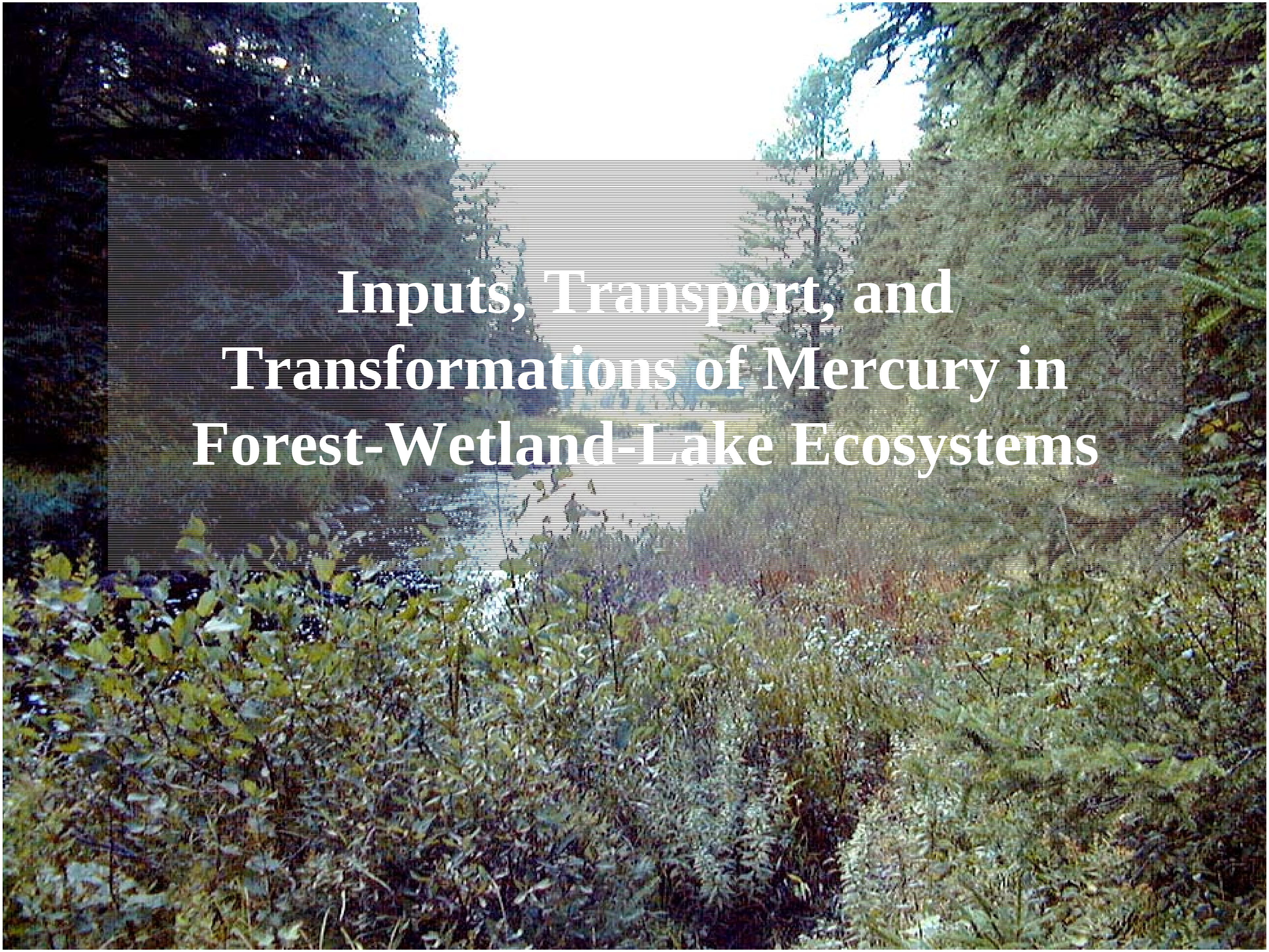
Inputs, Transport, and Transformations of Mercury in Forest-Wetland-Lake Ecosystems

