Aquatic Chemistry of Mercury

Factors Influencing the Reactivity and Fate of Mercury in Aquatic Systems

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Thanks to: All people in my lab and in others who have contributed data to this talk.
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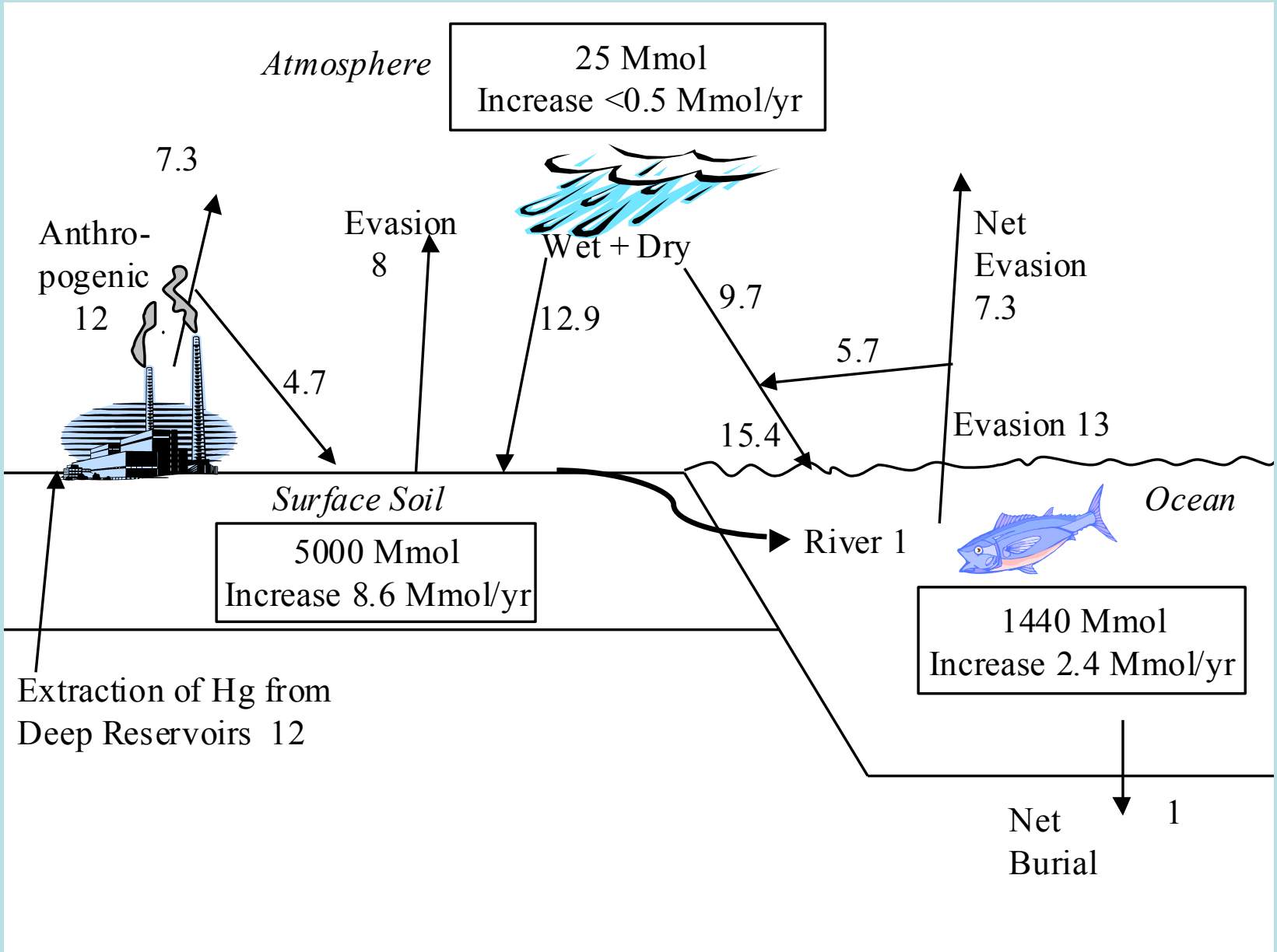


Mason and Sheu, 2002

Factors Controlling Mercury Fate, Transport And Net Methylation in Aquatic Systems

1. Source and Form of Mercury
2. Factors Controlling Air-Water Exchange and Mercury Evasion/Loss from the System
3. Factors Controlling Mercury Bioavailability
4. Factors Controlling Microbial Activity

Relative Sources and Sinks (as % of total) to Various Aquatic Systems

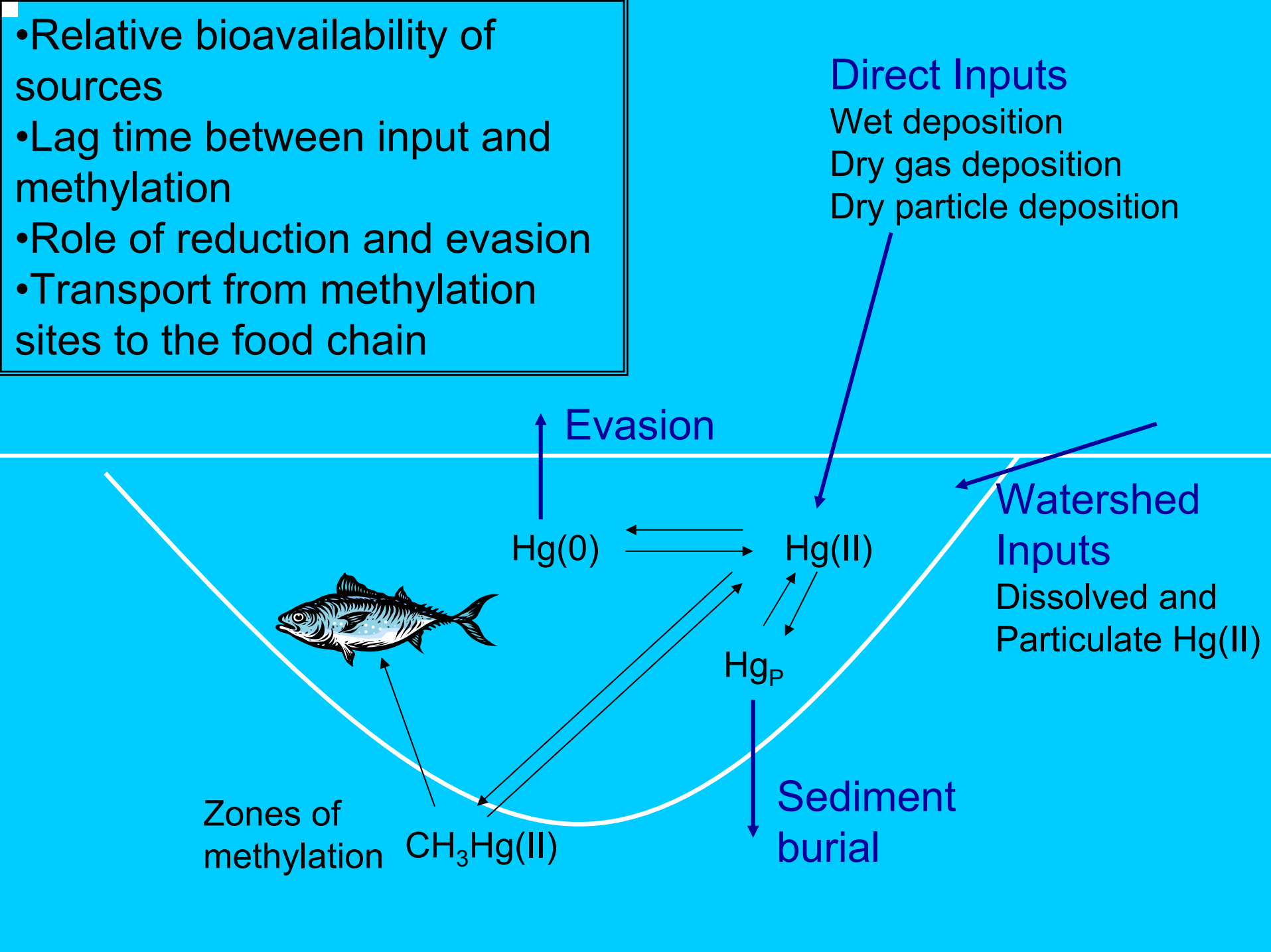
Site	Lake 658	Little Rock	Michigan	Ches. Bay
Inputs	(Gilmour)	(Fitz. et al)	(Mason&Sullivan)	(Mason et al)
Wet +Dry $	19	100	82	29
Watershed	74	-	17	41
Other Land #	7	-	1	8
Other *	-	-	-	21
Outputs				
Evasion	33	6	44	13
Sedimentation	50	87	54	43
Outflow	17	-	2	42
Fish	-	13	-	1

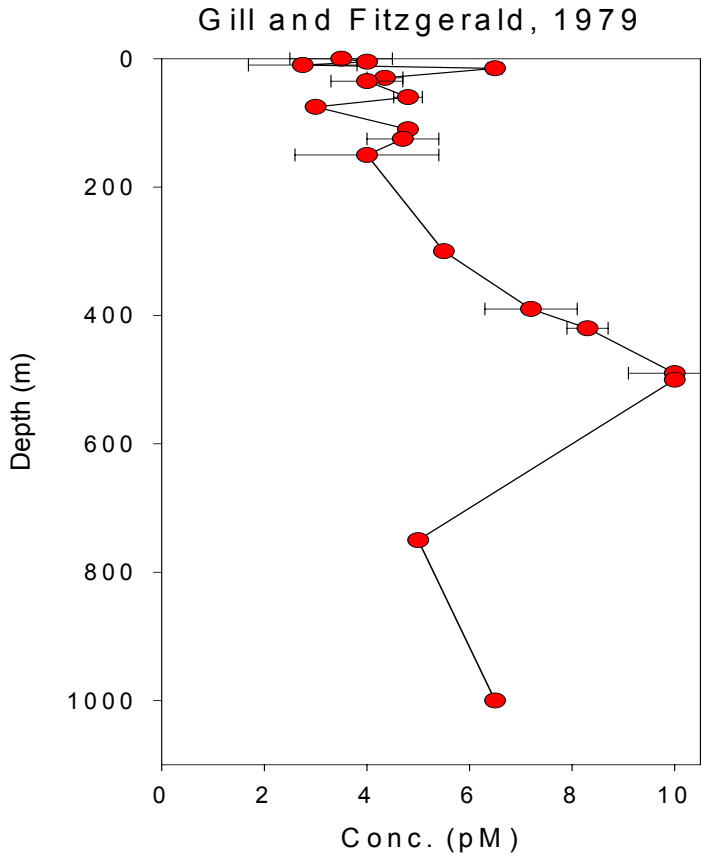
Notes: $ Estimates do not include dry deposition of RGHg which could be significant for the Chesapeake Bay

\# Either wetland inputs or groundwater inputs

* Input from ocean for the Chesapeake Bay

- Relative bioavailability of sources
- Lag time between input and methylation
- Role of reduction and evasion
- Transport from methylation sites to the food chain





