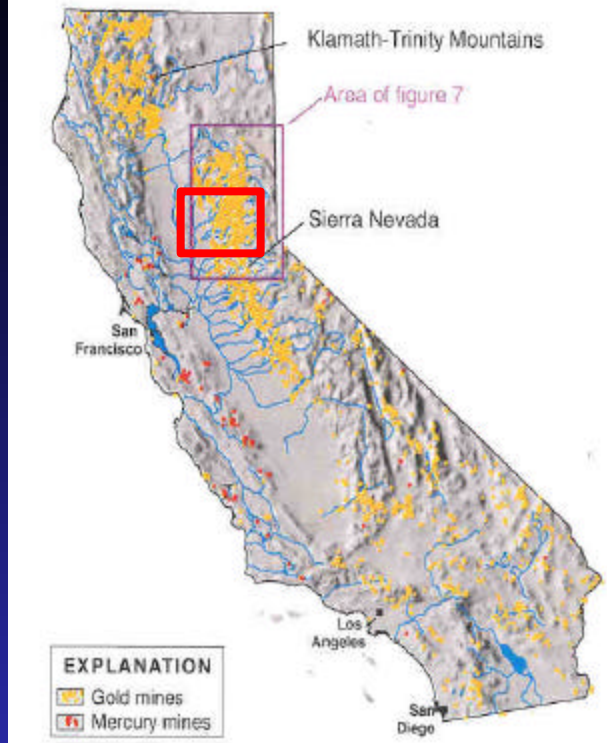


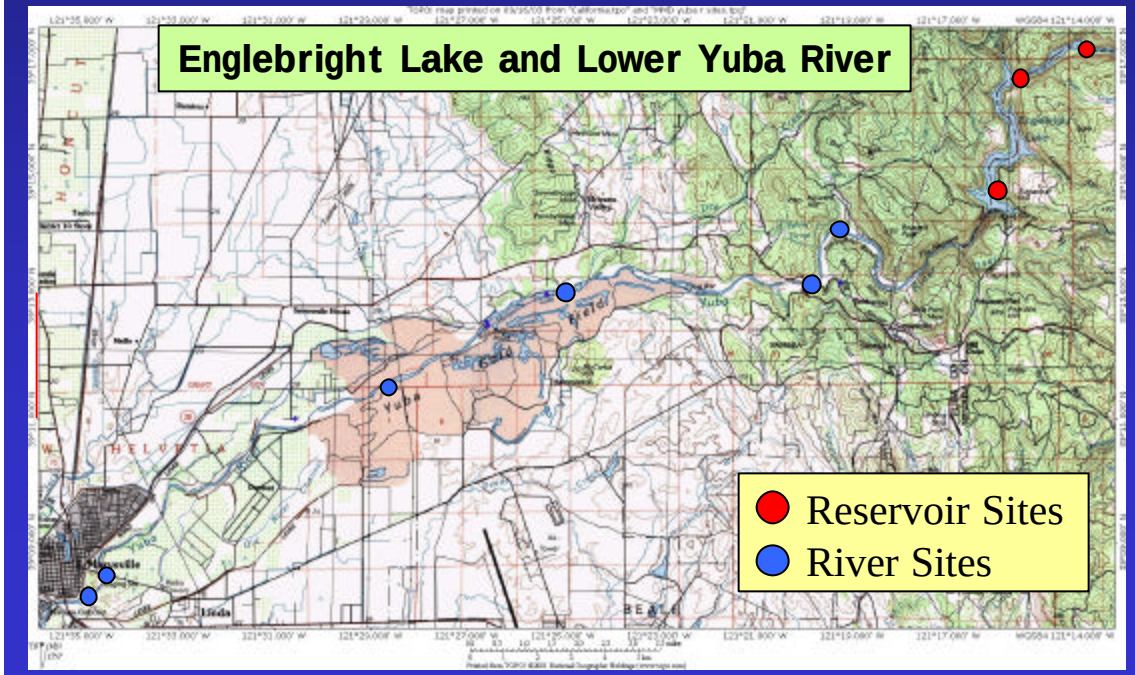
San Francisco Bay Watershed Mercury Cycling Study Regions

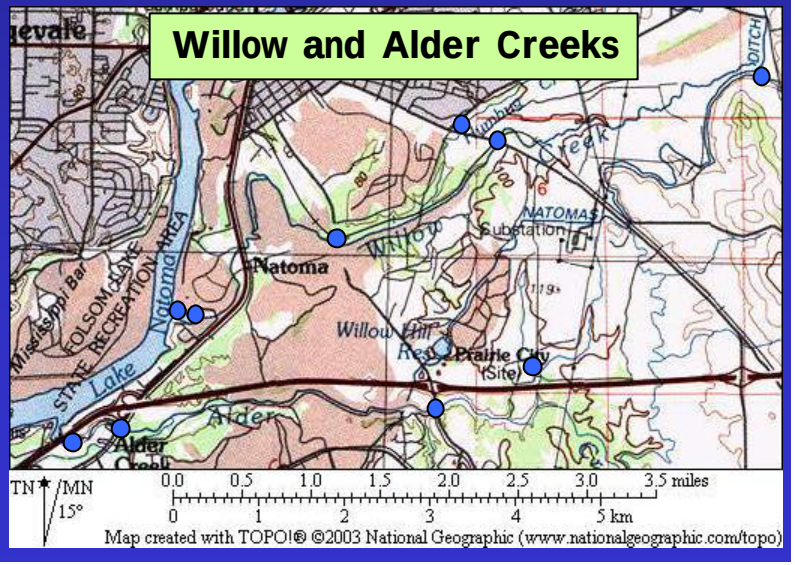


USGS

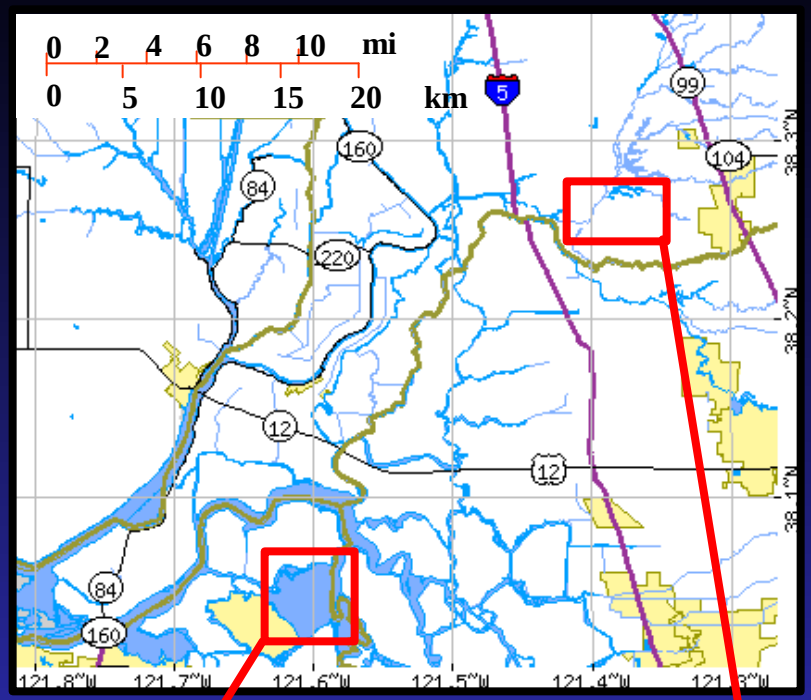

Camp Far West Reservoir


Klamath-Trinity Mountains
Area of figure 7
Sierra Nevada
San Francisco
Los Angeles
San Diego
EXPLANATION
Gold mines
Mercury mines

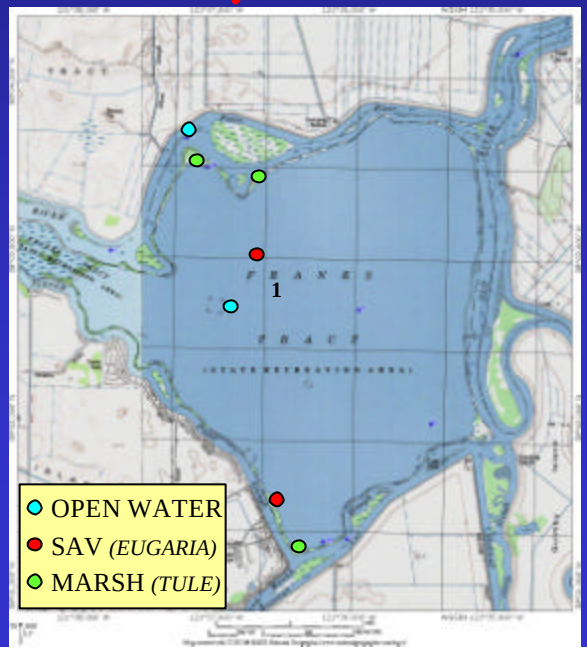

Englebright Lake and Lower Yuba River
Reservoir Sites
River Sites


Willow and Alder Creeks
Natoma
Prairie City (Site)
Alder Creek
Willow Hill Res.
NATOMAS Substation
FOLSOM LAKE STATE RECREATION AREA
Lake Natoma
TN MN 15°
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 miles
0 1 2 3 4 5 km
Map created with TOPO!® ©2003 National Geographic (www.nationalgeographic.com/topo)