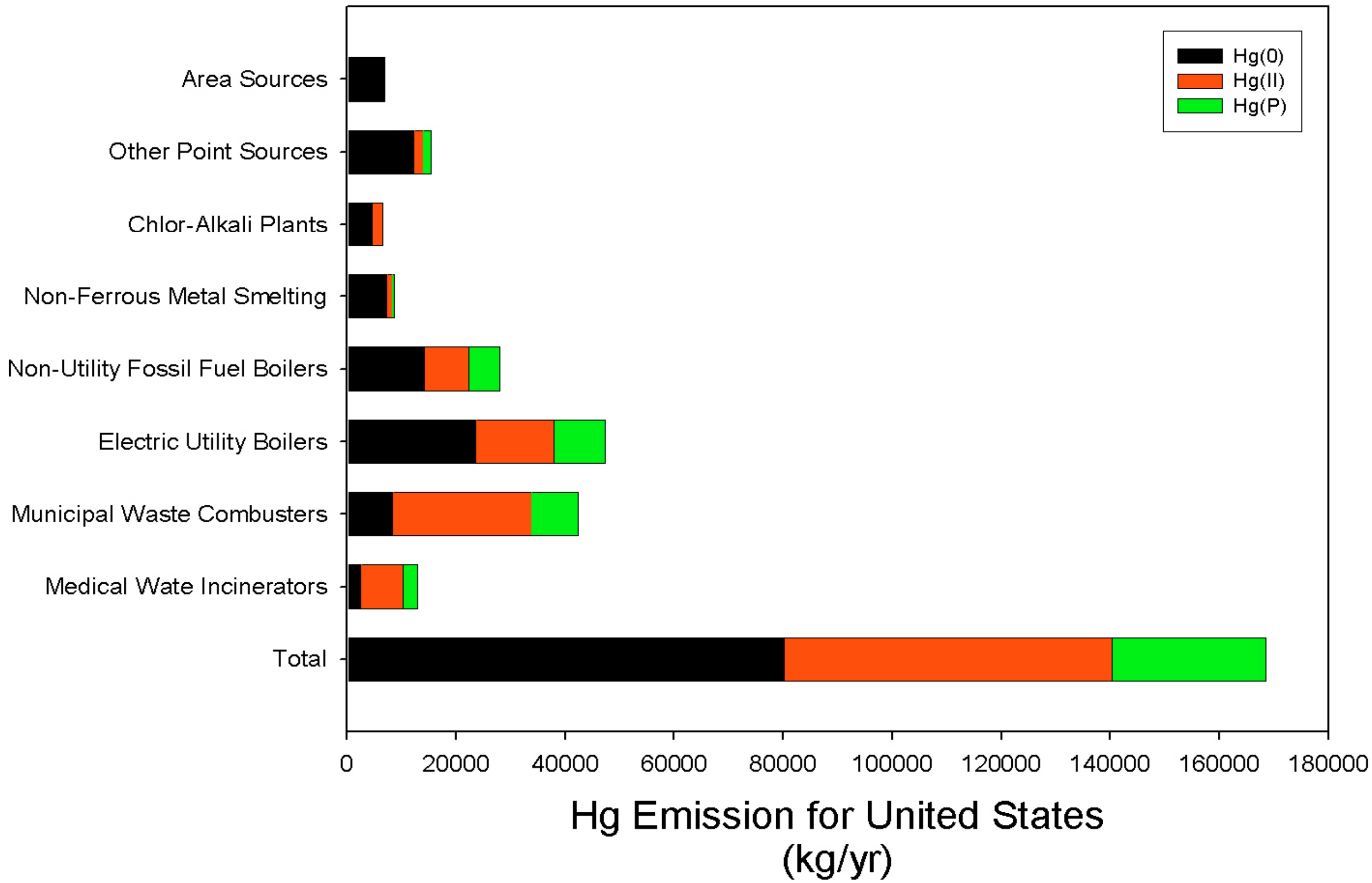


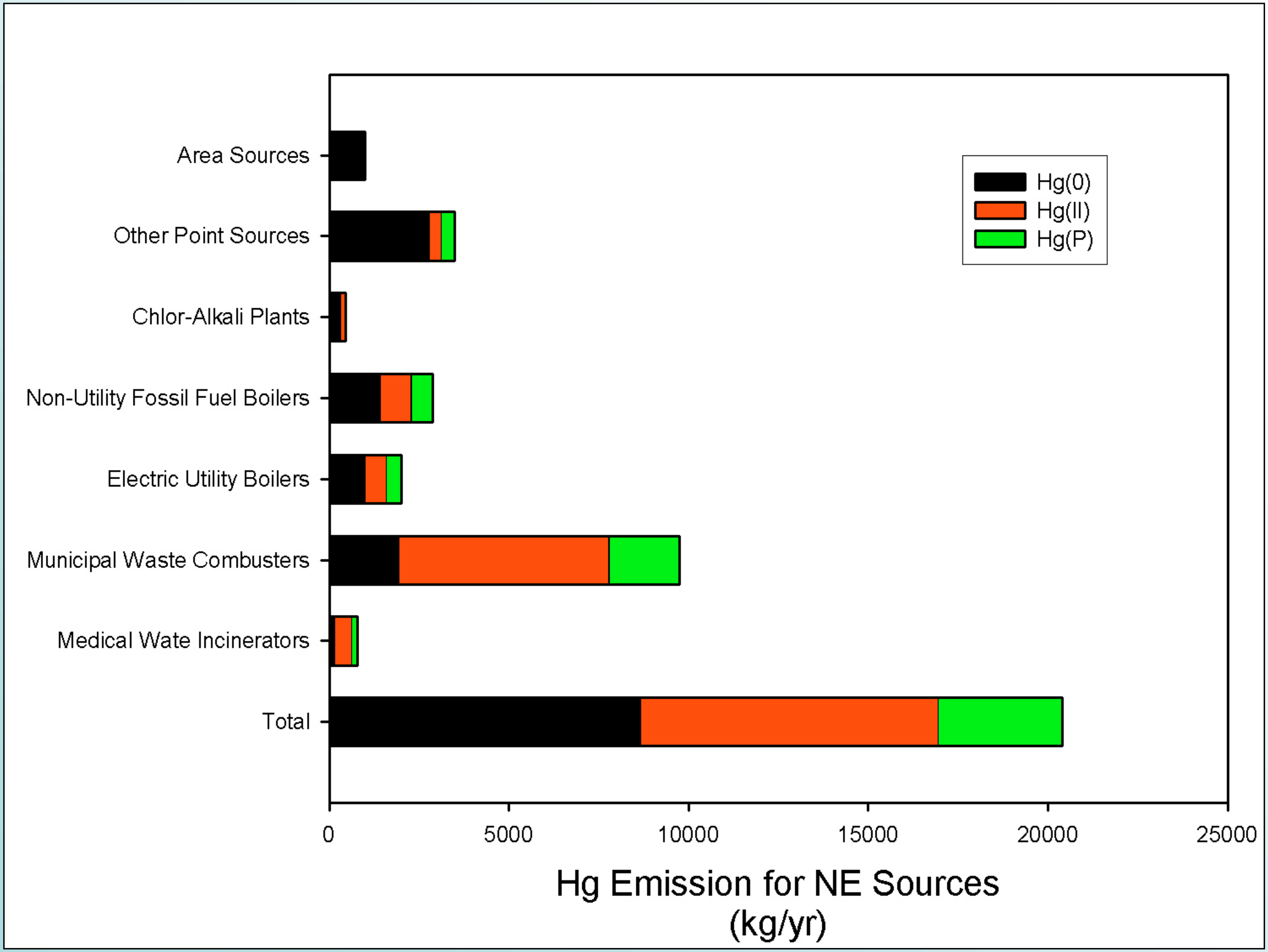
Outline

- Background
- Mercury in Adirondack Lake/Watersheds
- Historical Patterns of Mercury Deposition
- Utility Emission Controls
- Conclusions

Forms of Mercury

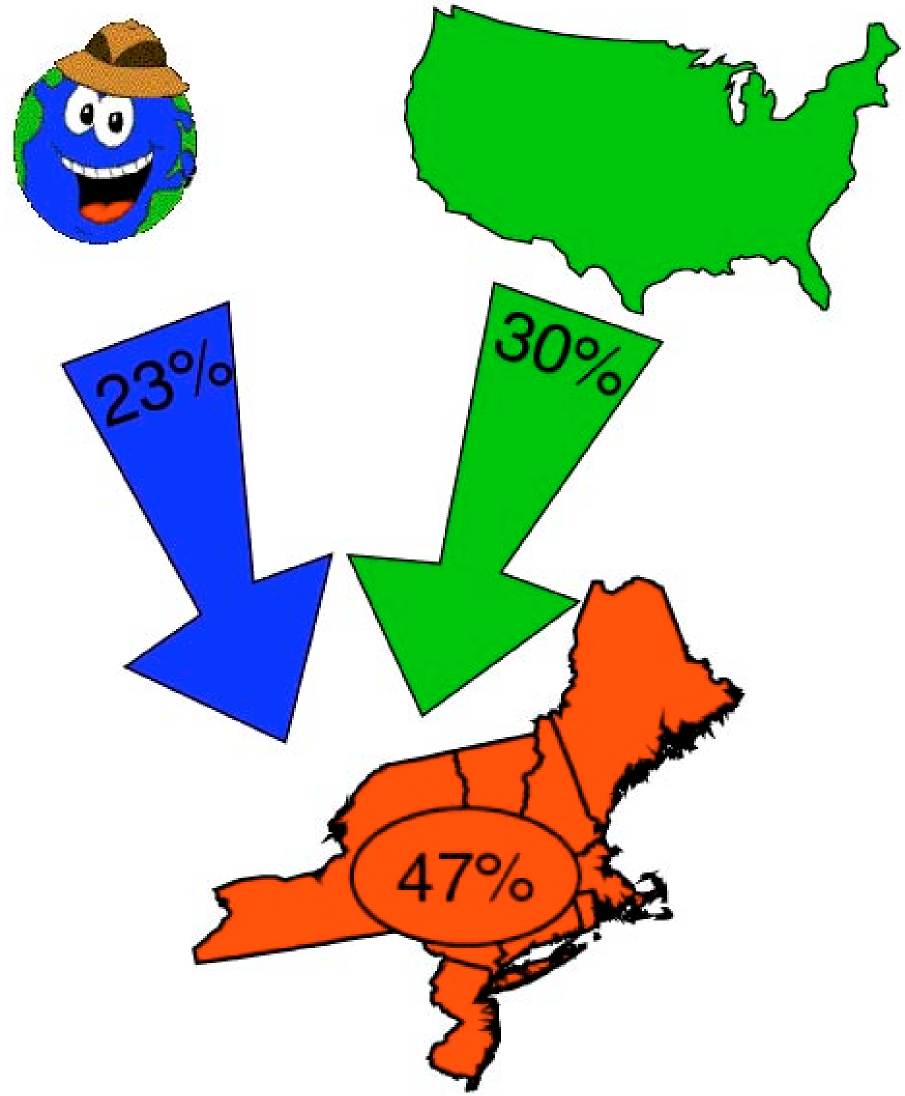
Hg^0	- Elemental Mercury
	- Gas phase, highly insoluble
	- Not highly toxic
	- High exposure to vapors cause a neurotoxic response, “mad hatter” syndrome
Hg^{2+}	- Ionic Mercury
	- Liquid phase, soluble
	- Not highly toxic
	- Damage g.i. tract, kidneys and liver
CH_3Hg^+	- Monomethyl Mercury
	- Biological tissue (muscle)
	- Neurotoxin – most toxic form of mercury