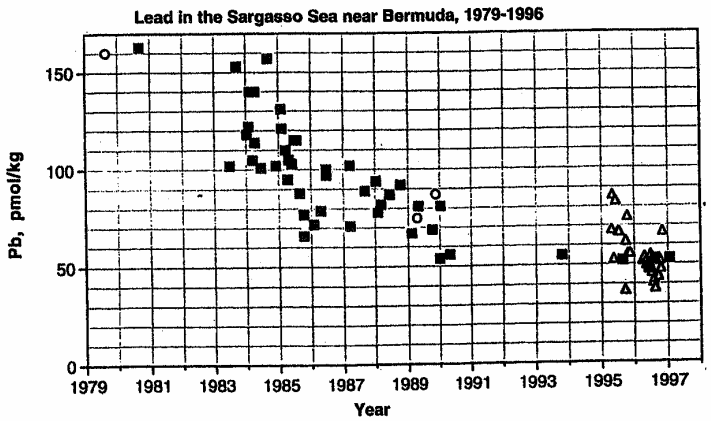
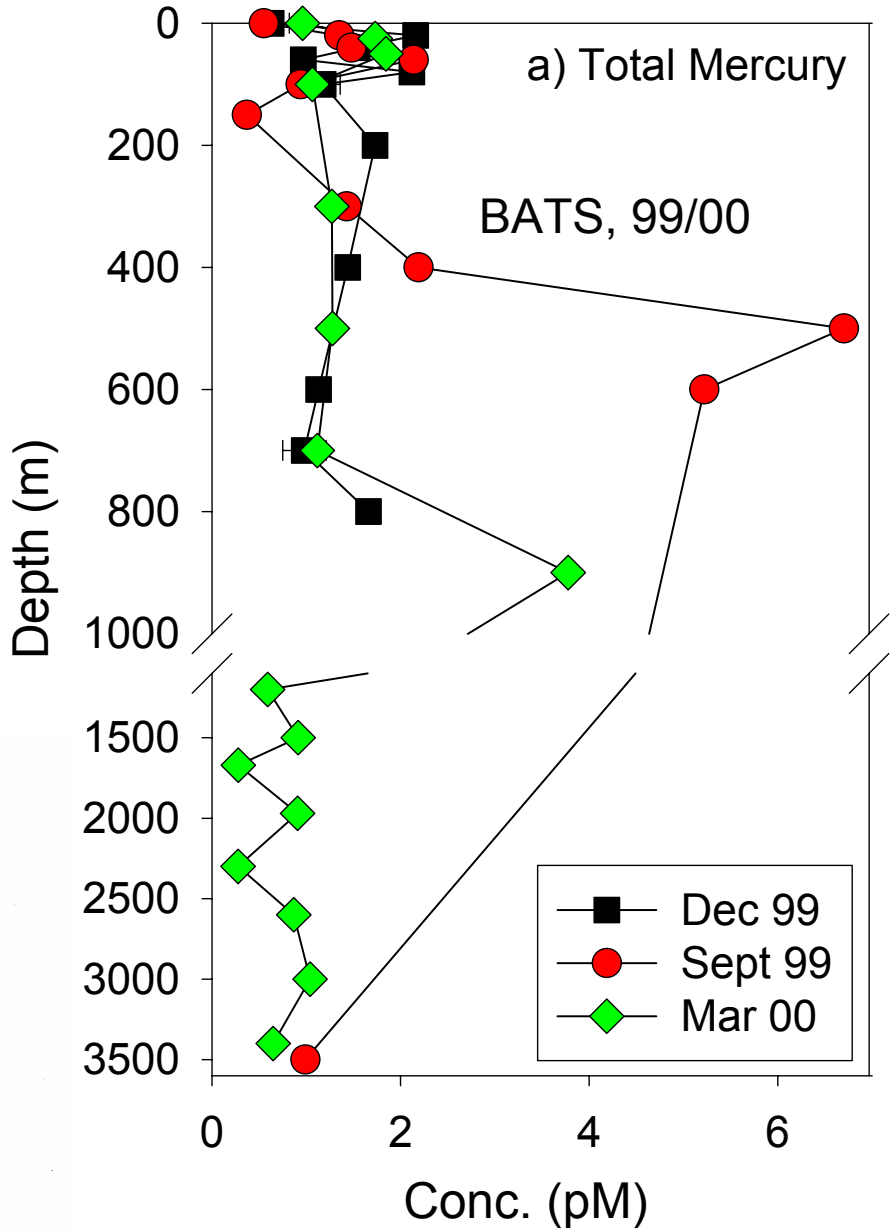


Fig. 3. Lead concentrations in surface water near Bermuda, 1979–1996. ■ surface samples collected and analyzed by MIT laboratory; ○ samples collected and analyzed by Cal Tech laboratory (Schaule and Patterson, 1983; Veron et al., 1993); △ moored sampler samples (44–51 m depth) Year mark and label on Jan. 1.

Mason et al, 2001



Factors Controlling Hg(II) Reduction and Hg(0) Evasion from Aquatic Systems

Light - photochemical and biological processes; diurnal cycle found in some aquatic systems

Water Chem. - DOC can enhance reduction, but also limits light penetration

- Dissolved constituents influence the extent of the "back reaction" – Hg(0) oxidation. This can also occur in the atmosphere leading to recycling

Wind Speed - Removes Hg(0) via evasion and prevents its oxidation and subsequent potential methylation

- Is the most important control over evasional flux, as are other factors that influence gas exch. coeff.

Terr. Surfaces-Evasion from land surfaces is also important

Estimated fluxes of elemental mercury for various water bodies. As fluxes are mostly from short-term measurements, they are scaled to a monthly rather than a yearly basis.

Location	Flux ($\mu g\ m^{-2}\ mth^{-1}$)	Ref.
Equatorial Pacific	0.7-7	1
North Pacific	<2	10
N. Atlantic - summer	12	2
S. Atlantic - summer	36	3
Bermuda	2.7	4
Long Island Sound, USA	2.1	5
Scheldt Estuary, Belgium	1.2-2.4	6
Chesapeake Bay, USA	0.8	7
St. Lawrence River/Lake Ontario	2.1	8
Lakes/Wetlands	0.2-2	9

Notes:References: #1= *Mason and Fitzgerald*, 1993; #2= *Mason et al.*, 1998; #3= *Lamborg et al.*, 1999; 4 = *Mason et al.*, 2001; #5= *Rolfhus and Fitzgerald*, 2001; #6= *Baeyens and Leemakers, 1998*; #7= *Mason et al.*, 1999; #8= *Poissant et al.*, 2000; #9= *Zhang and Lindberg*, 1999 and reference therein; #10 = Laurier et al., unpublished data.

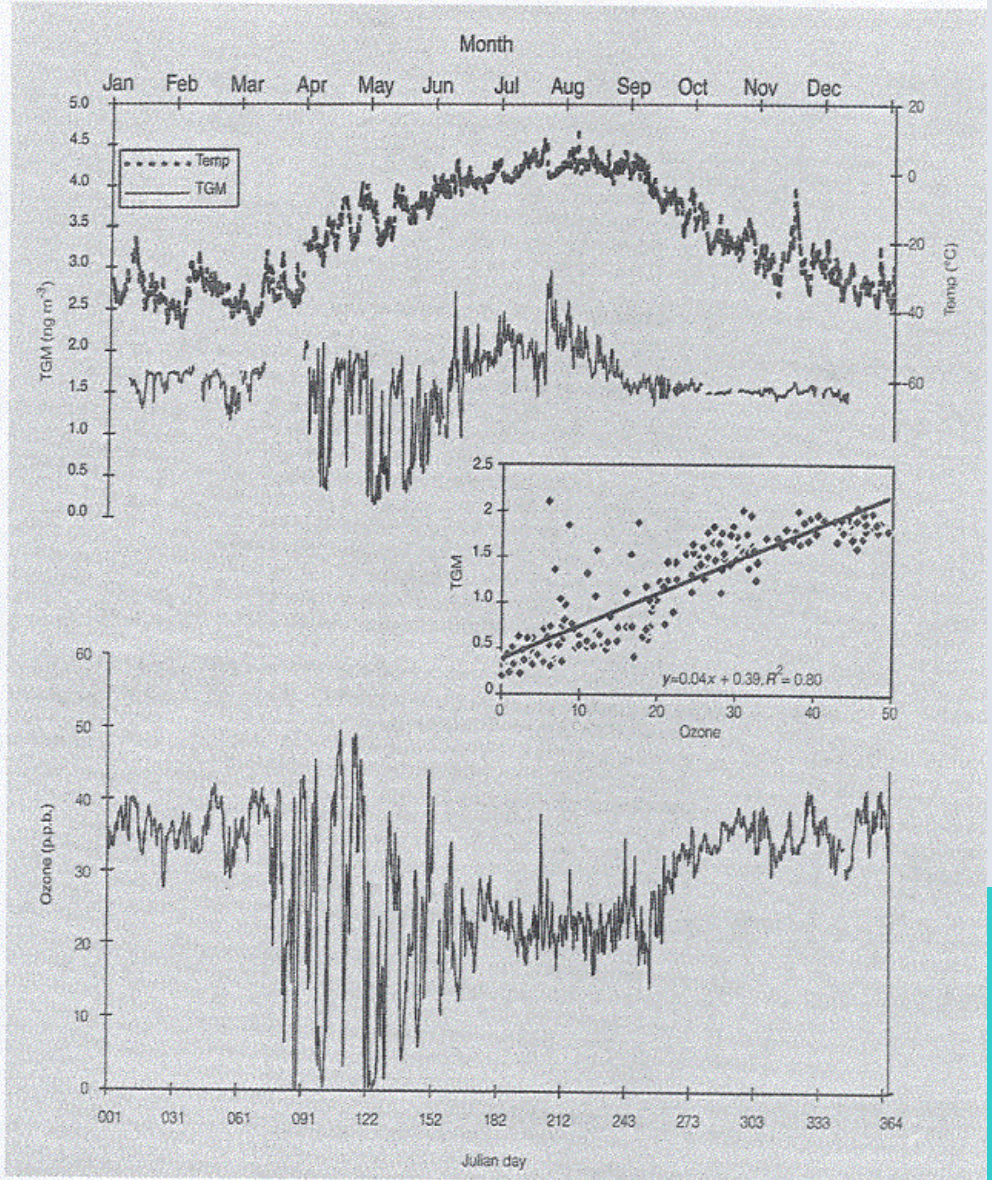


Figure 1 Time series of six-hour average values for air temperature and for total gaseous mercury (TGM) and ozone concentrations at Alert, Canada, in 1995. The inset shows concentrations of TGM versus ozone at Alert for the period from 9 April 1995 to 29 May 1995. (Note $R^2 = 0.8$ for the correlation between TGM and ozone concentrations during this period.)

Mercury and ozone during polar sunrise at Alert, Canada.