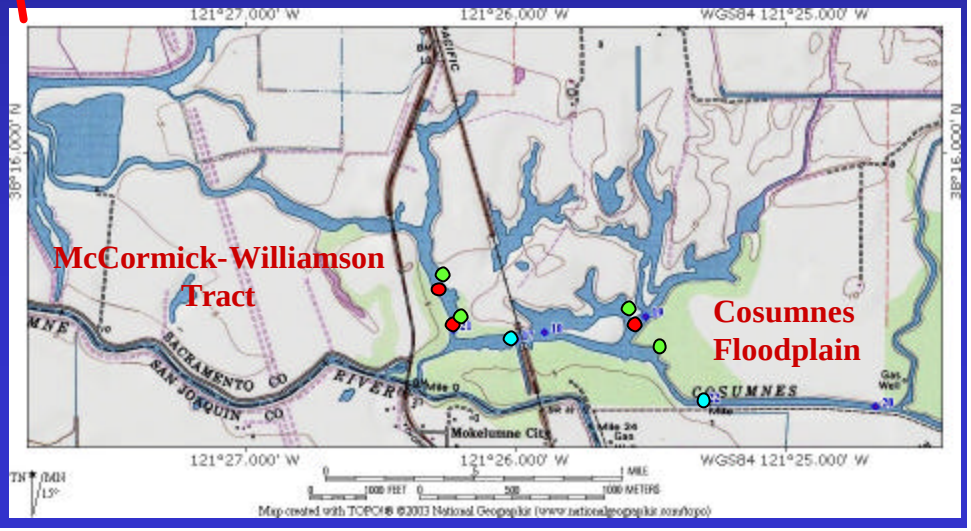
SFB - Delta



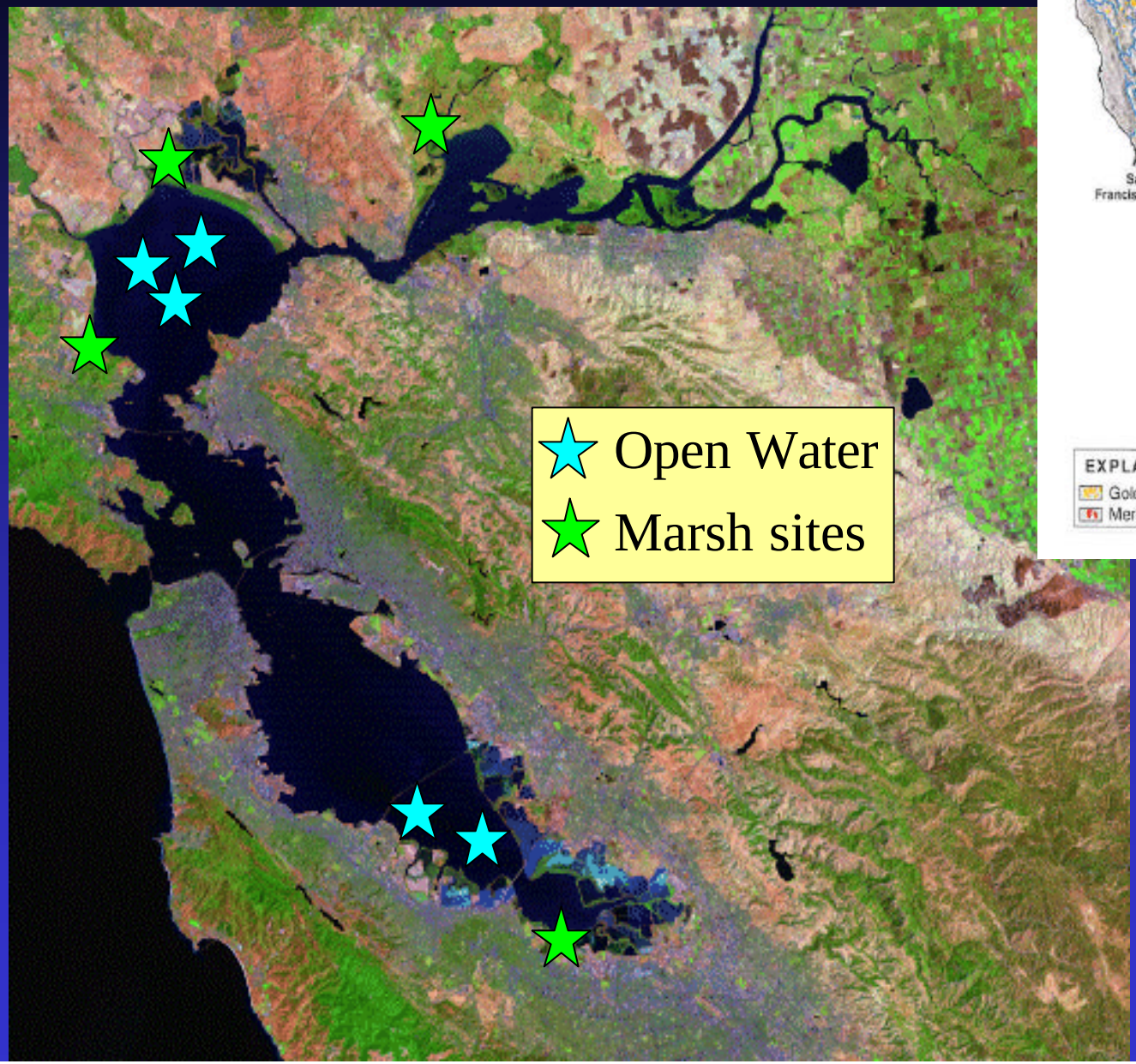
Frank's Tract



Cosumnes River

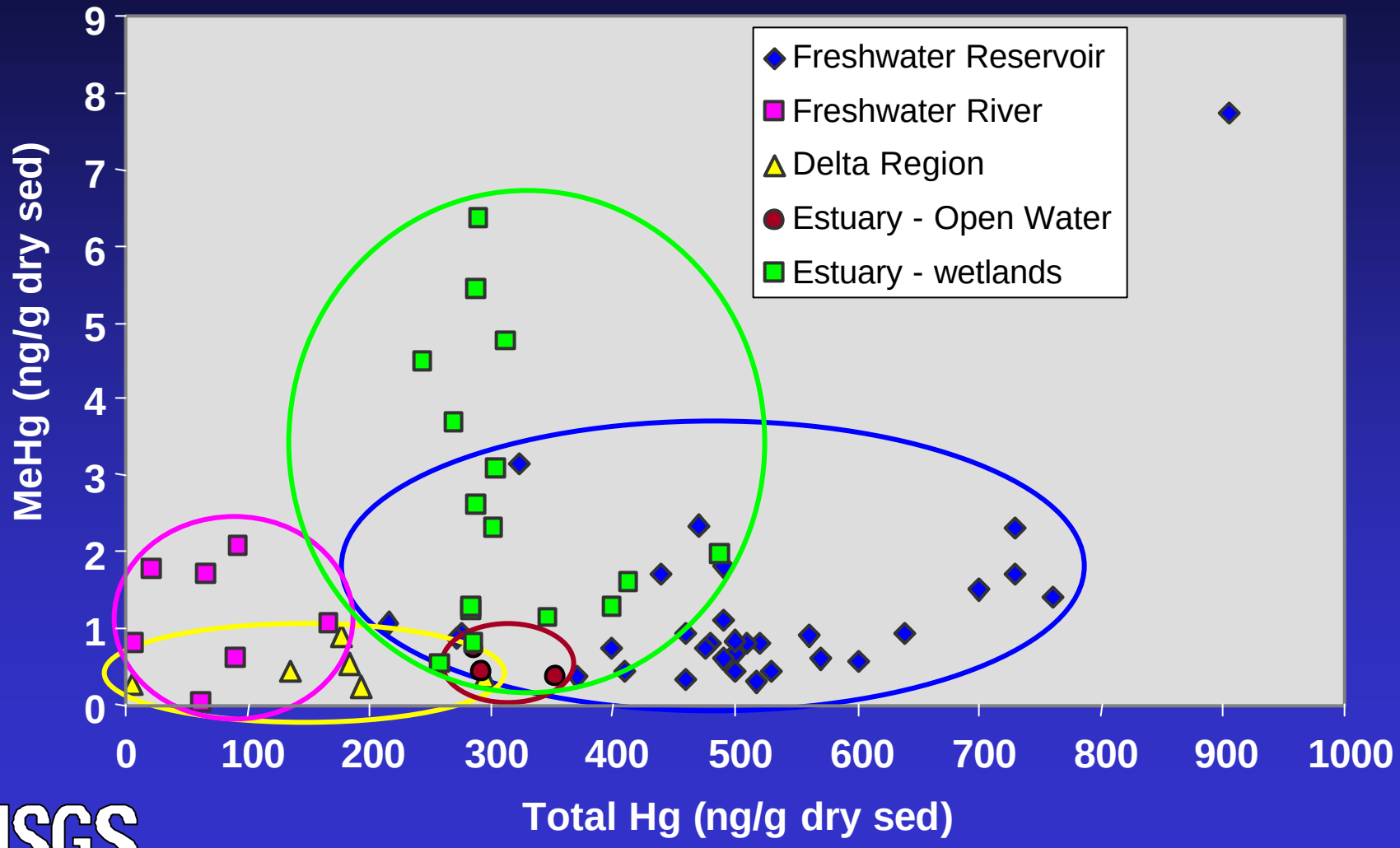


San Francisco Bay (CA)

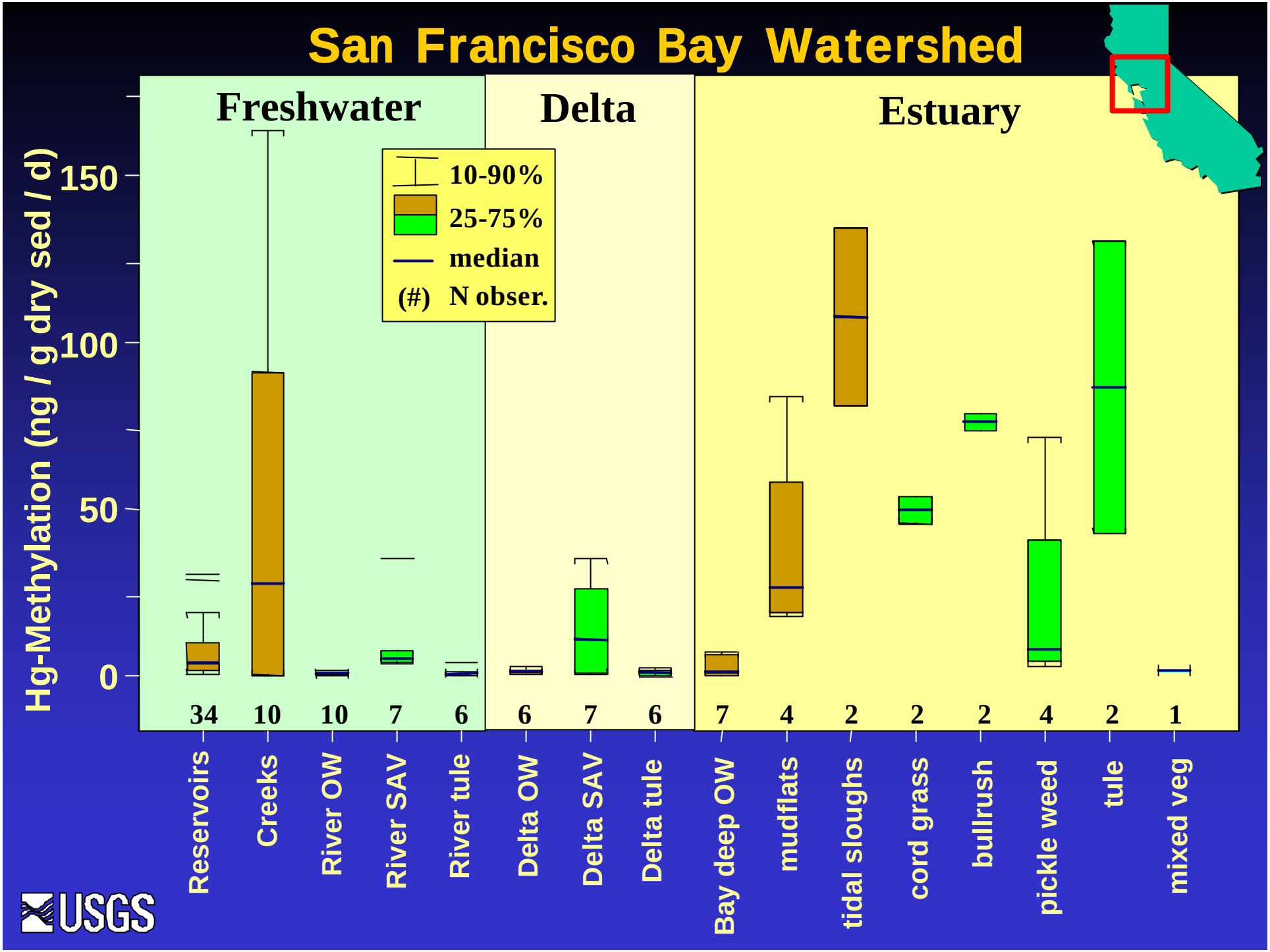


USGS

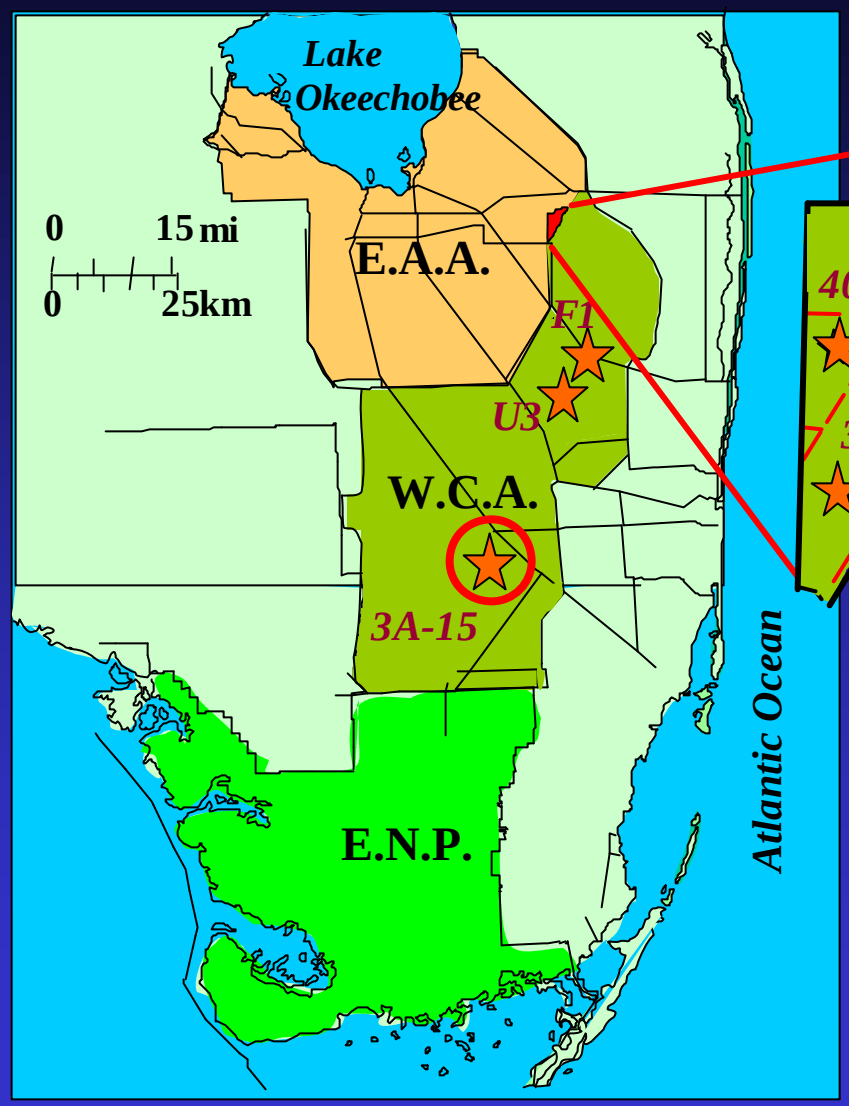
Total Hg vs MeHg
SFB Watershed

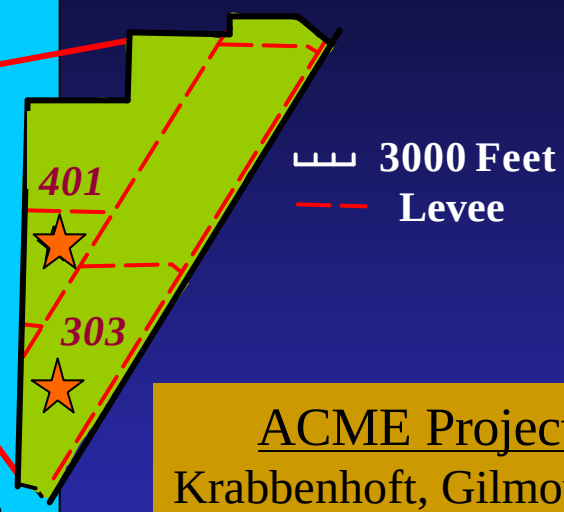


USGS


San Francisco Bay Watershed
Freshwater
Delta
Estuary
10-90%
25-75%
median
(#) N obser.
Hg-Methylation (ng / g dry sed / d)
150
100
50
0
34
10
10
7
6
6
7
6
7
4
2
2
2
4
2
1
Reservoirs
Creeks
River OW
River SAV
River tule
Delta OW
Delta SAV
Delta tule
Bay deep OW
mudflats
tidal sloughs
cord grass
bullrush
pickle weed
tule
mixed veg
USGS