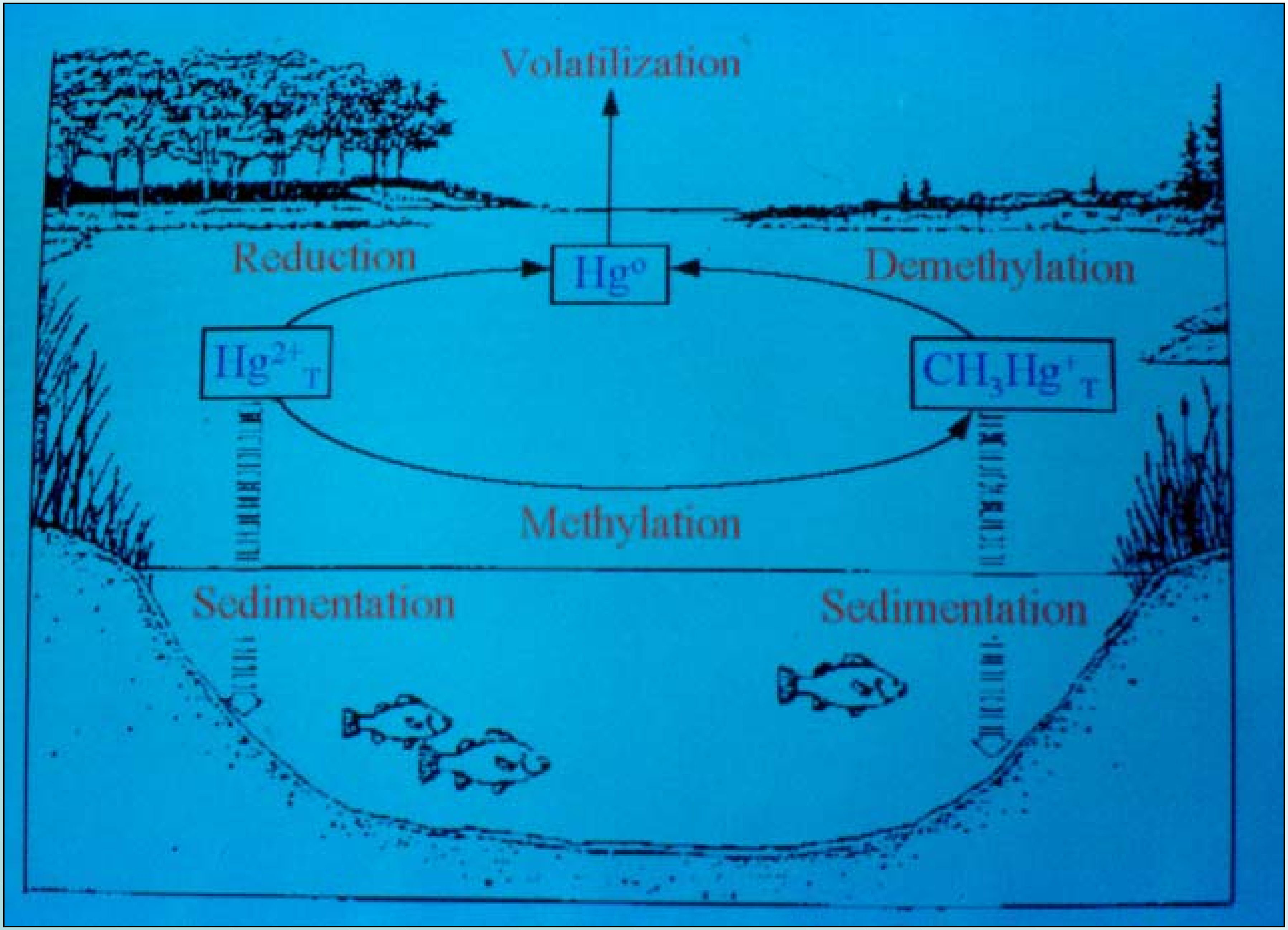

Area Sources
Other Point Sources
Chlor-Alkali Plants
Non-Ferrous Metal Smelting
Non-Utility Fossil Fuel Boilers
Electric Utility Boilers
Municipal Waste Combusters
Medical Wate Incinerators
Total
Hg(0)
Hg(II)
Hg(P)
0
20000
40000
60000
80000
100000
120000
140000
160000
180000
Hg Emission for United States
(kg/yr)



Area Sources
Other Point Sources
Chlor-Alkali Plants
Non-Utility Fossil Fuel Boilers
Electric Utility Boilers
Municipal Waste Combusters
Medical Wate Incinerators
Total
Hg(0)
Hg(II)
Hg(P)
0
5000
10000
15000
20000
25000
Hg Emission for NE Sources
(kg/yr)

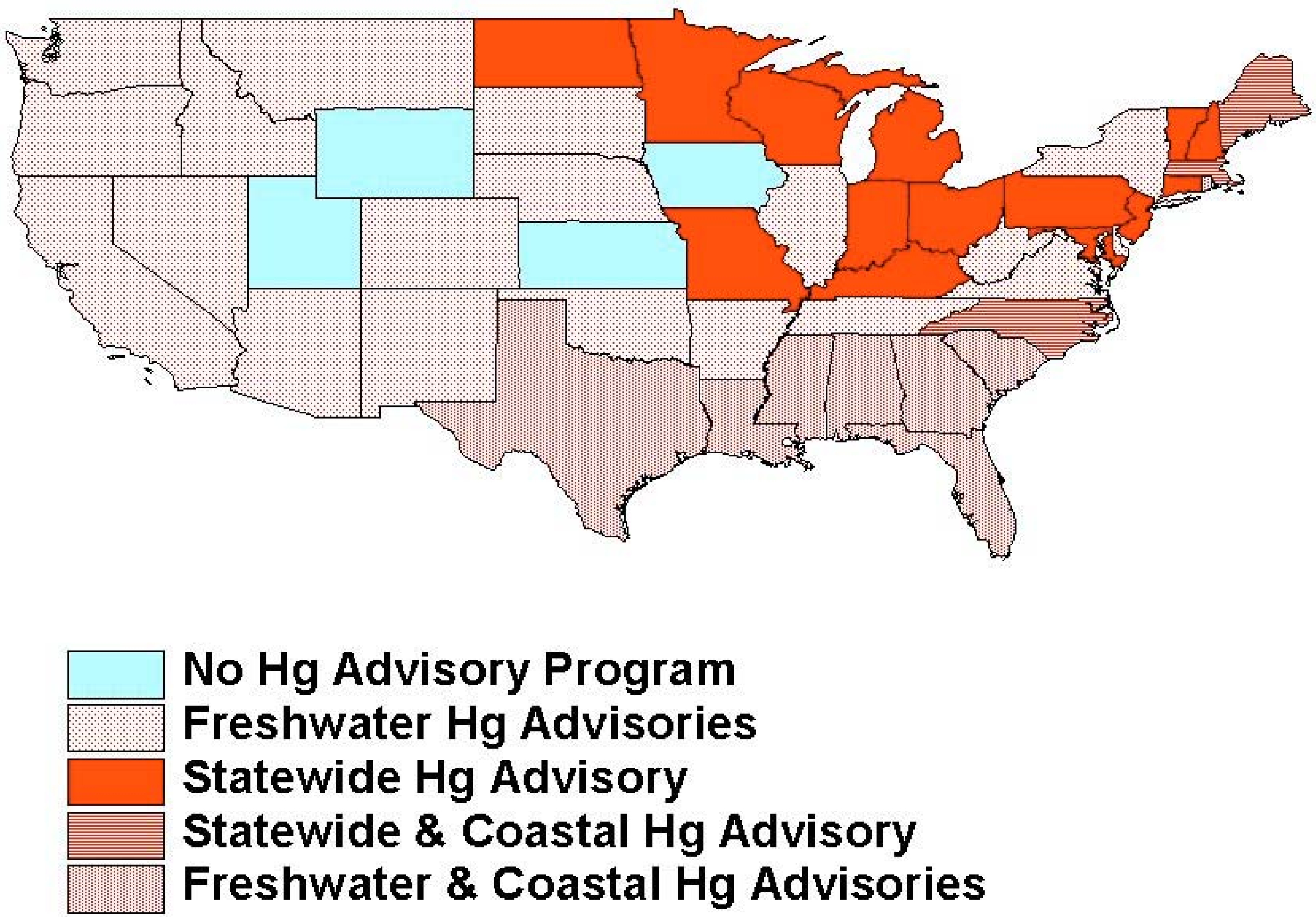
Sources of Hg Deposition in the Northeast