From Schroeder et al., 998

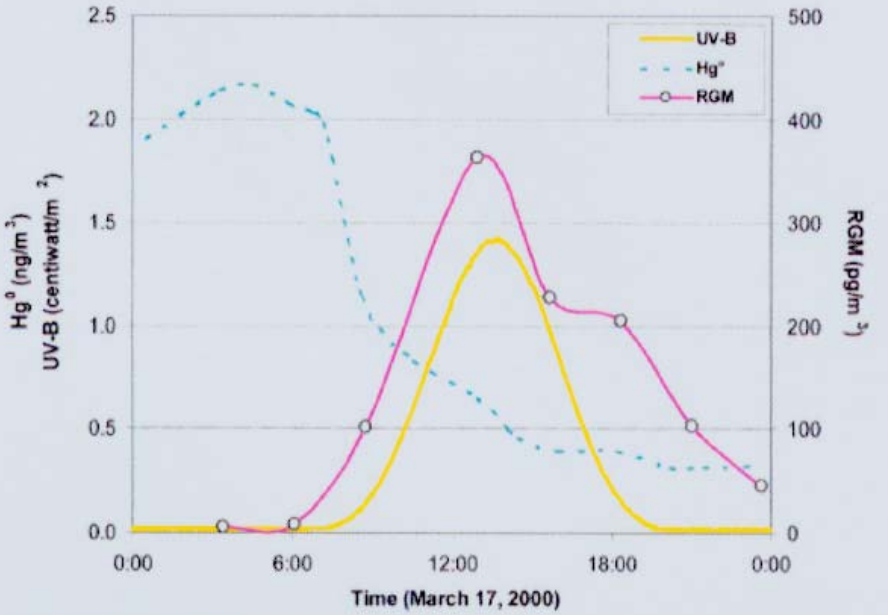
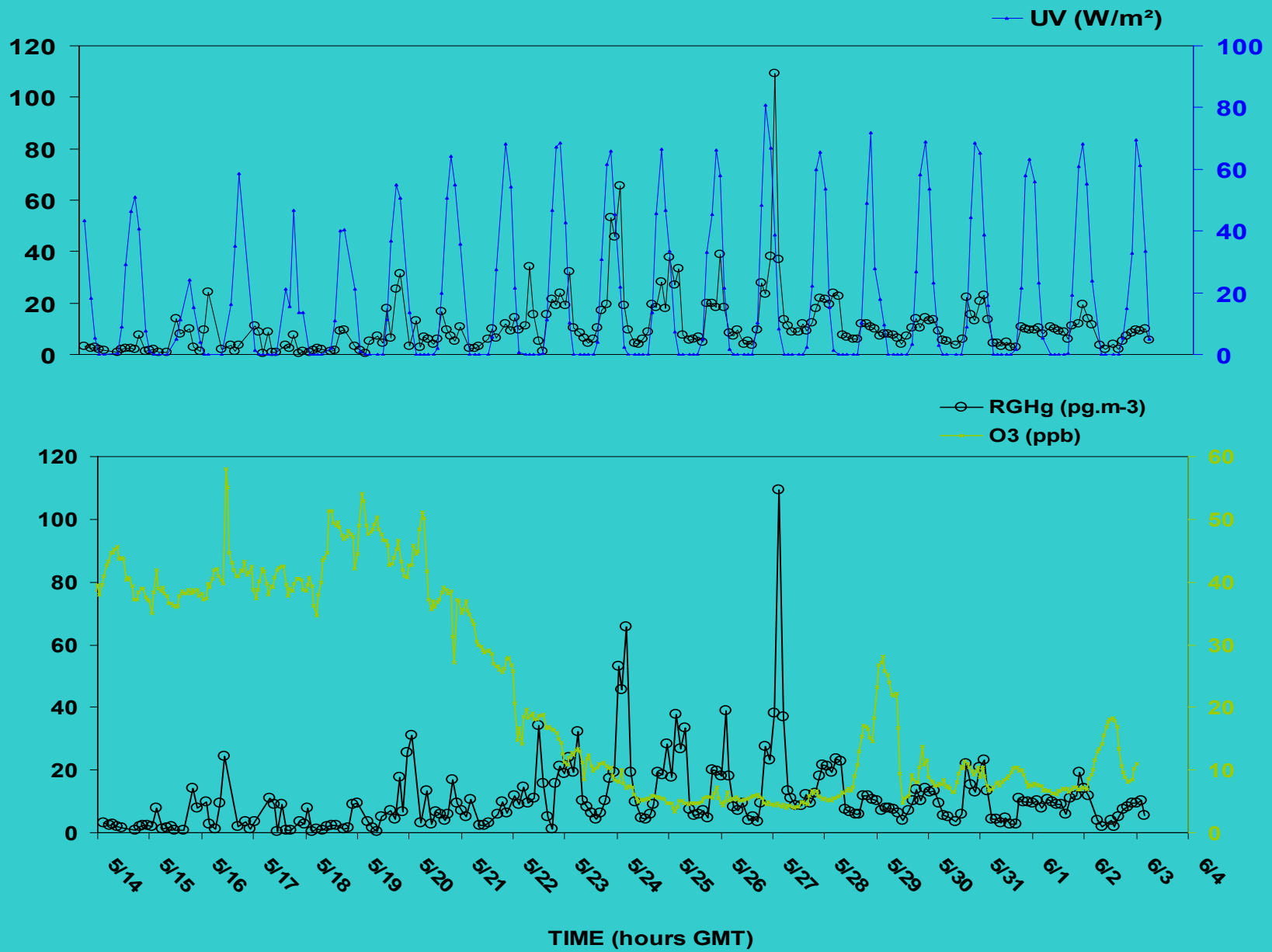


FIGURE 4. Typical diel cycle of tropospheric gaseous Hg species and UV-B at Barrow (UV is measured in near-realtime, while Hg^0 and RGM represent integrated samples of 5 min and 2 h, respectively, as described in the text).

Diel Cycle of Atmospheric Hg at Barrow, Alaska

Lindberg et al., 2002

Reactive Gaseous Mercury – Equatorial Pacific



Forms of Atmospheric Hg

*Elemental Hg – Hg^0. Dominant species. Low deposition velocity

*Ionic Hg

Gaseous Hg(II) – RGHg. A few %, typically. High deposition velocity.

Particulate bound. A few %, typically. Lower deposition velocity - ~10x less than RGHg

*Hg in Precipitation. Often the dominant source to aqueous systems.

Property	Hg^0	$HgCl_2$
Melting Point (°C)	-39	277
Boiling Point (°C)	357 @ 1 atm	303 @ 1 atm
Vapor Pressure (Pa)	0.18 @ 20°C	8.99×10^{-3} @ 20°C
Water Solubility($g\cdot L^{-1}$)	49.4×10^{-6} @ 20°C	66 @ 20°C
Henry's Law C. ($mol\cdot m^{-3}\cdot Pa^{-1}$)	1.37×10^{-3} @ 20°C	2.71×10^{4} @ 20°C

Estimated Depositional Fluxes for Mercury for Various Locations (in ug/m^2/yr)

From Mason et al., 2001; Sheu, 2001; St. Louis et al., 2001 and unpubl. data

Site	Wet	RGHg	Part.	Total	%Dry
CBL, MD, rural	12.6	11.7	1.6	25.9	51
STP, MD, "rural"	14	7.5	2.5	24	42
SC in Baltimore	30	28	3.5	61.5	51
ELA, Canada	7	<1	<1	<9	<22
Average ocean	5.3	3.2	0.06	8.6	38

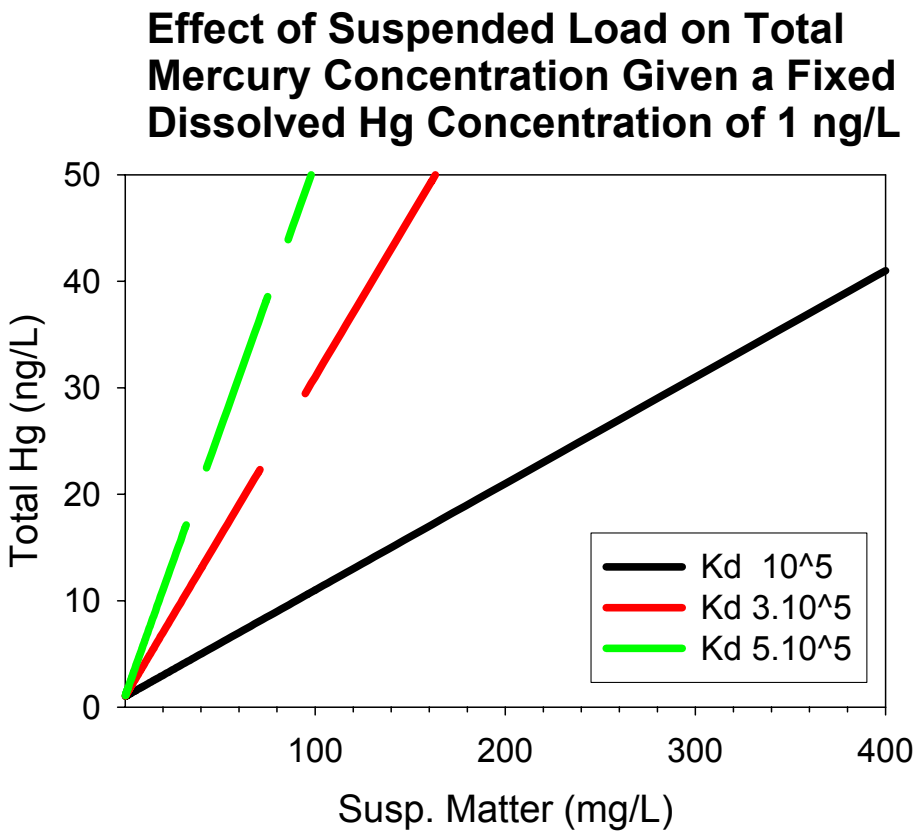
Estimated Wet and Throughfall Depositional Fluxes for Mercury for Various Locations (in ug/m^2/yr)

Site	Wet	Thru'fall	%Dry
ELA	7	8	13
Inland Rural USA	6.5-10	12-14	30-45
Rural Sweden	7-10	15-23	50-60
Western MD	15	25	40

From St. Louis et al., 2001 and references therein and Lawson et al., 2001

Factors Controlling Bioavailability

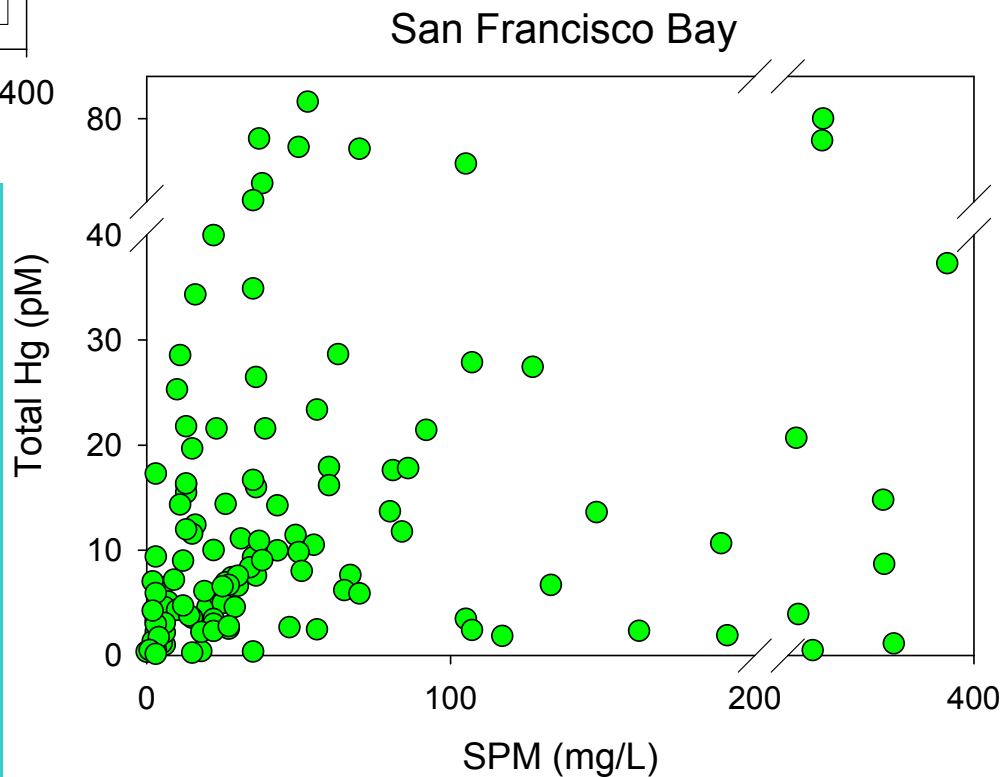
1. Partitioning to the Solid Phase
2. Dissolved Hg Speciation