Florida Everglades





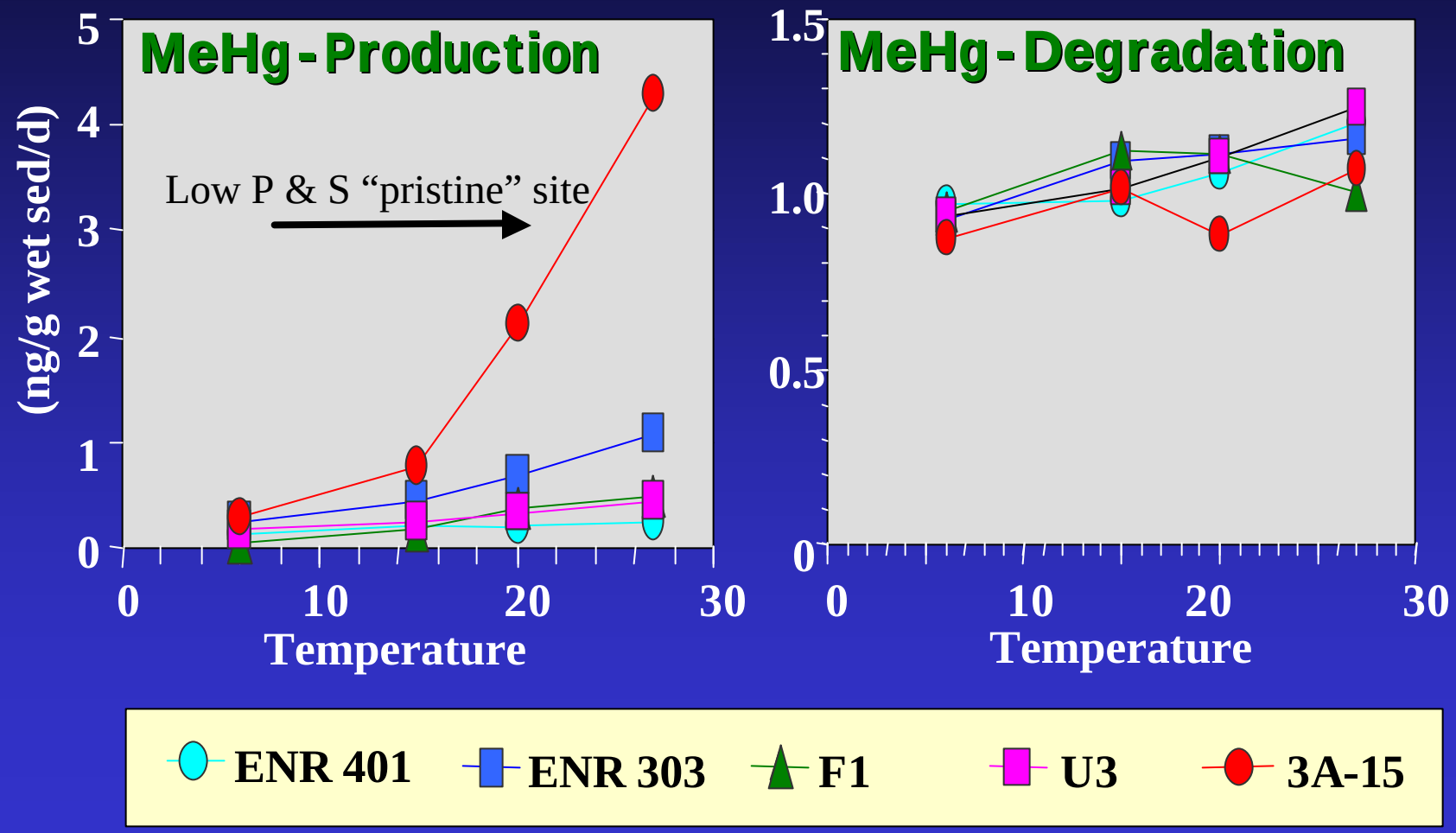
ACME Project (1995-98):
Krabbenhoft, Gilmour, Orem, Aiken, Marvin-DiPasquale, Kendall, et al.

North → South Gradients in:

- Nutrients (PO_4^{-3})
- Macrophytes
- Sulfur
- Hg-methylation

USGS

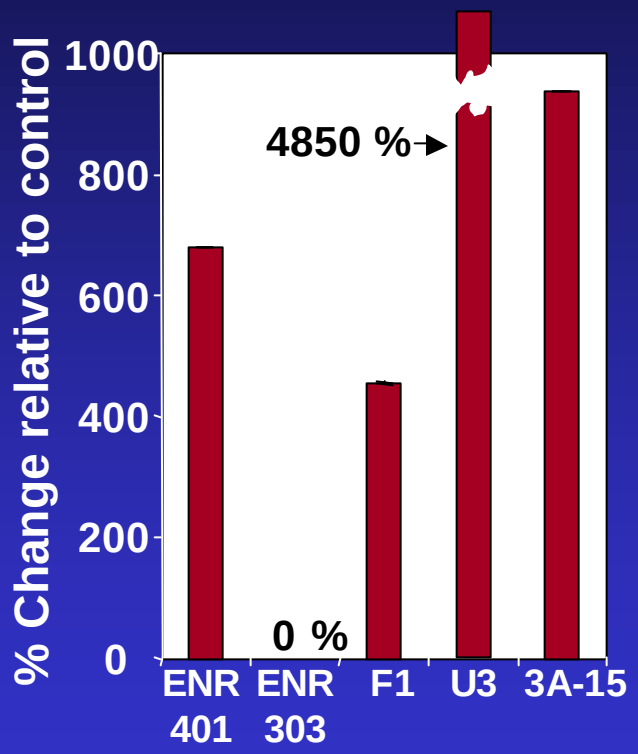
Florida Everglades
Temperature Response Curves