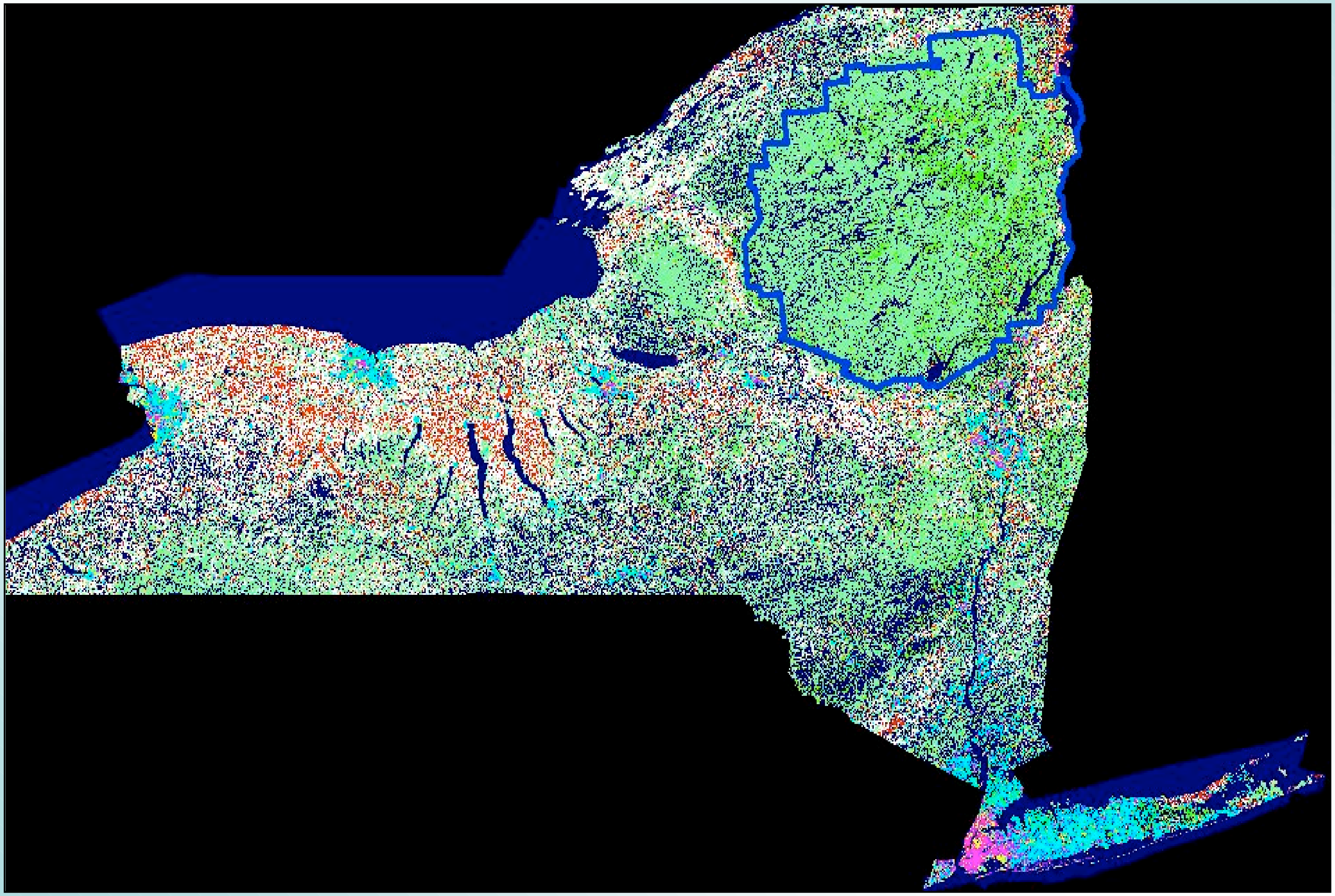


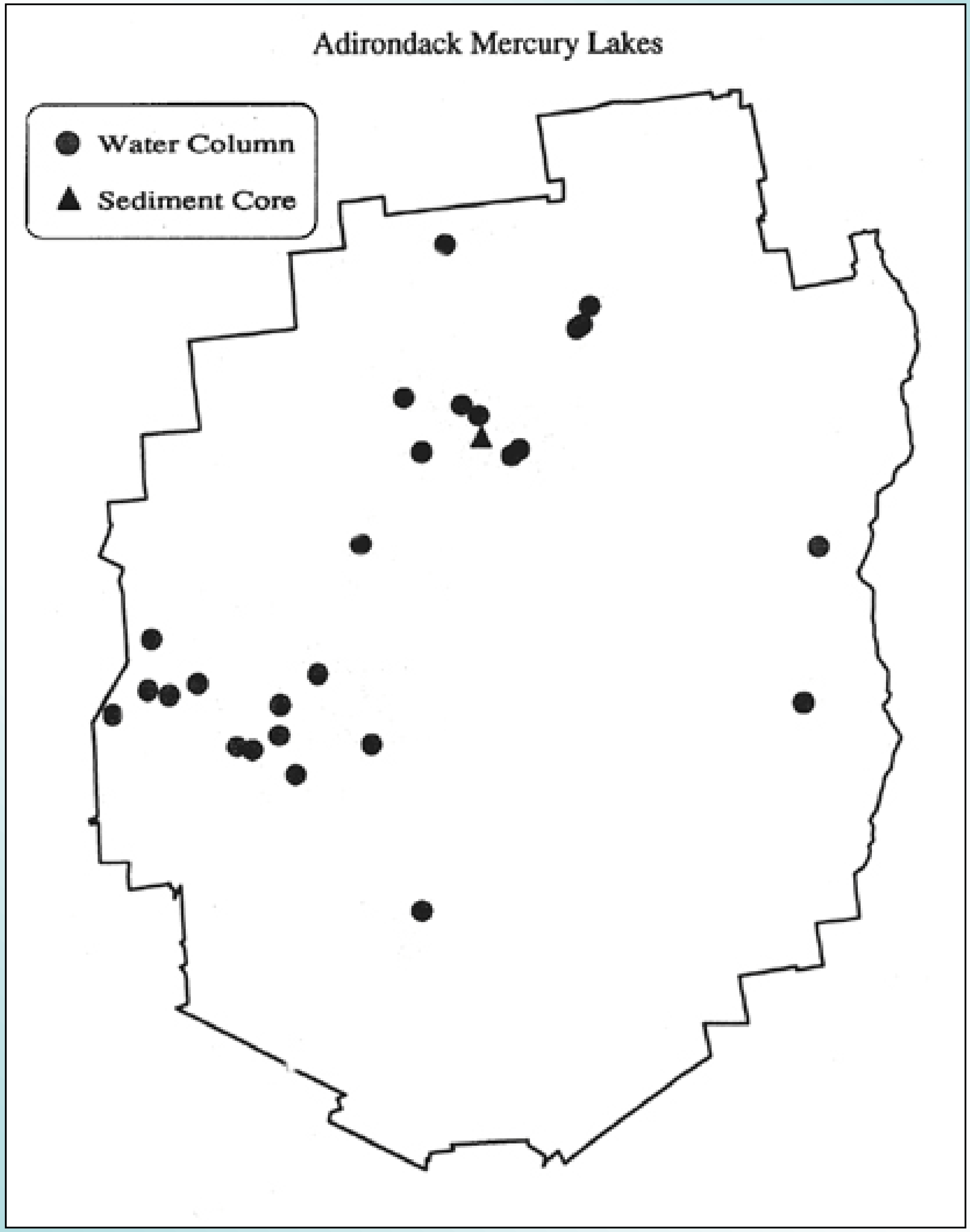
Volatilization
Reduction
Hg^{o}
Demethylation
Hg^{2+}_{T}
$CH_3Hg^{+}_{T}$
Methylation
Sedimentation
Sedimentation