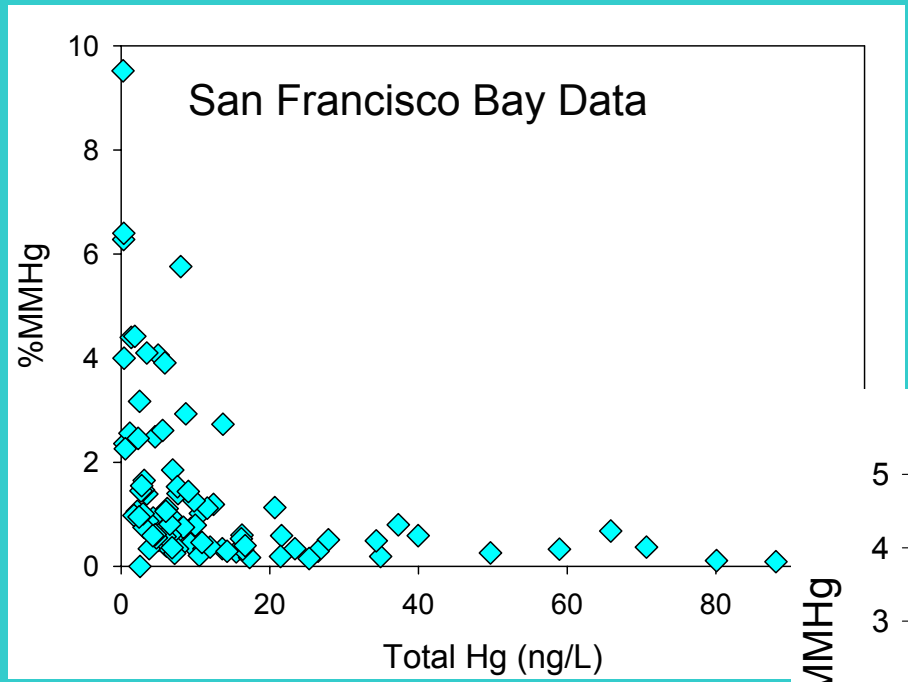


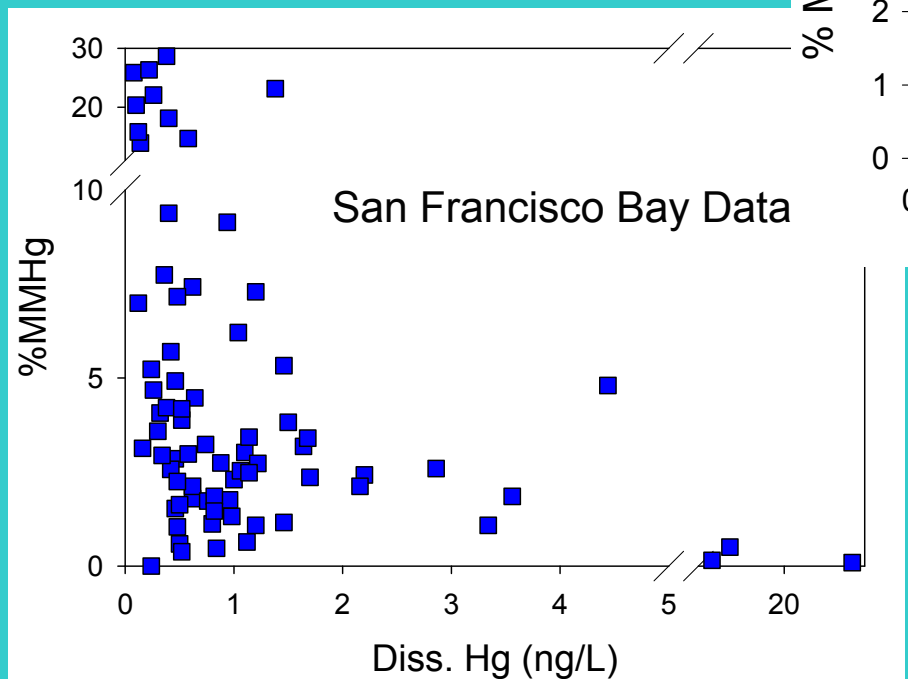
Mercury is very particle reactive and is not easily released from particles into solution. MethylHg Is less strongly associated with particles.

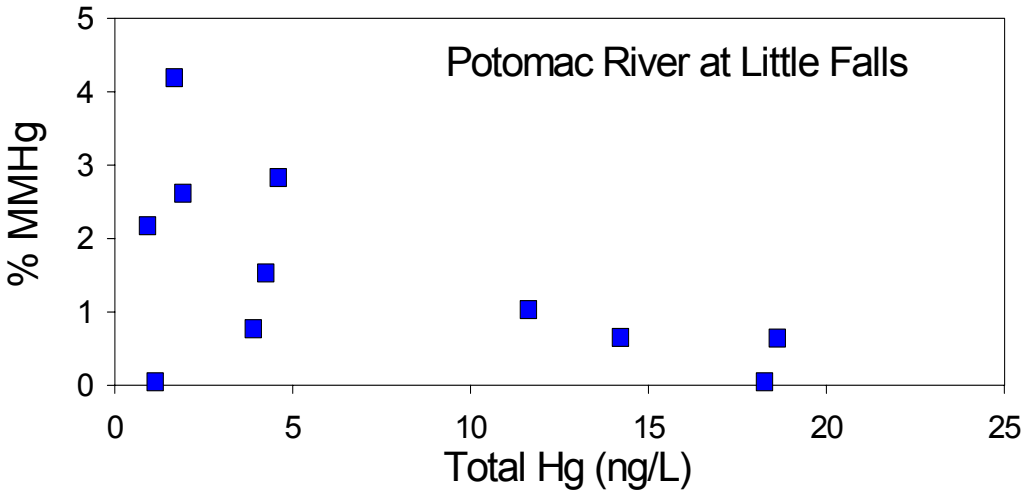
Observed relationship between total mercury and suspended particulate load in San Francisco Bay

From Conaway et al., 2002



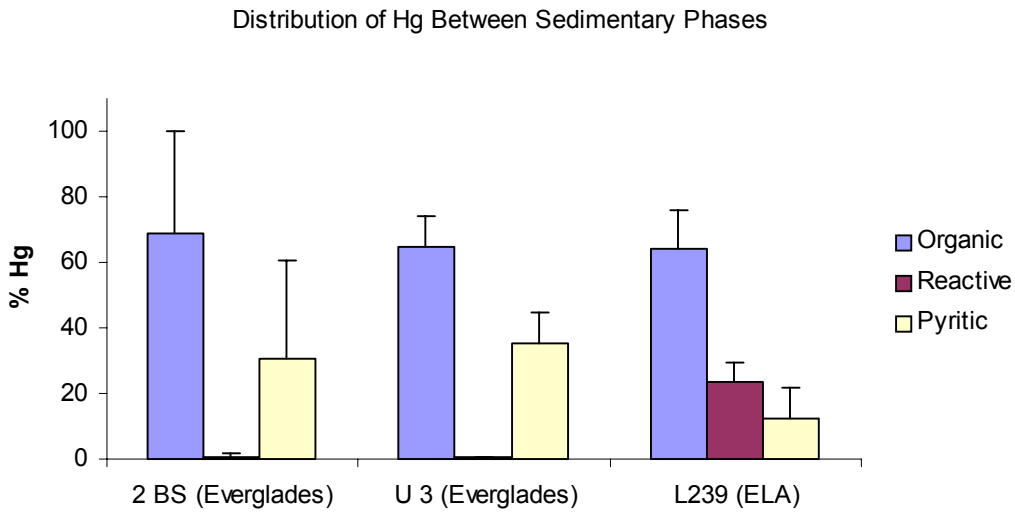






From Conaway et al., 2002
and Lawson et al., 2001

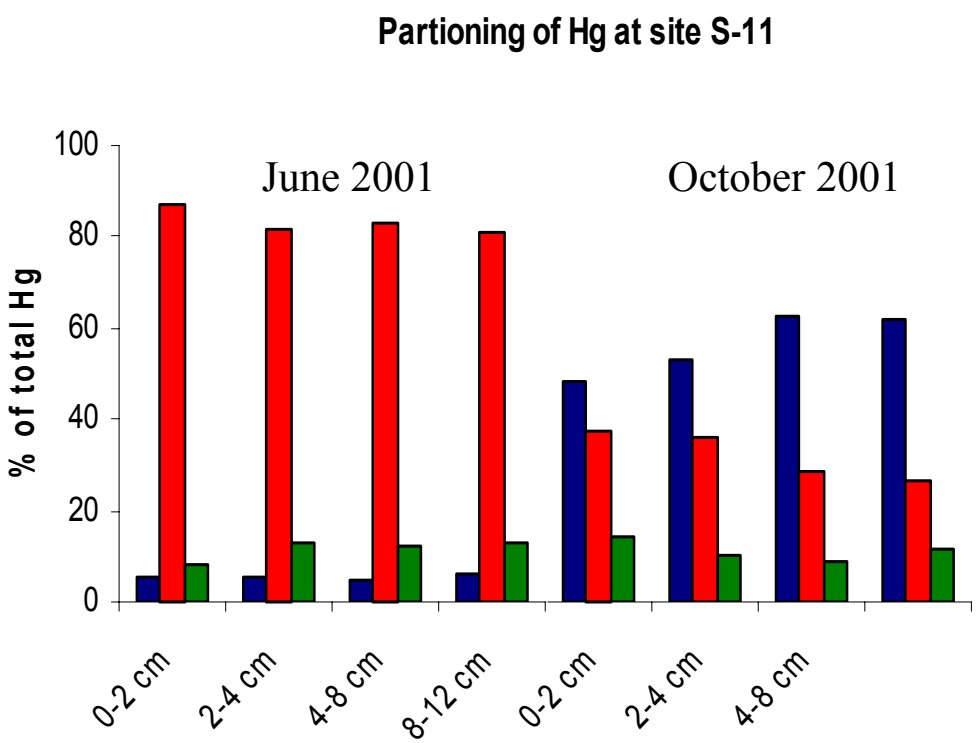
Sequential Extraction Results



Fraction 1: Organics, 1M KOH
Fraction 2: Reactive Species, 3M HCl
Fraction 3: Pyritic, 1 mL conc. HCl + 9 mL conc. HNO_3; heat

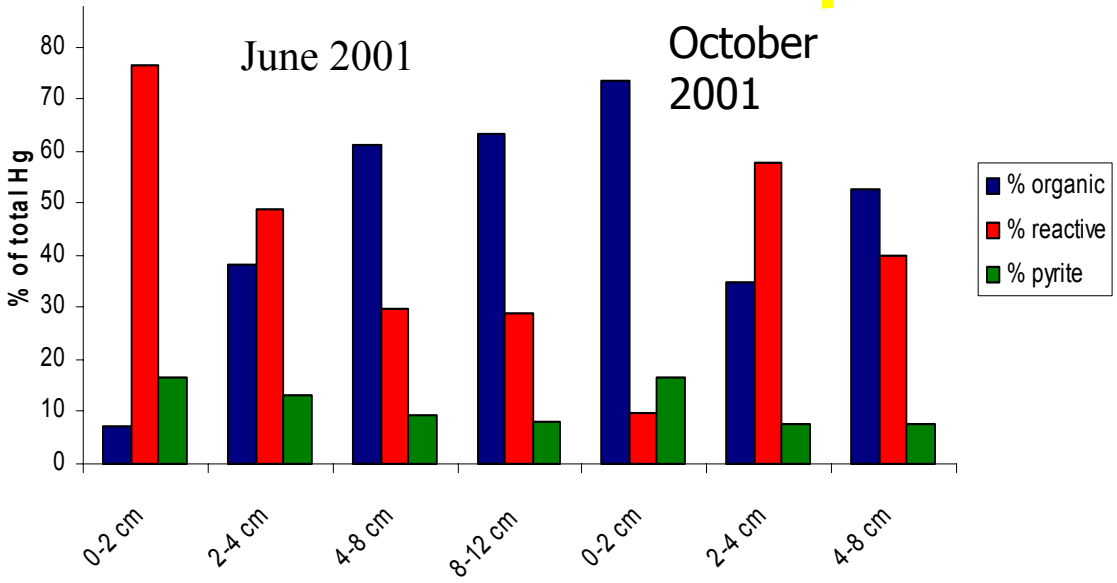
Site	**LOI**	**AVS**	**CRS**
2BS	11.5	2.23	91
U3	10.6	22.9	235
L239	3.3		

LOI as %; AVS & CRS as umol/g dry



Hudson River Estuary

Sites N3 (erosional) and S11 (depositional)



Relationship between total mercury and methylmercury for different locations and environments