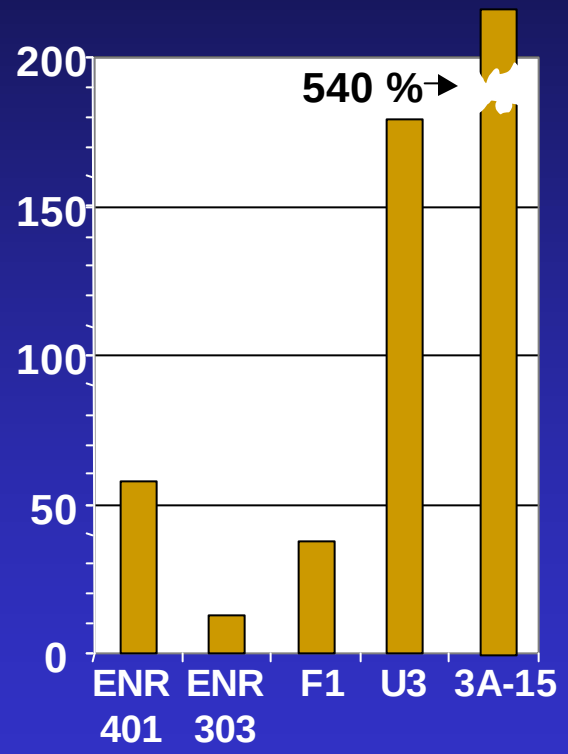
USGS

Sulfate Addition to Everglades Sediment

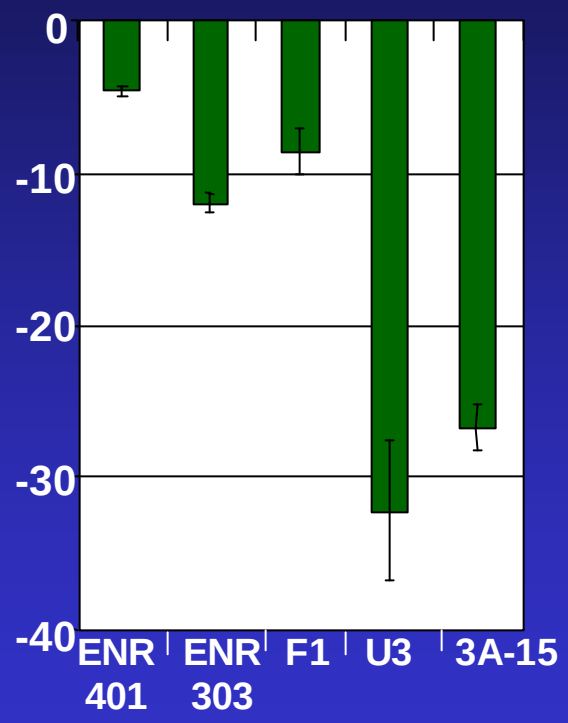
Increased Microbial SR…



…which Increased Sulfide Production



…and Decreased Hg Methylation

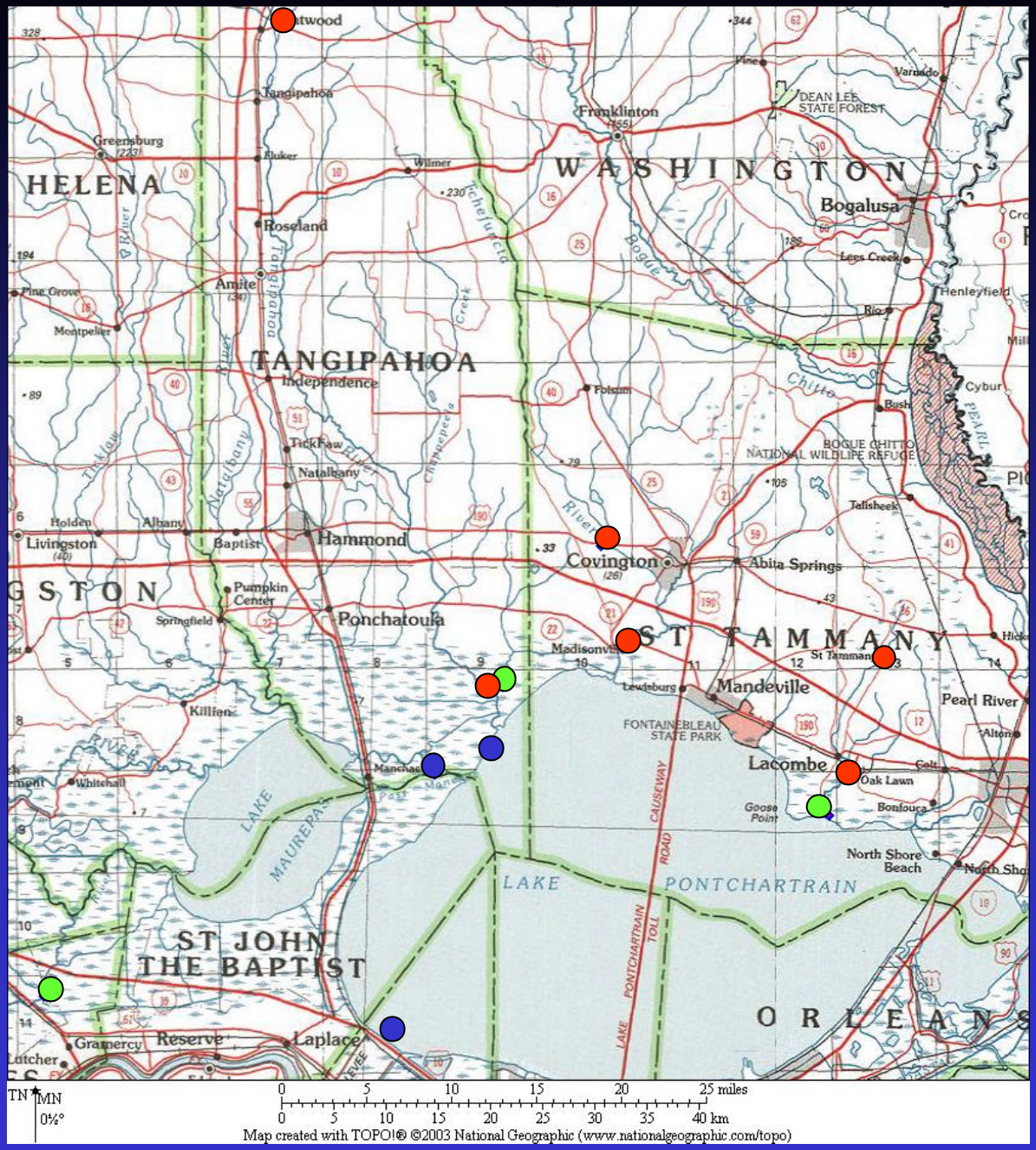


SO_4^{2-} Amendment: 20 mmol/g sed. slurry, Incubation Time = 18 hours

USGS

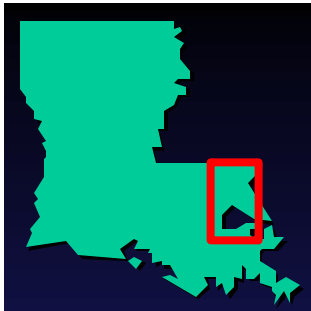
Lake Pontchartrain Watershed (LA) (August '03)