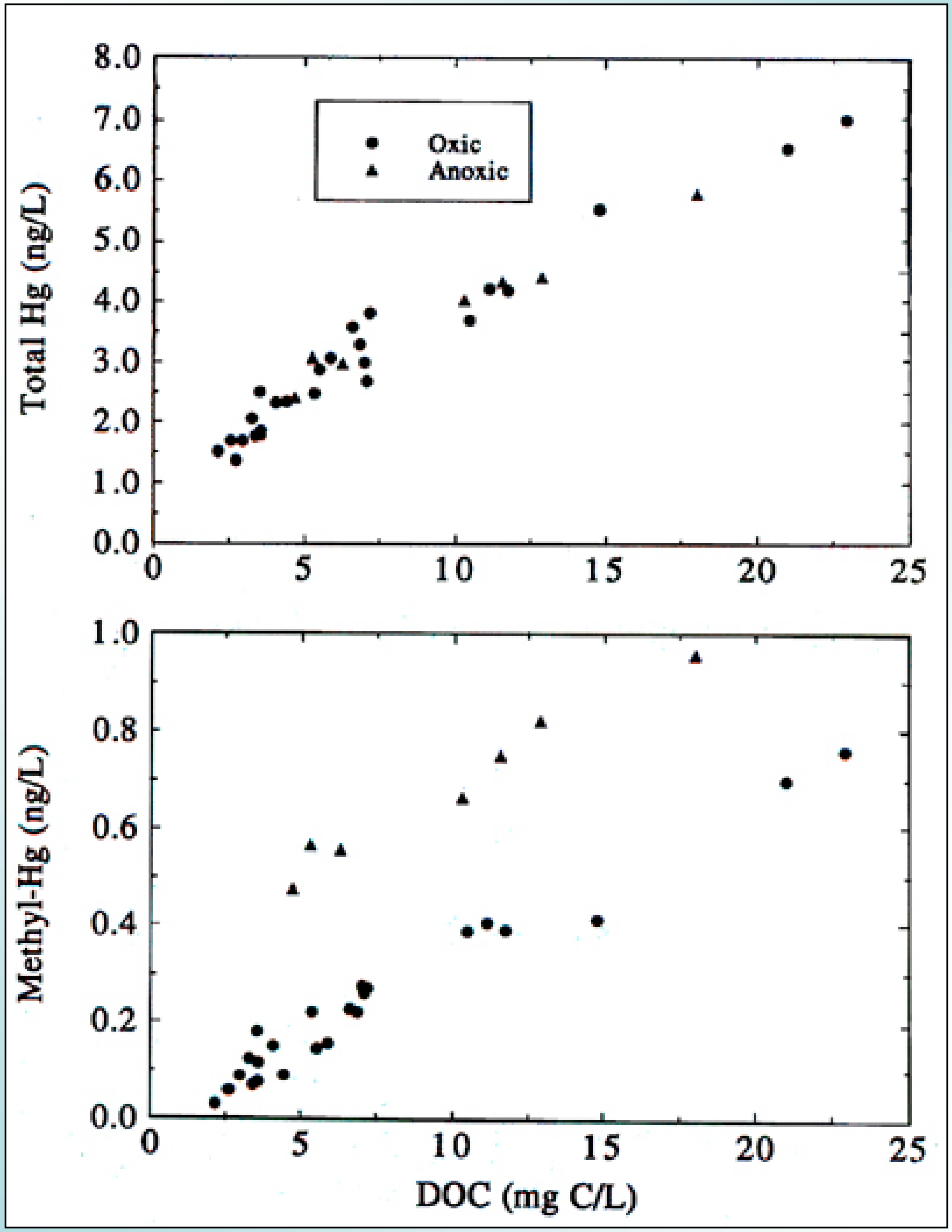
$$\text{Bioconcentration Factor (BF)} = \log\left(\frac{CH_3Hg - \text{fish}}{CH_3Hg - \text{water}}\right)$$


No Hg Advisory Program
Freshwater Hg Advisories
Statewide Hg Advisory
Statewide & Coastal Hg Advisory
Freshwater & Coastal Hg Advisories