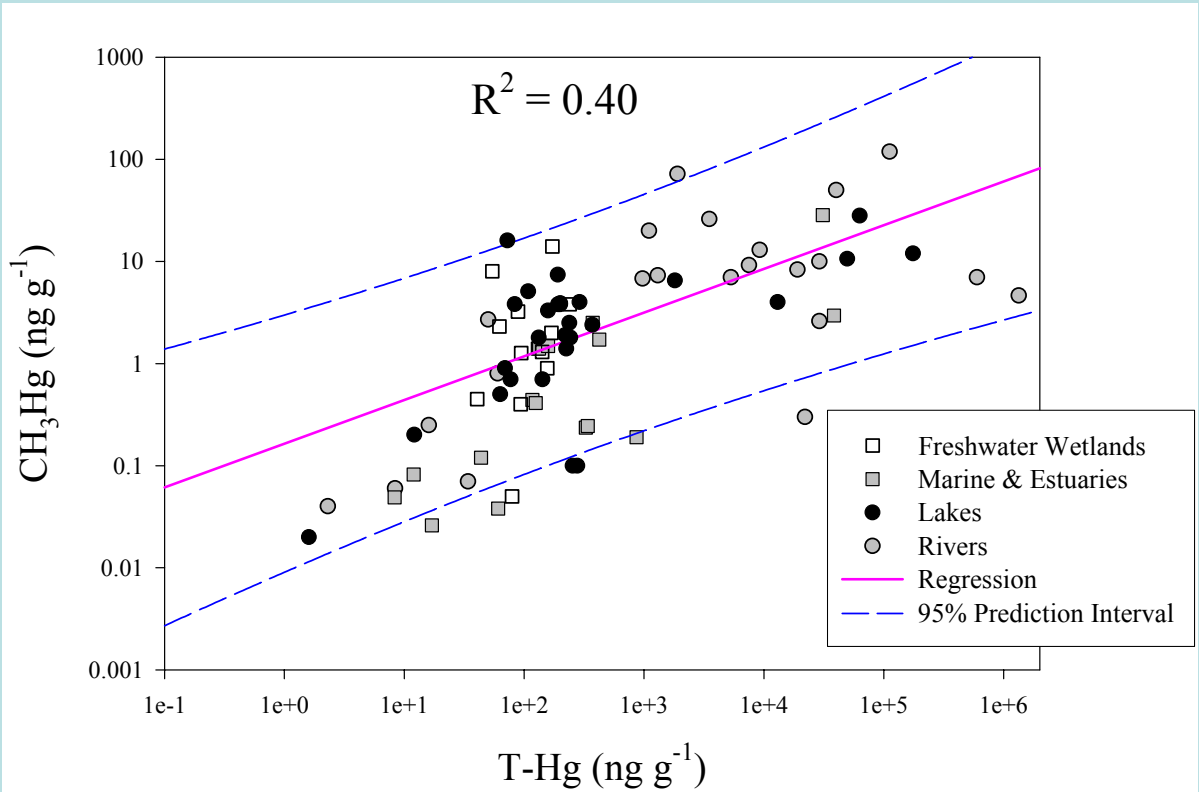


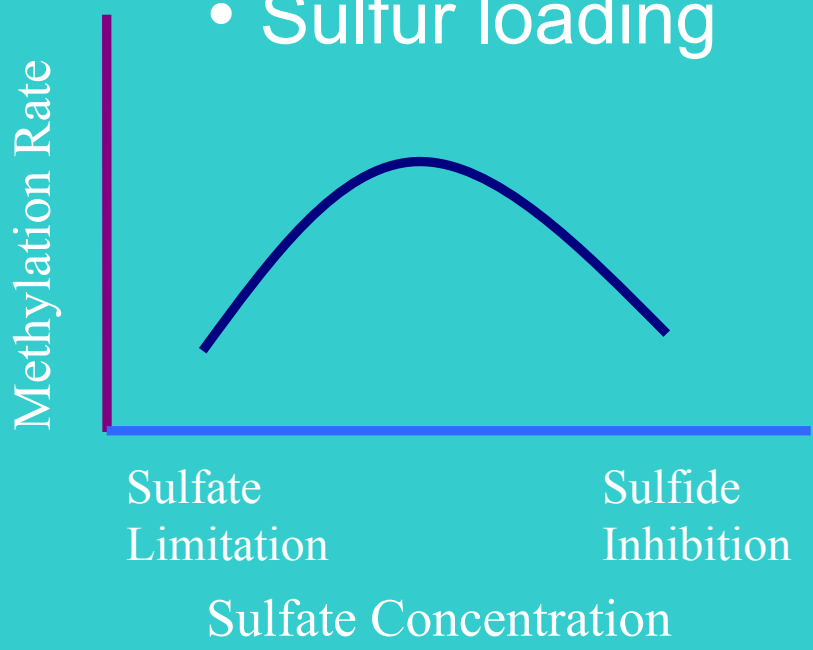
Figure 1. Mercury (Hg) and methylmercury (CH_3Hg) in near surface (0-4 cm) sediment in:

1. Freshwater wetlands from: North and South Carolina, Ontario, Canada, Florida Everglades;
2. Marine and estuarine sediments from: coastal N. and S. Carolina, the Chesapeake Bay and its estuaries, coastal Florida, coastal Texas, Slovenia coast, coastal Poland, coastal Malaysia, Anadyr Estuary, Russia;
3. Lakes: New Jersey, New York State,Wisconsin, California, Finland, Poland;
4. Rivers: S. Carolina, Wisconsin, Nevada, Alaska, Germany, Poland.

From Benoit et al., 2003

Variability in MeHg production among ecosystems is a function of:

- Hg loading
  - Atmospheric
  - Point sources
- Basin geomorphology
  - Wetland area
  - Littoral area
  - Watershed area
- Sulfur loading



- Controls on microbial activity
  - Temperature
  - Trophic status

Hg bioavailability to the bacteria is important, but intracellular processes also influence the net rate of methylation

Bioaccumulation

$Hg(SR)_n^{2-2n}$

$Hg(OH)_2^o$, $HgClOH^o$

Inorganic complexes

$HgCl_2^o$, $HgCl_4^{2-}$

CH_3HgX

Influenced by DOC, pH

Porewater

Hg^{2+}

Influenced by Cl, pH

Influenced by Sulfide, pH

k_M

k_D

Hg_C → CH_3HgX

k_B

HgSX

Cell

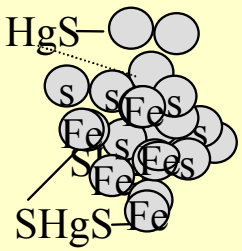
HgS^o

$Hg(SH)_2^o$

$Hg^{2+} + xS^{2-} + yH^+ = HgS_xH_y^{2-2x+y}$

e.g HgS^o, HgS_6^{2-}, $HgSH_2^-$, $Hg(SH)_2^o$

S-Hg-S



Sediment

$Hg^{2+} + HSR^{n-} = HgSR^{2-n} + H^+$

$HgSR^{2-n} + HSR^{n-} = Hg(SR)_n^{2-2n} + H^+$

At steady state…

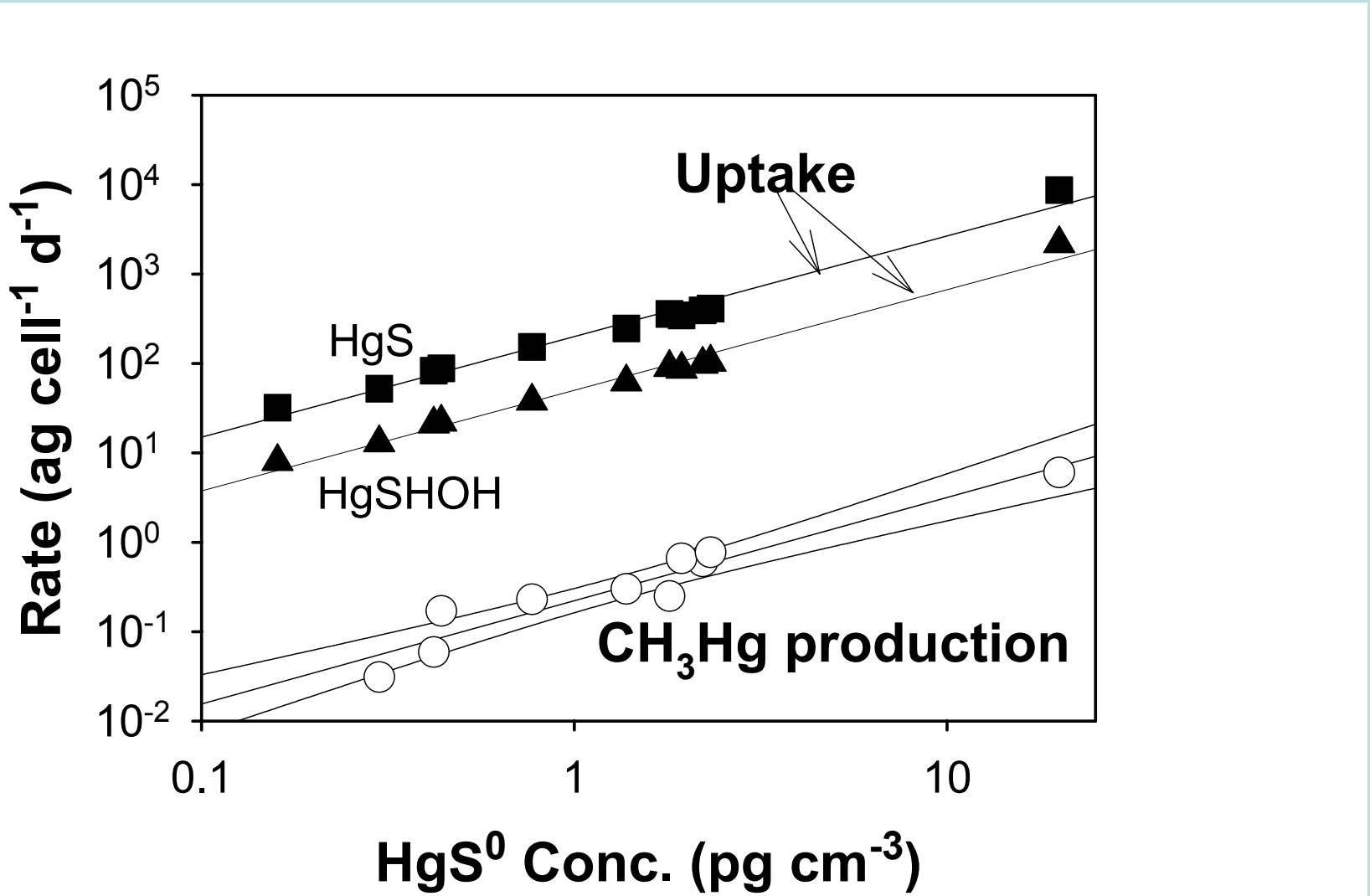
$[Hg_C] = k_D.[HgL_n]/(k_B + k_M)$

and

$d[CH_3Hg]/dt = k_M.[Hg_C]$

$= k_D.k_M.[HgL_n]/(k_B + k_M)$

Estimated mercury (Hg) uptake rate, assuming passive diffusion of neutral Hg complexes - either modeled as HgS^o or $HOHgSH^o$, and the simultaneous Hg methylation rate in pure cultures of *D. propionicus*.