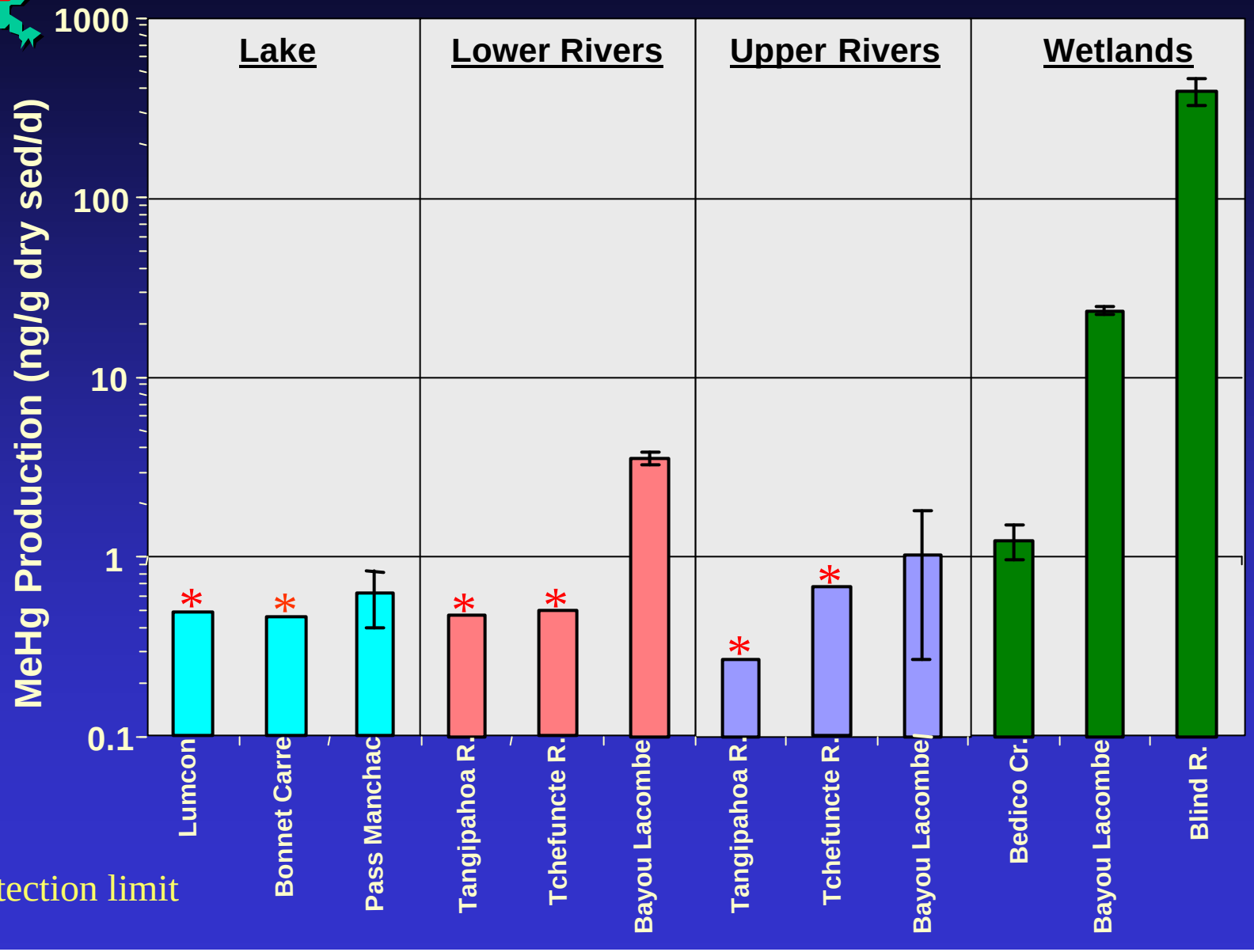
- Lake
- Wetlands
- Rivers



USGS

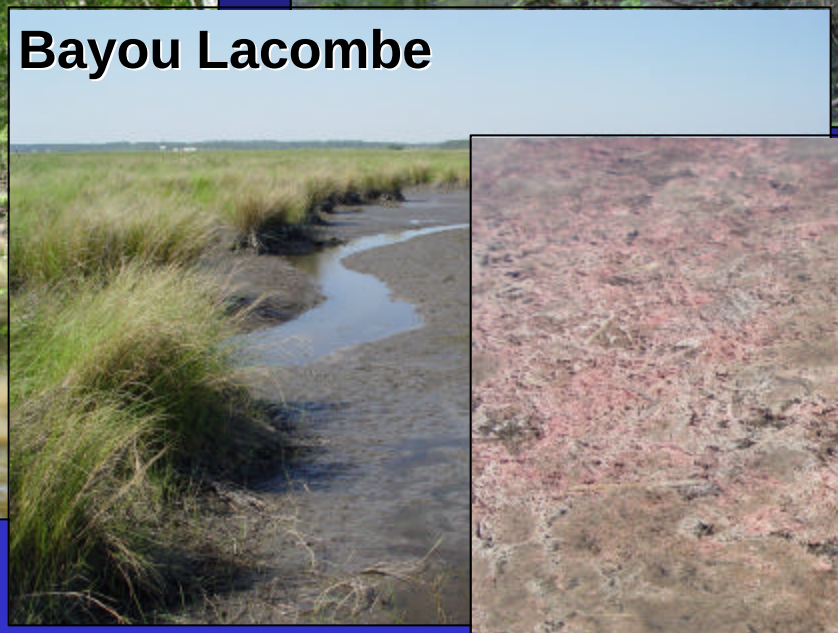
Lake Pontchartrain Watershed (LA), August '03
Hg-Methylation Potential Rates

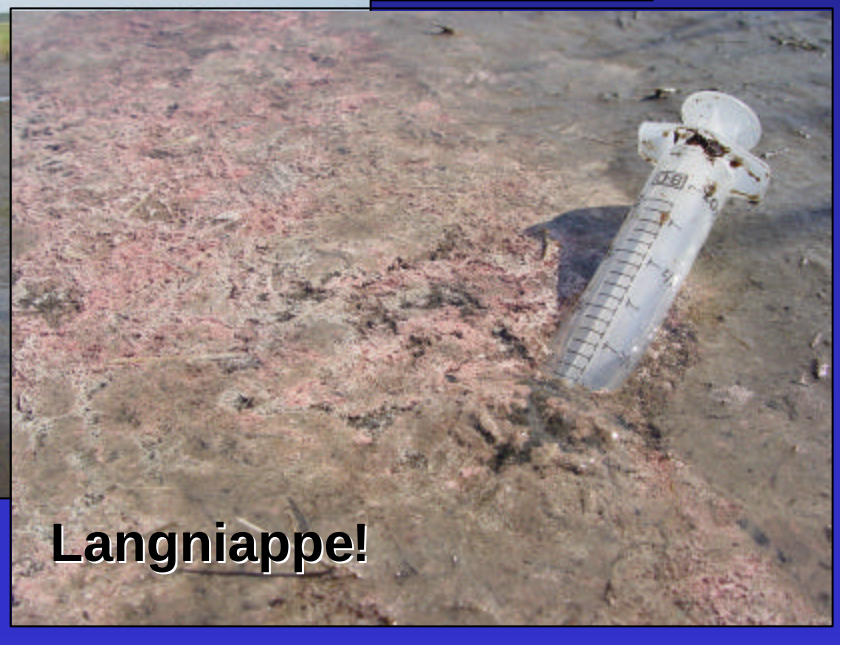




* = detection limit

Louisiana Wetlands (April '04)

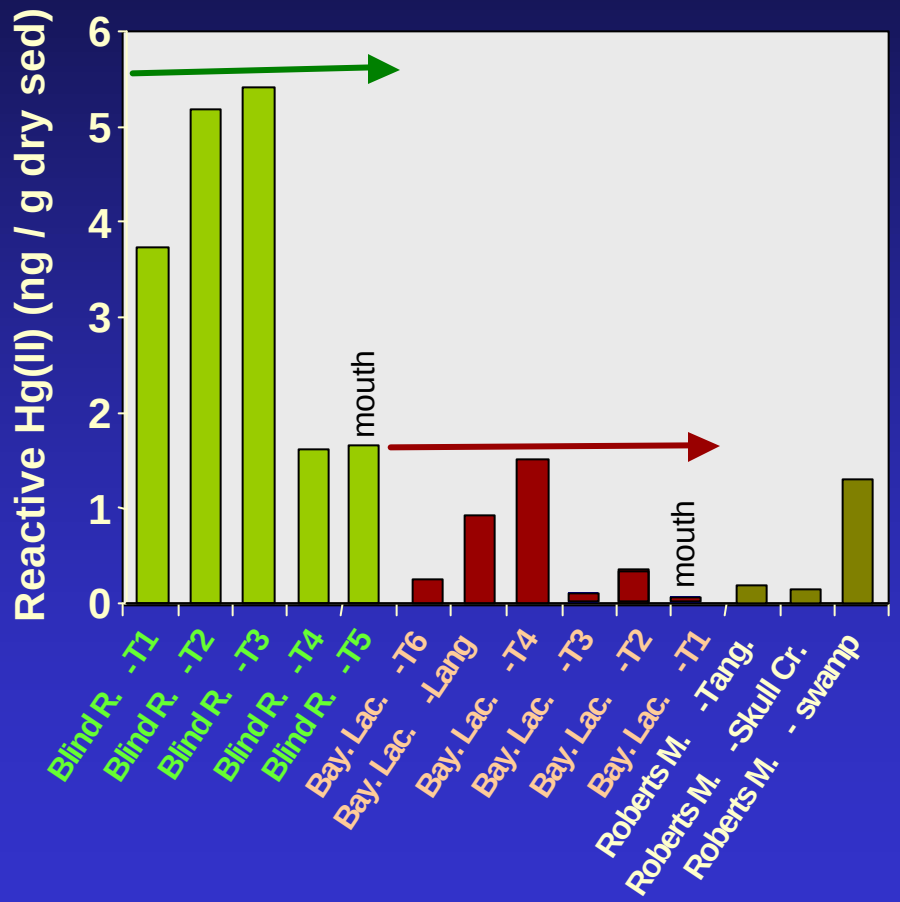


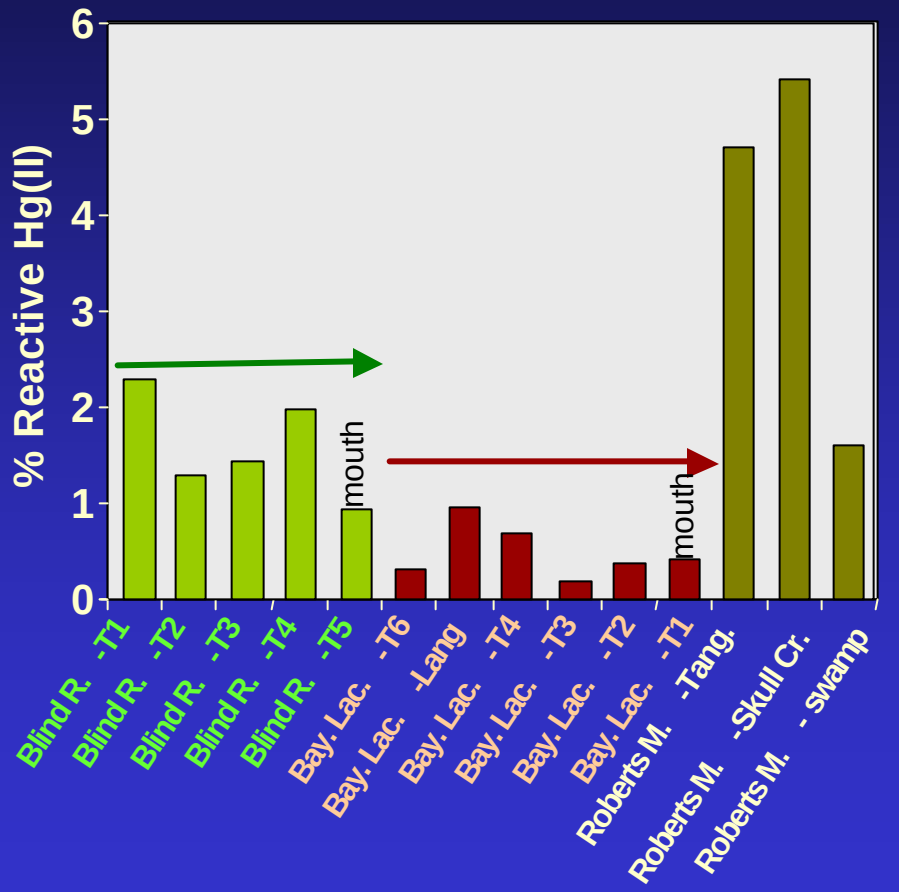


USGS

Reactive Hg(II): Louisiana Wetlands, April '04 (surface 0-2 cm interval)