Mercury in Adirondack Lake/Watersheds

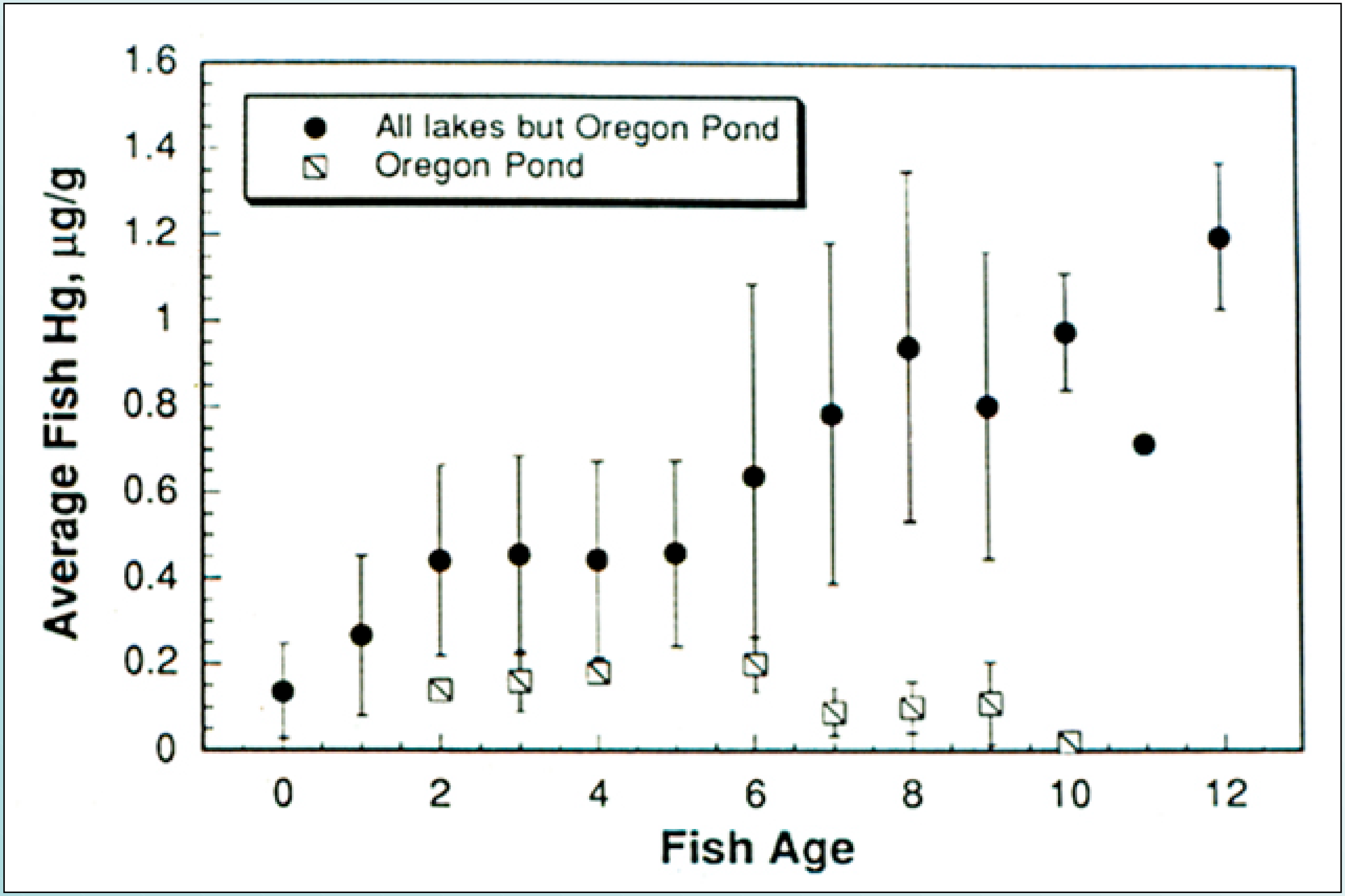


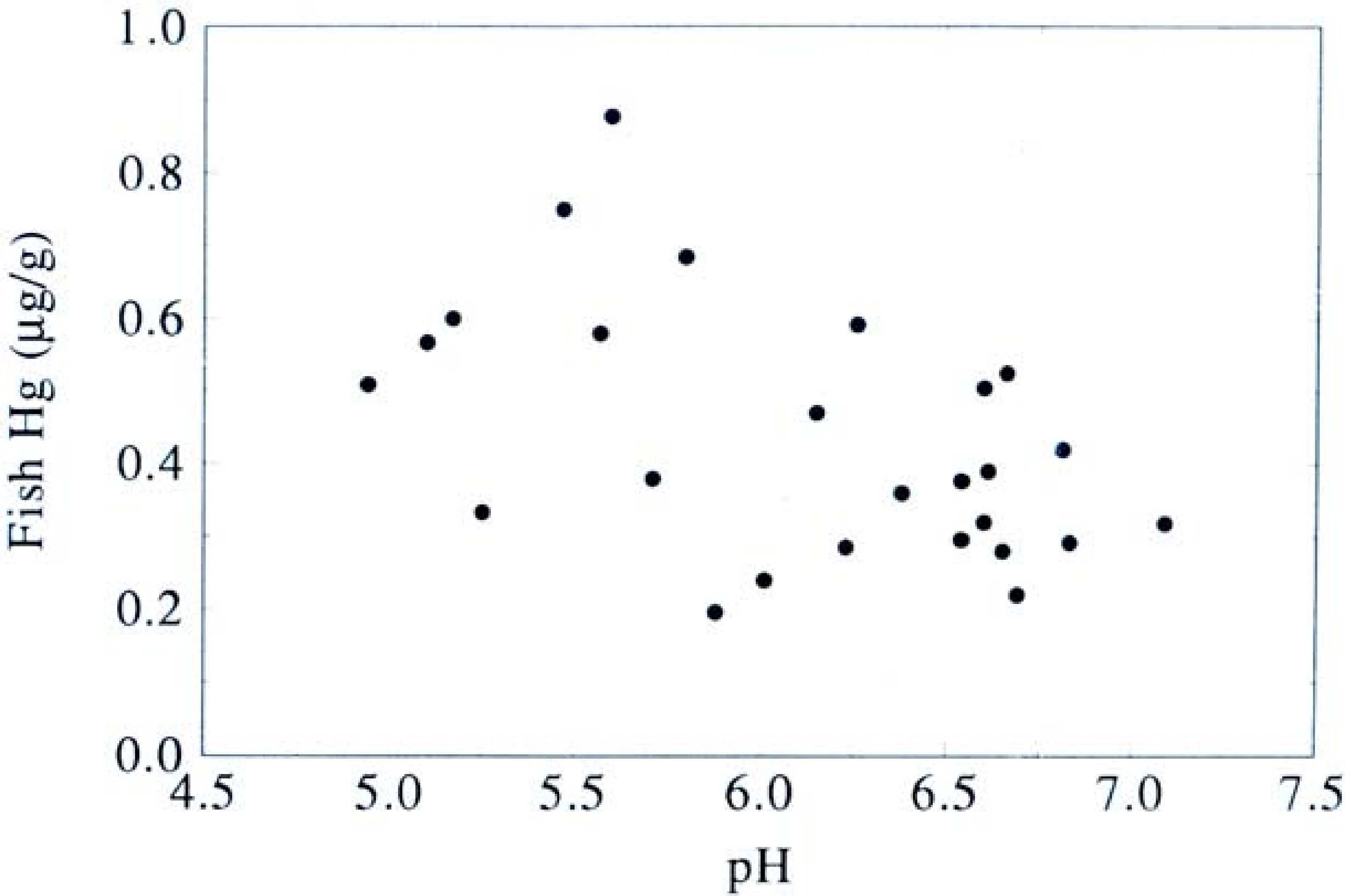

Adirondack Mercury Lakes
Water Column
Sediment Core

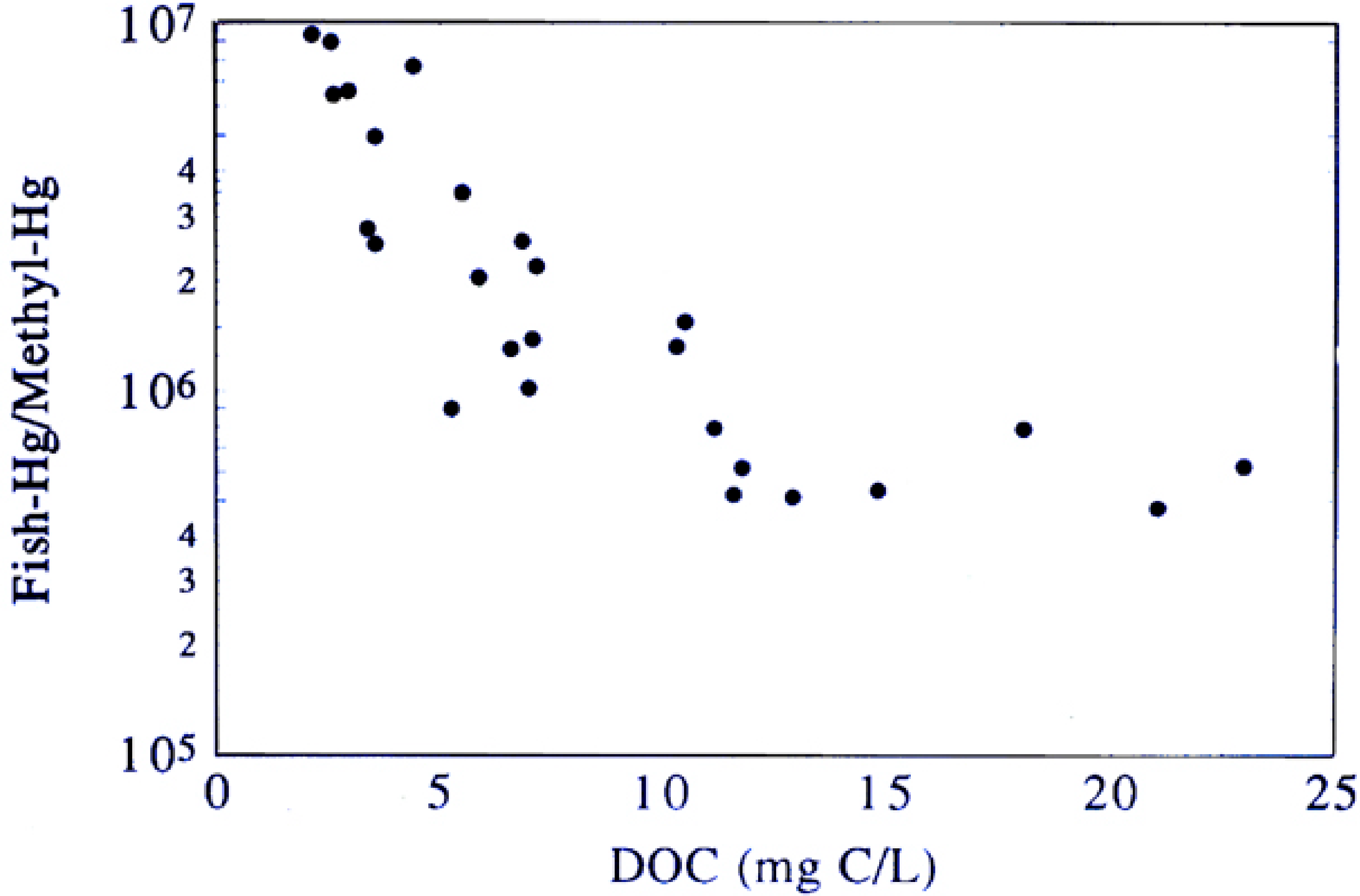

Oxic
Anoxic
Total Hg (ng/L)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
5
10
15
20
25
Methyl-Hg (ng/L)
1.0
0.8
0.6
0.4
0.2
0.0
DOC (mg C/L)

Fish Hg Concentrations

	Hg Concentrations	
	> 0.5 µg/g	> 1.0 µg/g
% fish	34	7.3
% lakes	96	65


1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Average Fish Hg, µg/g
All lakes but Oregon Pond
Oregon Pond
0
2
4
6
8
10
12
Fish Age