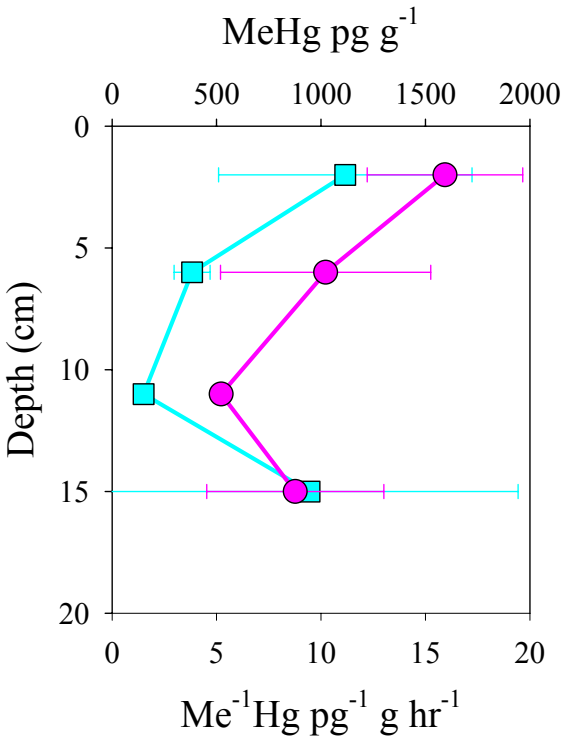


From Benoit et al., 2001

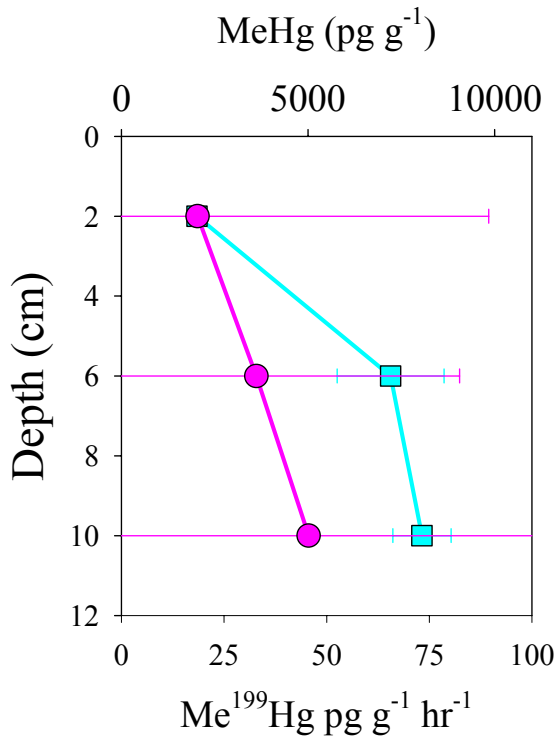
1. Hg methylation occurs in all parts of the watershed

2. Production of methylmercury from a Hg spike is correlated to in situ concentration

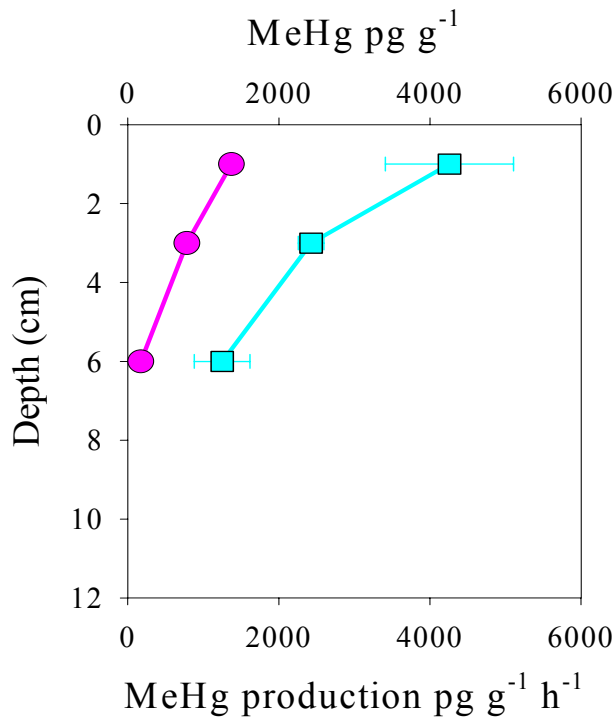
Upland



Wetland



Lake



Low oxygen? → No oxygen?

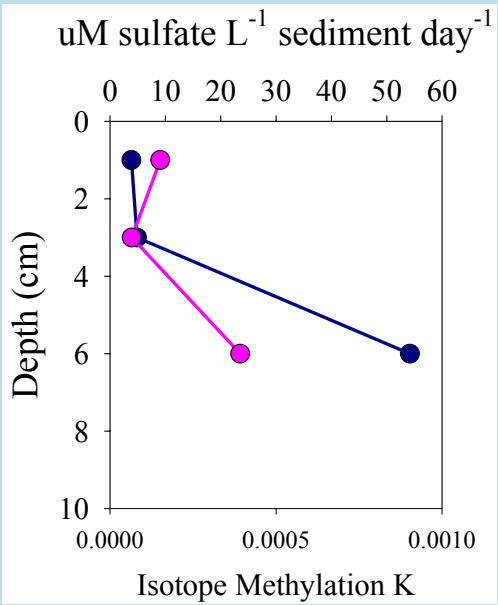
Ambient MeHg concentration

Isotope methylated during incubation

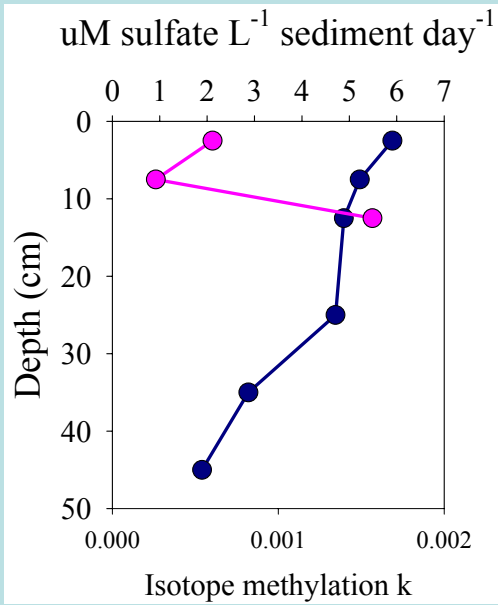
Activity of SRB in the watershed

Sulfate Reduction Rates

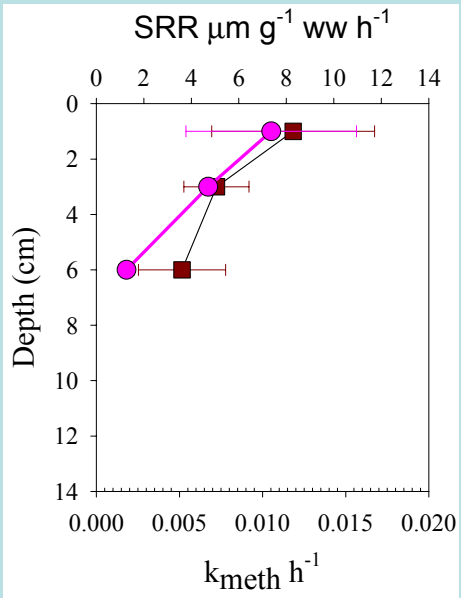
Upland
riparian zone



Wetland



Lake



Low oxygen? ⟶ No oxygen?

Not all SRB methylate Hg, so Hg methylation is not directly related to sulfate-reducing bacteria activity

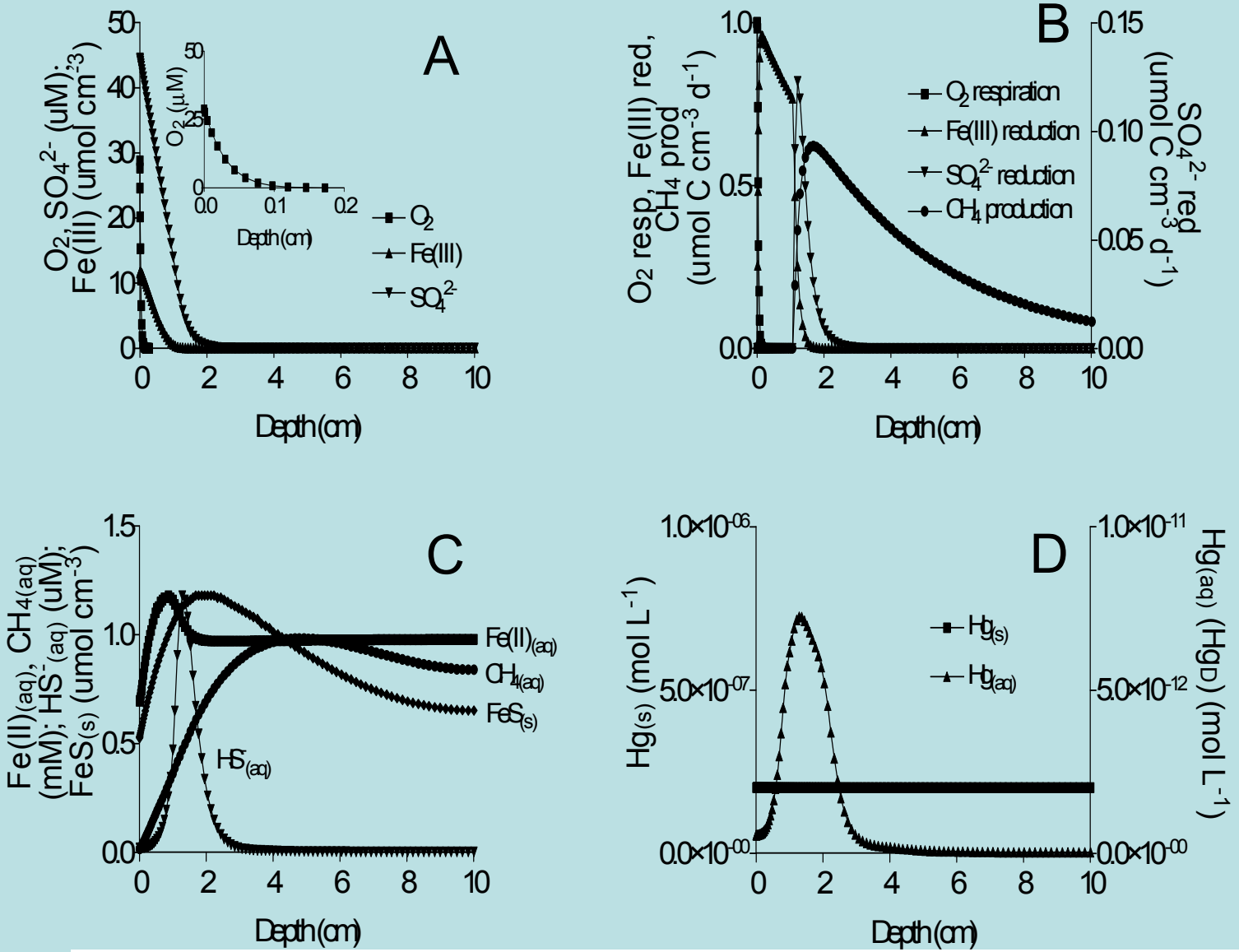
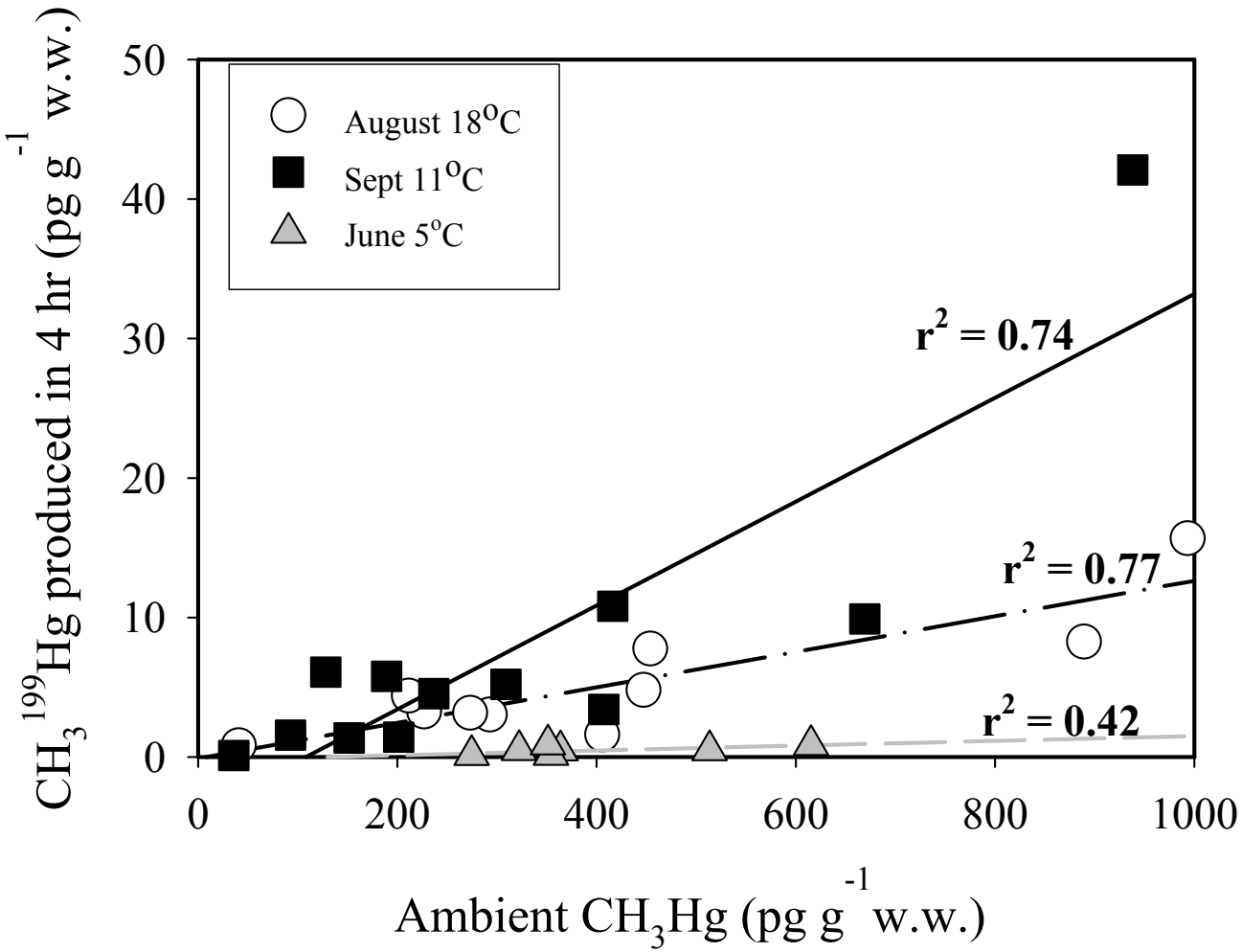