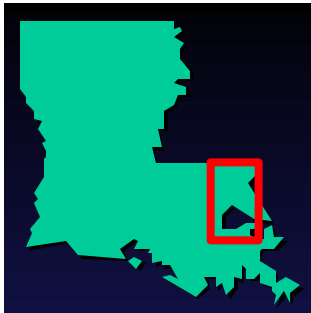
sediment-Hg(II) $\xrightarrow[\text{[SnCl}_2\text{]}]{\text{[0.06 M HCl]}}$ $Hg^0(g)$ $\xrightarrow{\text{[Au-trap]}}$ **CVAFS Detection**





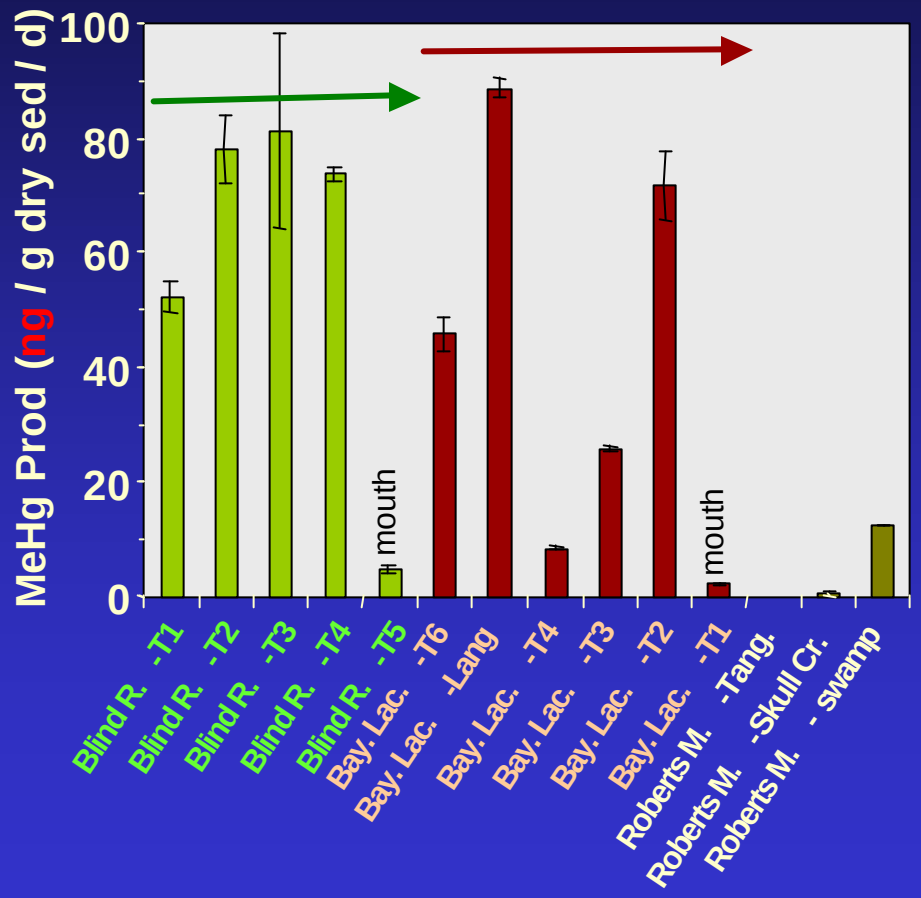
USGS

MeHg Production: Louisiana Wetlands, April '04
Dry Sediment Rates (surface 0-2 cm interval)



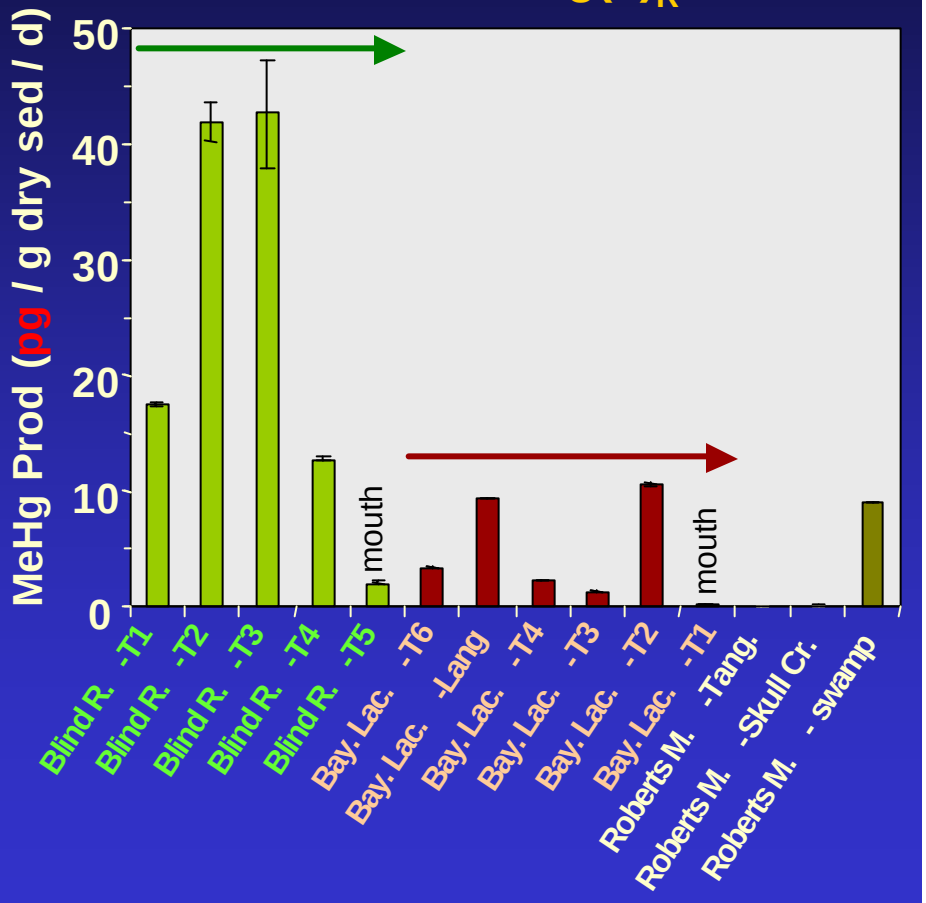
Based on ^{203}Hg(II) added *

MP = K x ^{203}Hg(II)



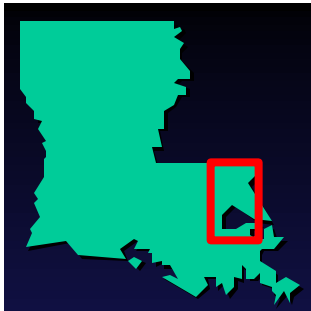
Based on REACTIVE Hg(II)