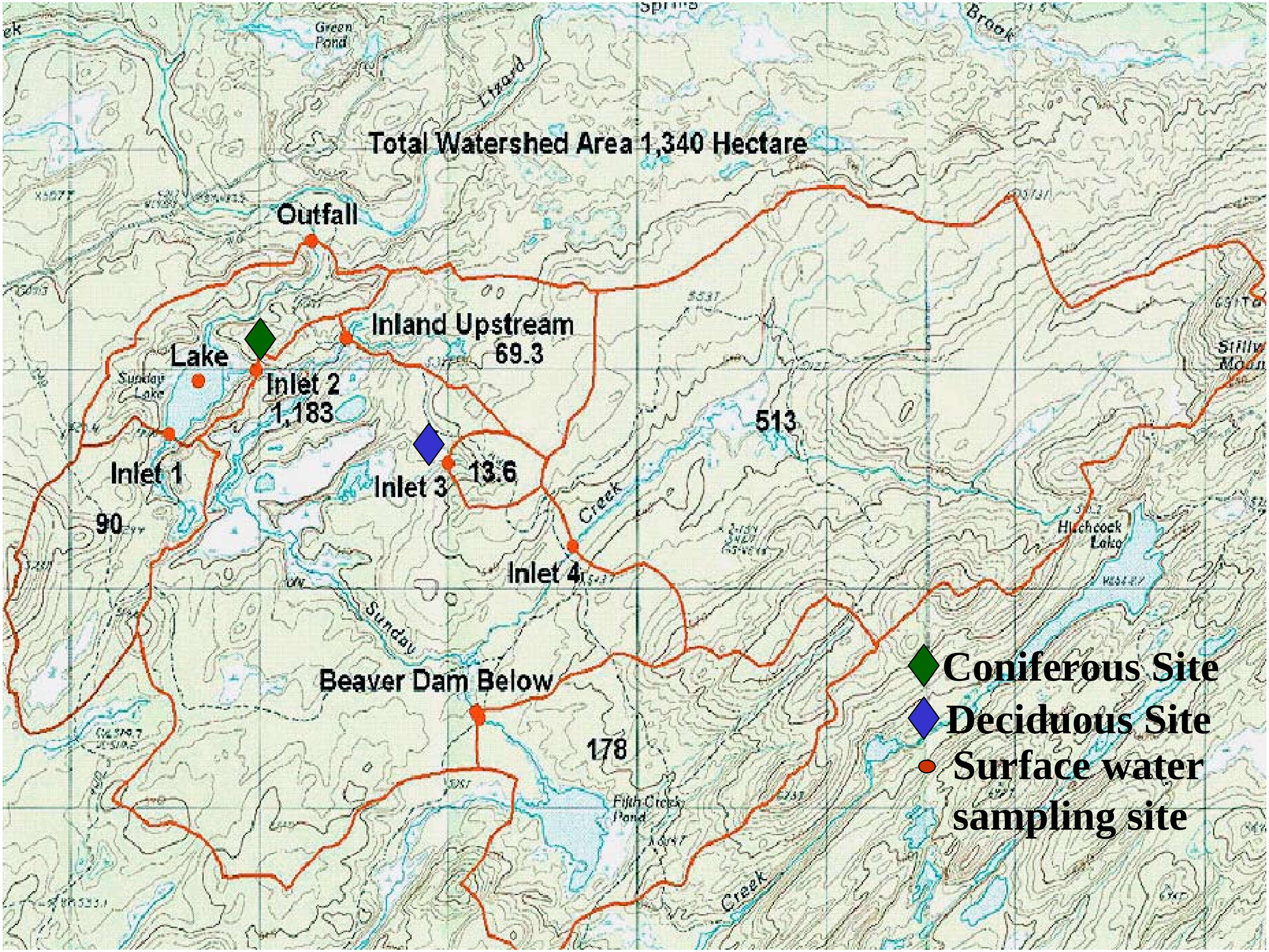

1.0
0.8
0.6
0.4
0.2
0.0
Fish Hg (µg/g)
4.5
5.0
5.5
6.0
6.5
7.0
7.5
pH

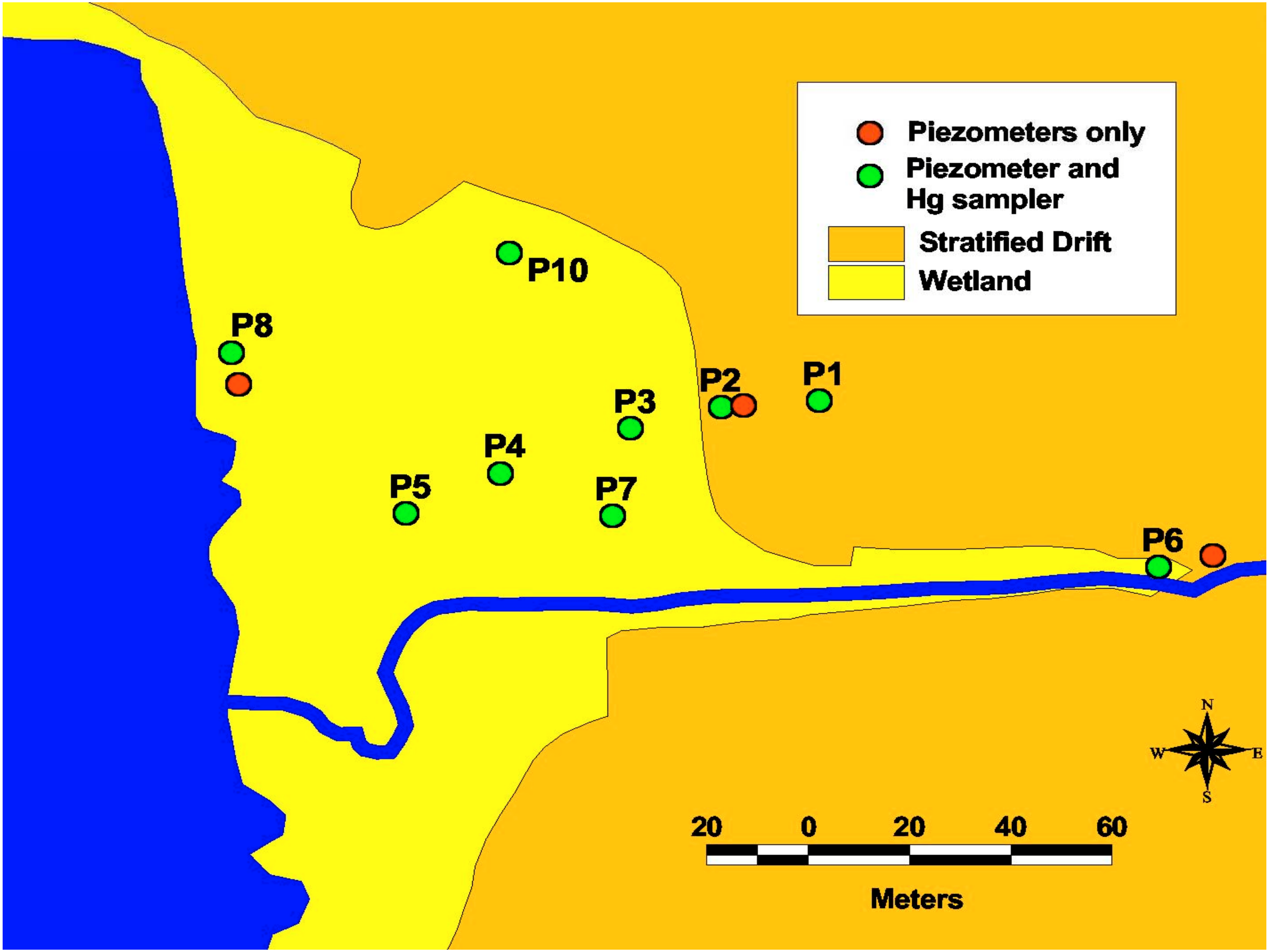


10^7
4
3
2
10^6
4
3
2
10^5
Fish-Hg/Methyl-Hg
0
5
10
15
20
25
DOC (mg C/L)