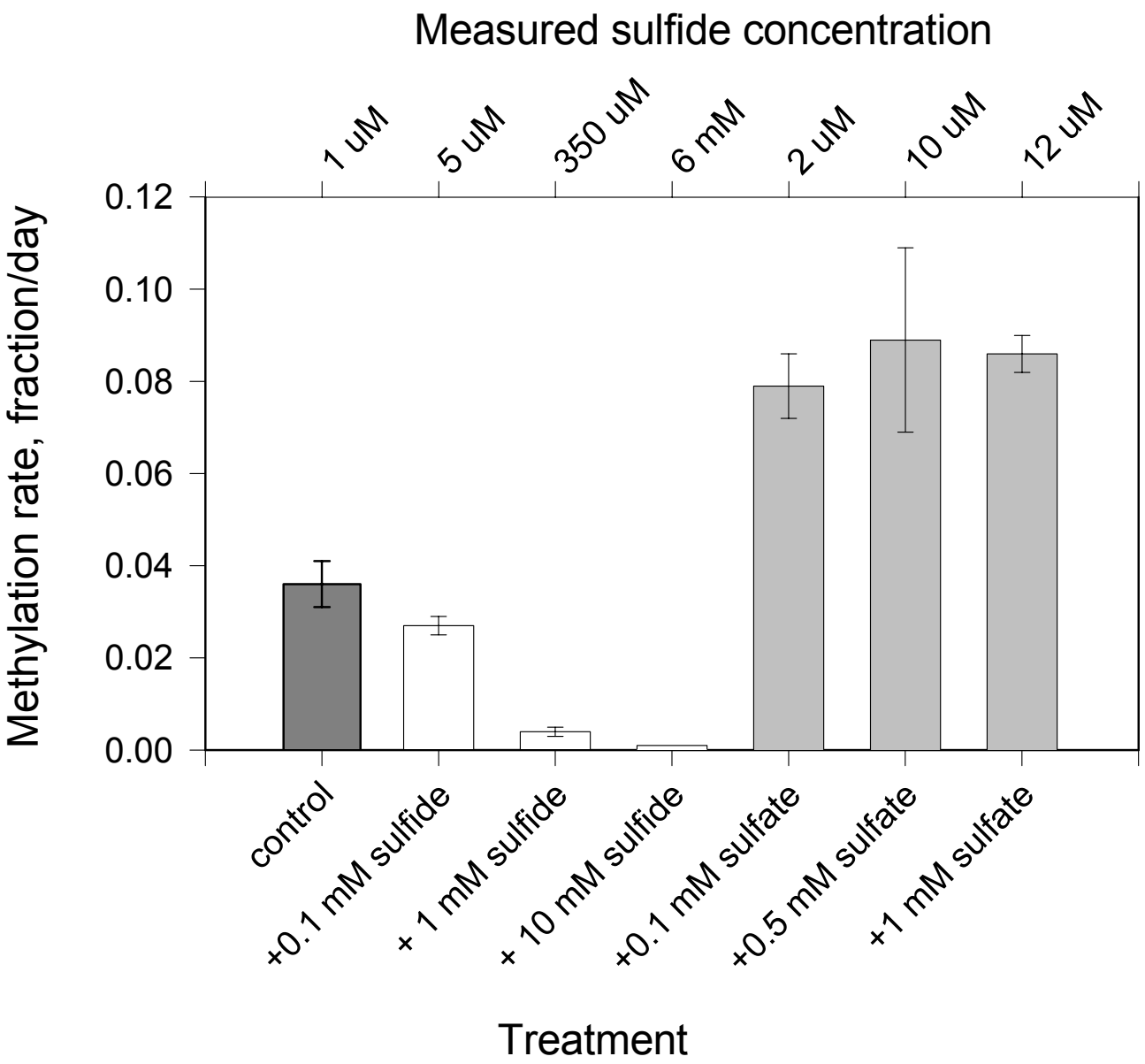
Fig. 1. Results of the preliminary lake sediment diagenetic model.

The relationship between production rate and in situ concentration changes with time



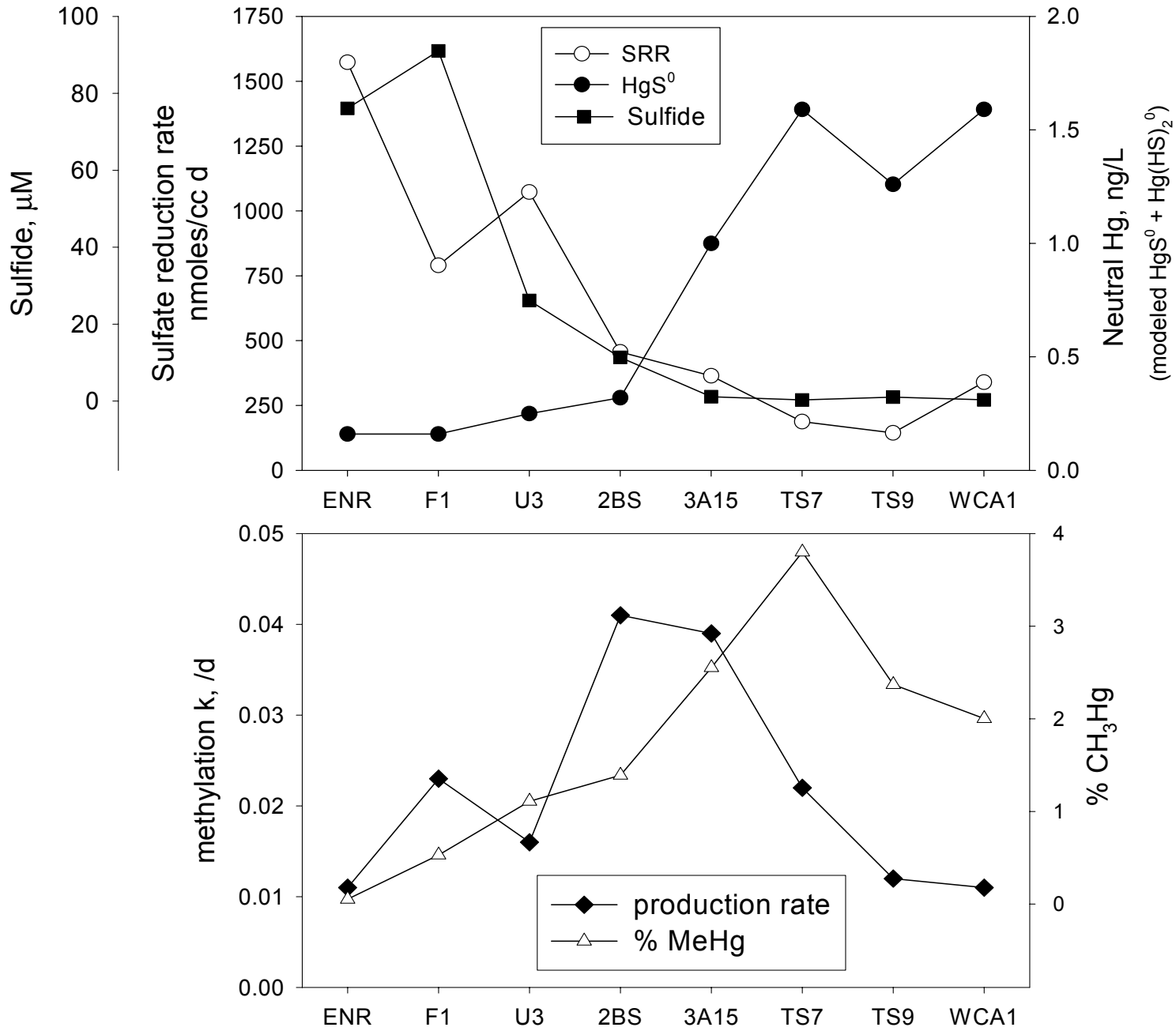
Native in situ methylmercury (CH_3Hg) concentration and excess $CH_3{}^{199}Hg$ produced from ^{199}Hg in 4 hrs, in peat collected in June, August and September, 2000, from a lakeside, sphagnum wetland (L115) at ELA in northwest Ontario.

From Benoit et al., 2003



Methylmercury production in Florida Everglades sediment cores after addition of either sulfate (light grey bars) or sulfide (white bars). Sediment cores, taken from the central area of the Loxahatchee National Wildlife Refuge (LNWR), were amended with either sodium sulfide or sodium sulfate (at neutral pH), by injection into the top 4 cm of sediment.