MP = K x $Hg(II)_R$

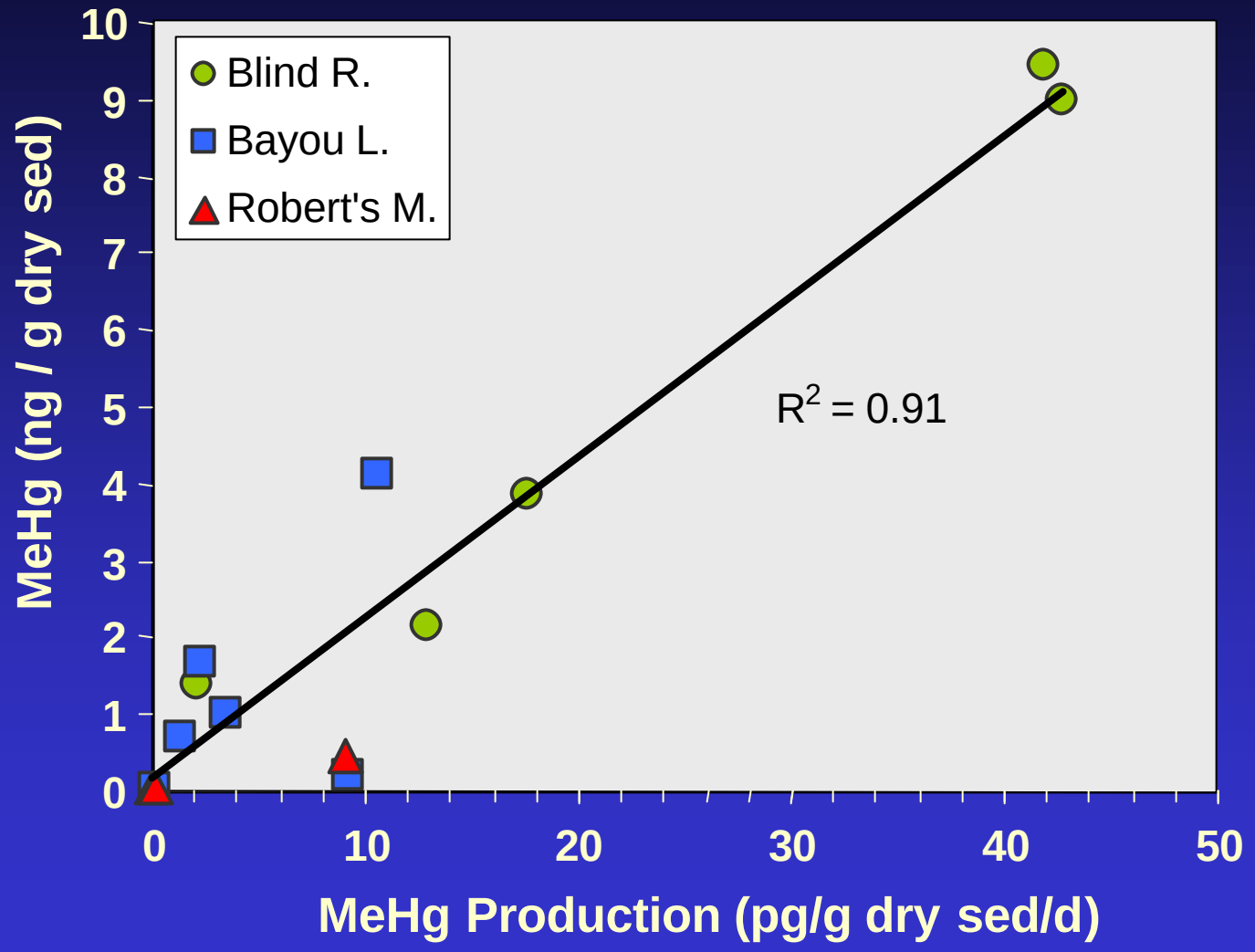


* ^{203}Hg(II) added = 500 ng / g wet sed

USGS

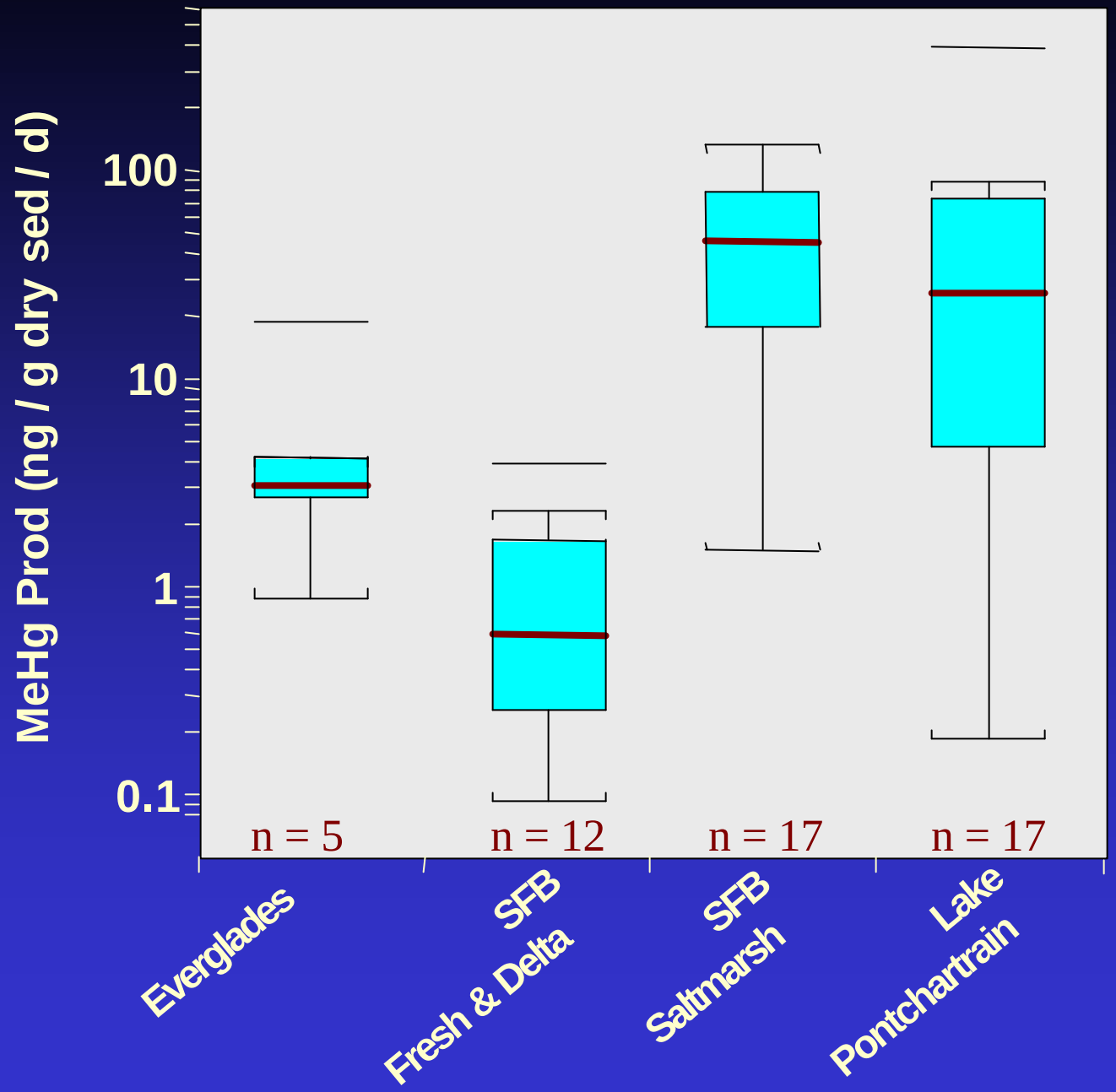


MeHg Production based on REACTIVE Hg(II) vs MeHg concentration (dry wt.)



USGS

Regional MeHg Production: The Big 3 Wetlands



USGS

Take Home Message

- MeHg production / degradation rates vary widely among <u>and</u> within wetland ecosystems

- Plant root zones can have a substantial effect on MeHg production (both + and -).

- Reactive-Hg(II) varies with substrate (£ 5% of total Hg)

- Wetland Restoration: Success will depend on understanding the Hg cycle in various sub-habitats that comprise a wetland

USGS

So Many "Thank You's", So little time…

Collaborators

D. Krabbenhoft – *USGS, Middleton WI*
C. Alpers – *USGS, Sacramento CA*
J. Kuwabara – *USGS, Menlo Park CA*
R. Stewart – *USGS, Menlo Park CA*
B. Jaffe – *USGS, Santa Cruz CA*
G. Aiken – *USGS, Boulder CO*
D. Wentz – *USGS, Portland OR*
L. Chasar – *USGS, Tallahassee FL*
B. Scudder – *USGS, Middleton WI*
M. Brigham – *USGS, Mounds View MN*
B. Hall – *Univ. WI (Madison)*
R. Mason – *Univ. MD (Solomons)*
A. Heyes – *Univ. MD (Solomons)*

Technical Support

USGS – Menlo Park, CA
J. Agee
L.H. Kieu
H. Harms
B. Topping
USGS, Middleton WI
M. Olson
S. Olund
J. DeWild
M. Lutz
USGS, Baton Rouge LA
D. Demcheck
C. Demas

Funding

CALFED / CBDA
SFWMD
CA State Water Resources Control Board
Bureau of Reclamation
CA Dept. of Fish and Game
CA Dept. of Water Resources
USGS Toxics Program
USGS Congressional Earmark's for the Lower Mississippi

USGS