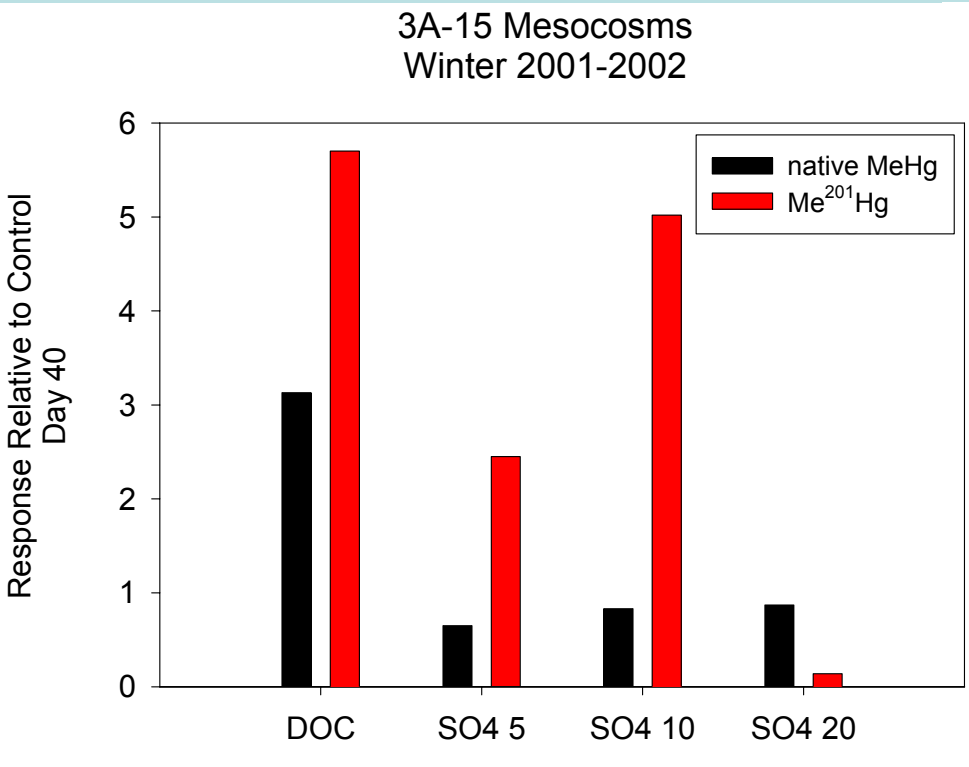
From Benoit et al., 2003

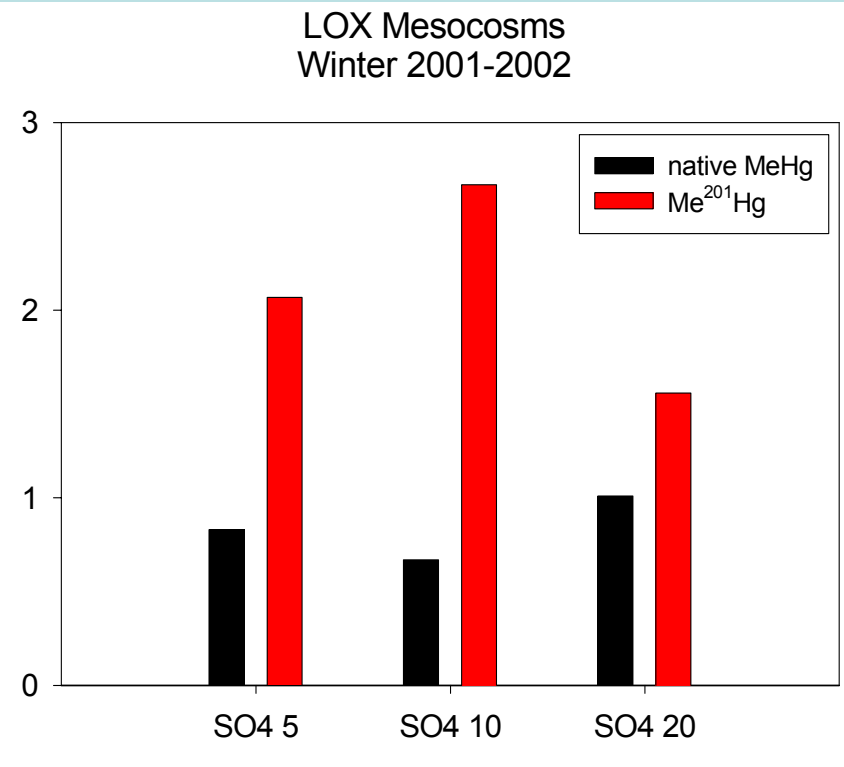


From Benoit et al., 2003

Measured sulfate reduction rate, porewater sulfide concentration, percent methylmercury (%CH_3Hg), mercury methylation rate and modeled porewater HgS^o in the upper 4 cm of Florida Everglades sediments at 8 ACME sites. Everglades sites are arranged from left to right by average surface water sulfate concentration (highest concentrations on the left). With the exception of the WCA 1 site, this represents a north to south transect, running from the Everglades Nutrient Removal Project (ENR) and Water Conservation Area 2A (F1, U3) in the north, through Water Conservation Areas 2B (2BS) and 3A (3A15), and to Taylor Slough in Everglades National Park (TS7, TS9) in the south. Data shown are averages from three years (1995-1998) of bi- to tri-annual sampling.

MeHg Spiked into Everglades Sediment Mesocosms



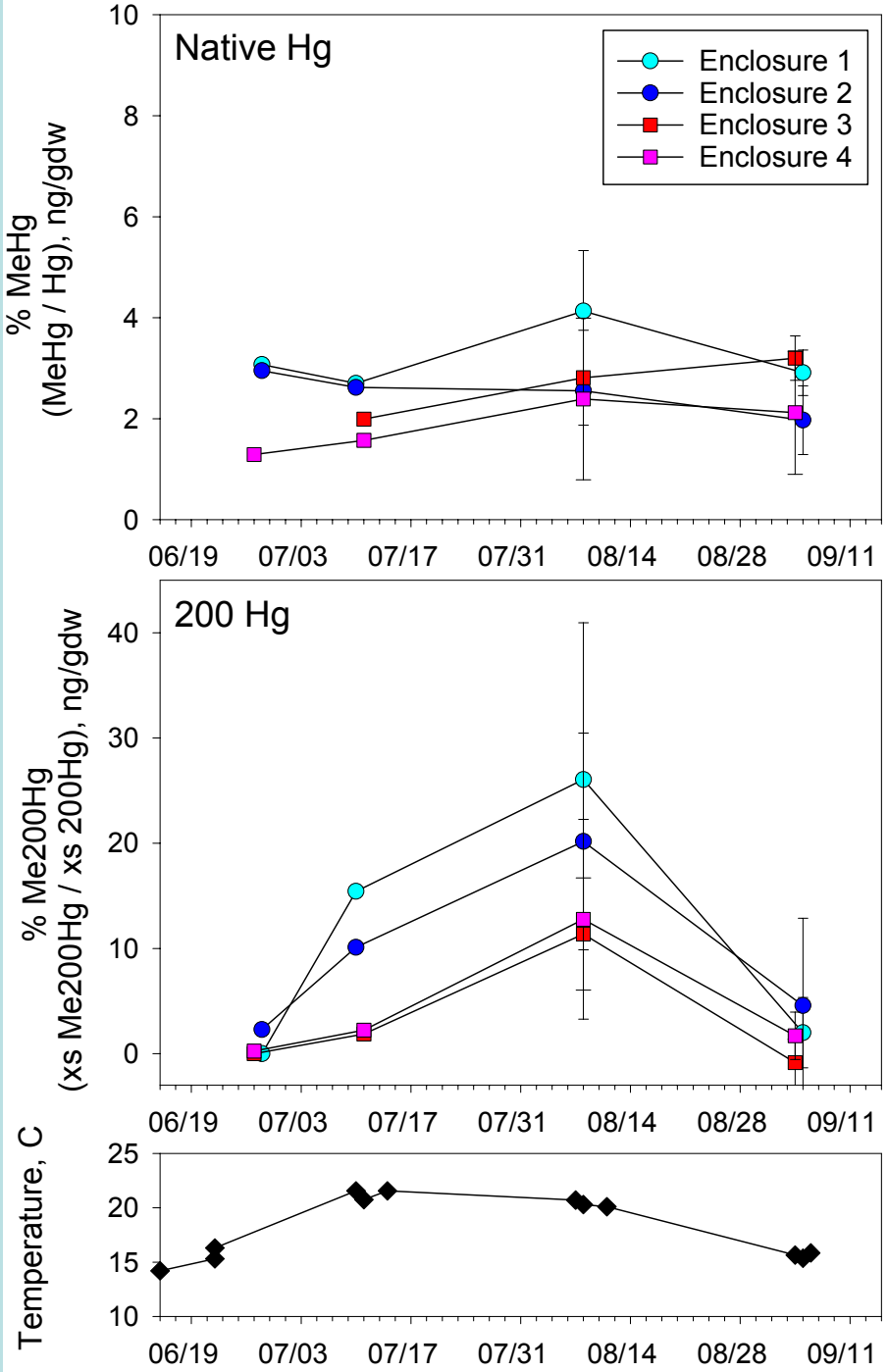


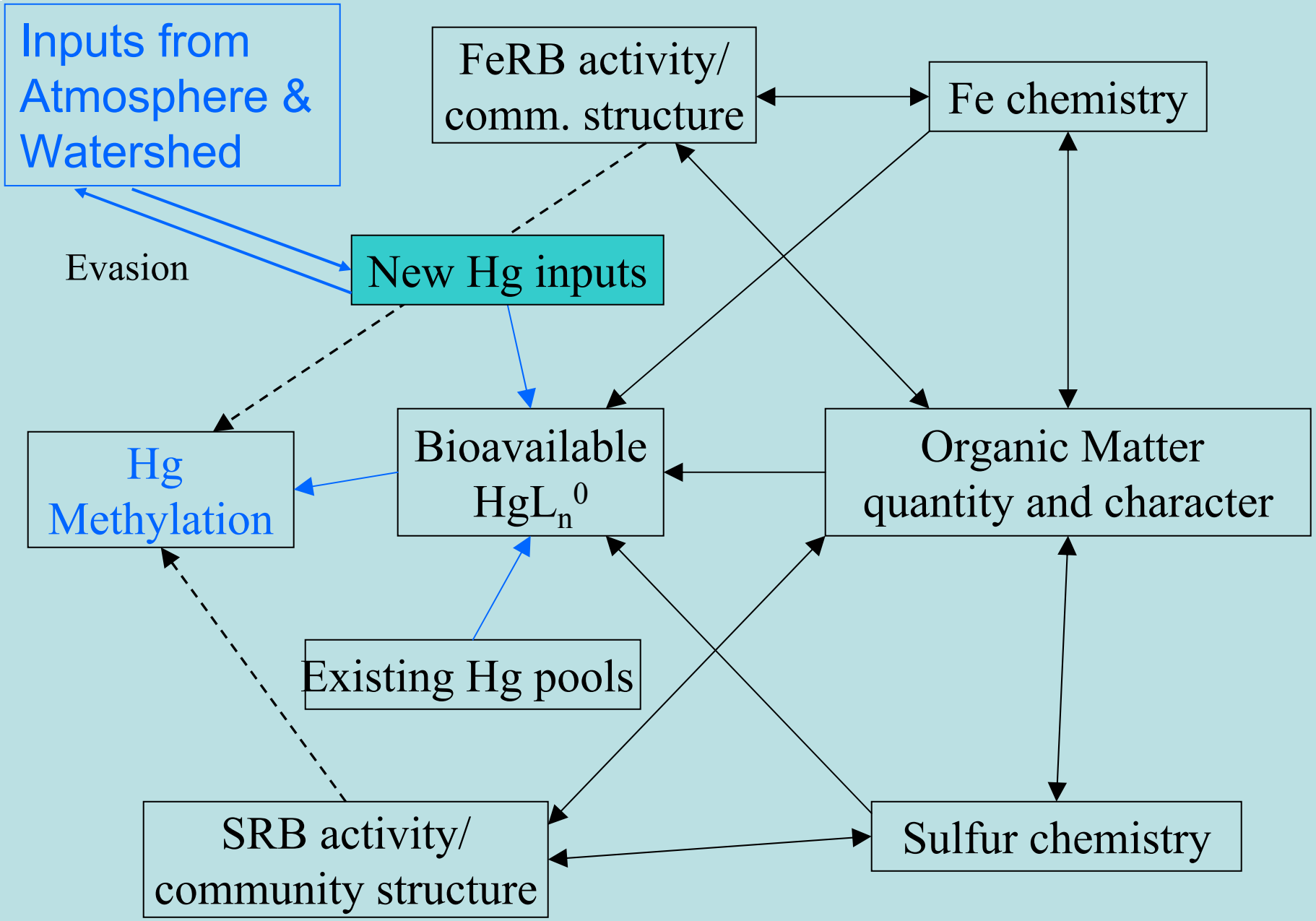
- New ^{201}Hg is more readily methylated than existing Hg
- DOC and SO_4 additions affect methylation of new ^{201}Hg more than existing Hg
- DOC stimulates production of MeHg from old and new pools
- SO_4 stimulated MeHg production from new pools only
- High SO_4 additions produce sulfide that inhibits methylation

Spiked Enclosure Experiments at ELA

Fraction of "old" Hg in sediments as MeHg: average 3.5%

Fraction of "new" Hg in sediments as MeHg: midsummer average ~15% declines later inthe season but is still more "available" the next year





A conceptual summary…….

Summary

1. The bioavailability/reactivity of Hg on entering an aquatic system depends on its form and whether input is direct or indirect
2. Mercury reduction and subsequent evasion removes Hg that might otherwise be methylated
3. Mercury binds strongly to particles and the type and nature of the particle influences its subsequent bioavailabilty
4. Total Hg concentration is not the only variable influencing methyl-mercury concentration.
5. Bacteria influence Hg bioavailability by changing sediment chemistry – converting sulfate to sulfide, consuming and altering organic matter, reducing iron oxides
6. Not all sulfate-reducing bacteria methylate Hg so, in addition to microbial activity, the makeup of the bacterial consortium also influences methylation
7. Sediment chemistry, and physical processes, influence the rate of transport of the methylmercury from the site of accumulation to the site of methylation.