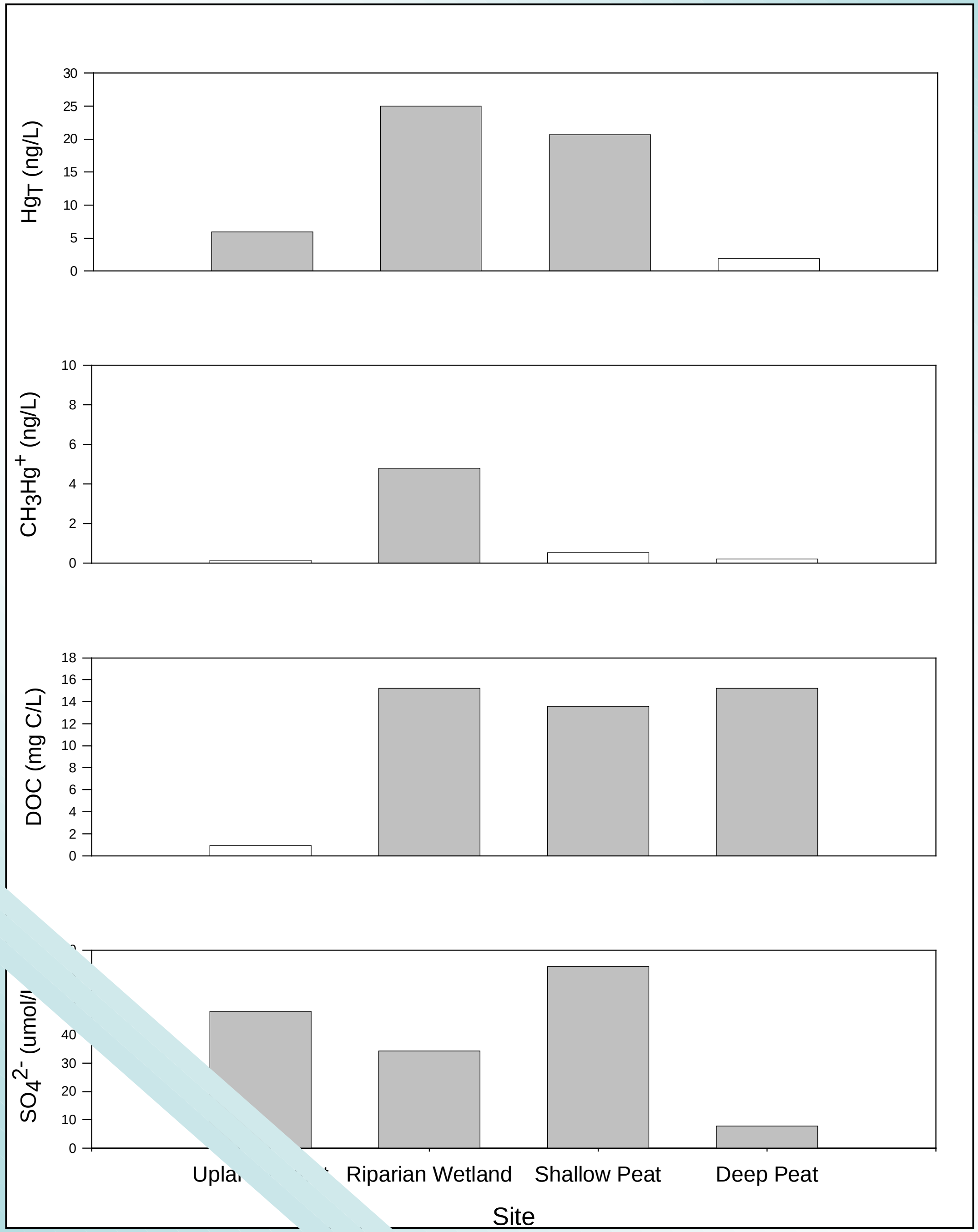
Sunday Lake Watershed

Watershed	-	1340 ha
Upland vegetation	-	second growth forest deciduous – 70% coniferous – 30%
Wetlands	-	20.5% of watershed palustrine forest and shrub conifers, riparian, beaver impoundments
Lake		
Surface area	-	7.7 ha
Mean depth	-	2.5 m
Chemistry	pH	5.6
	ANC	20 µeq/L
	DOC	10.3 mg C/L
Fish Hg		
Mean 3+ to 5+ yellow perch		0.88 µg/g

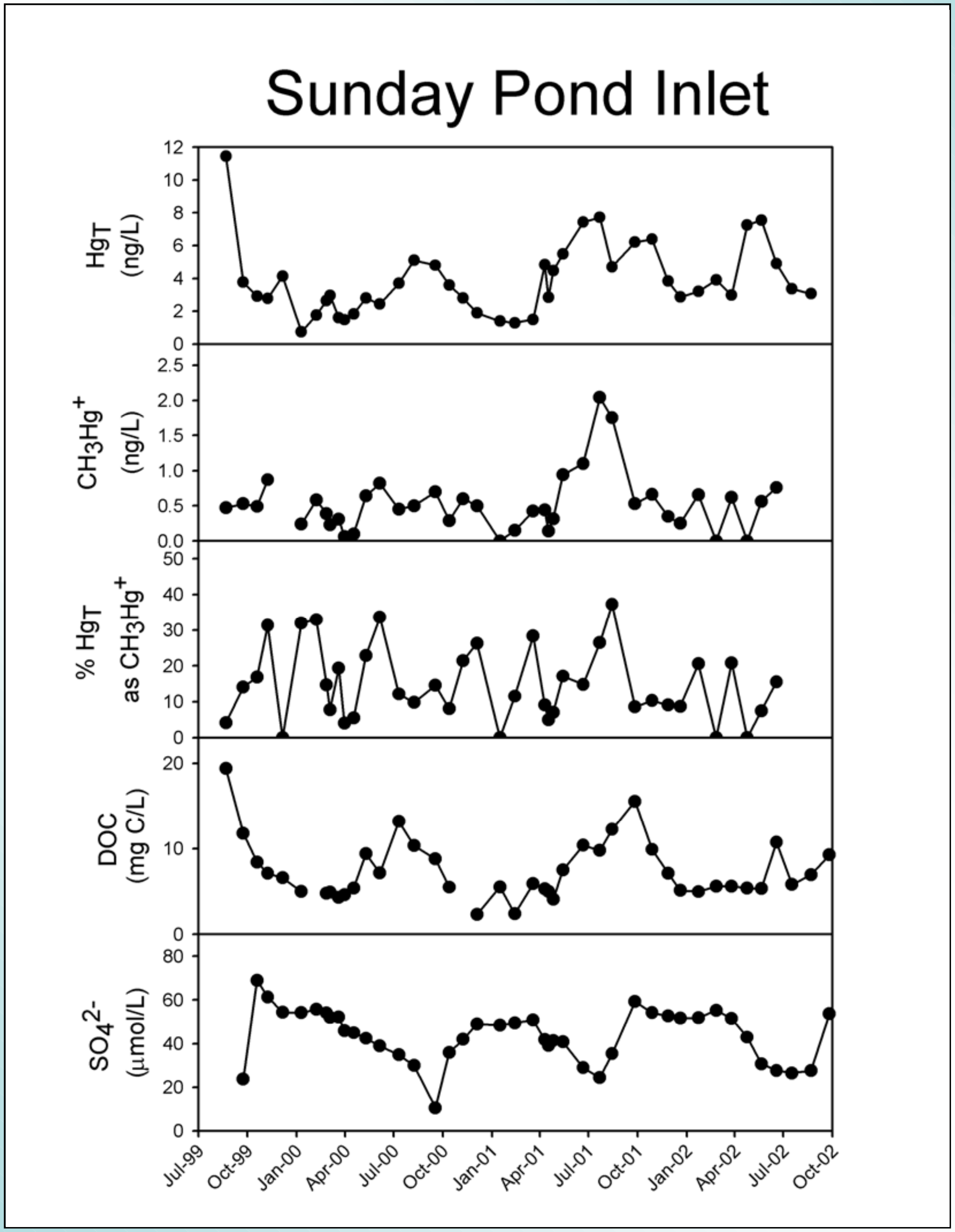

Total Watershed Area 1,340 Hectare
Outfall
Inland Upstream
69.3
Lake
Inlet 2
1,183
Inlet 1
90
Inlet 3
13.6
513
Inlet 4
Beaver Dam Below
178
Coniferous Site
Deciduous Site
Surface water sampling site



Piezometers only
Piezometer and Hg sampler
Stratified Drift
Wetland
P10
P8
P2
P1
P3
P4
P5
P7
P6
N
W
E
S
20 0 20 40 60
Meters

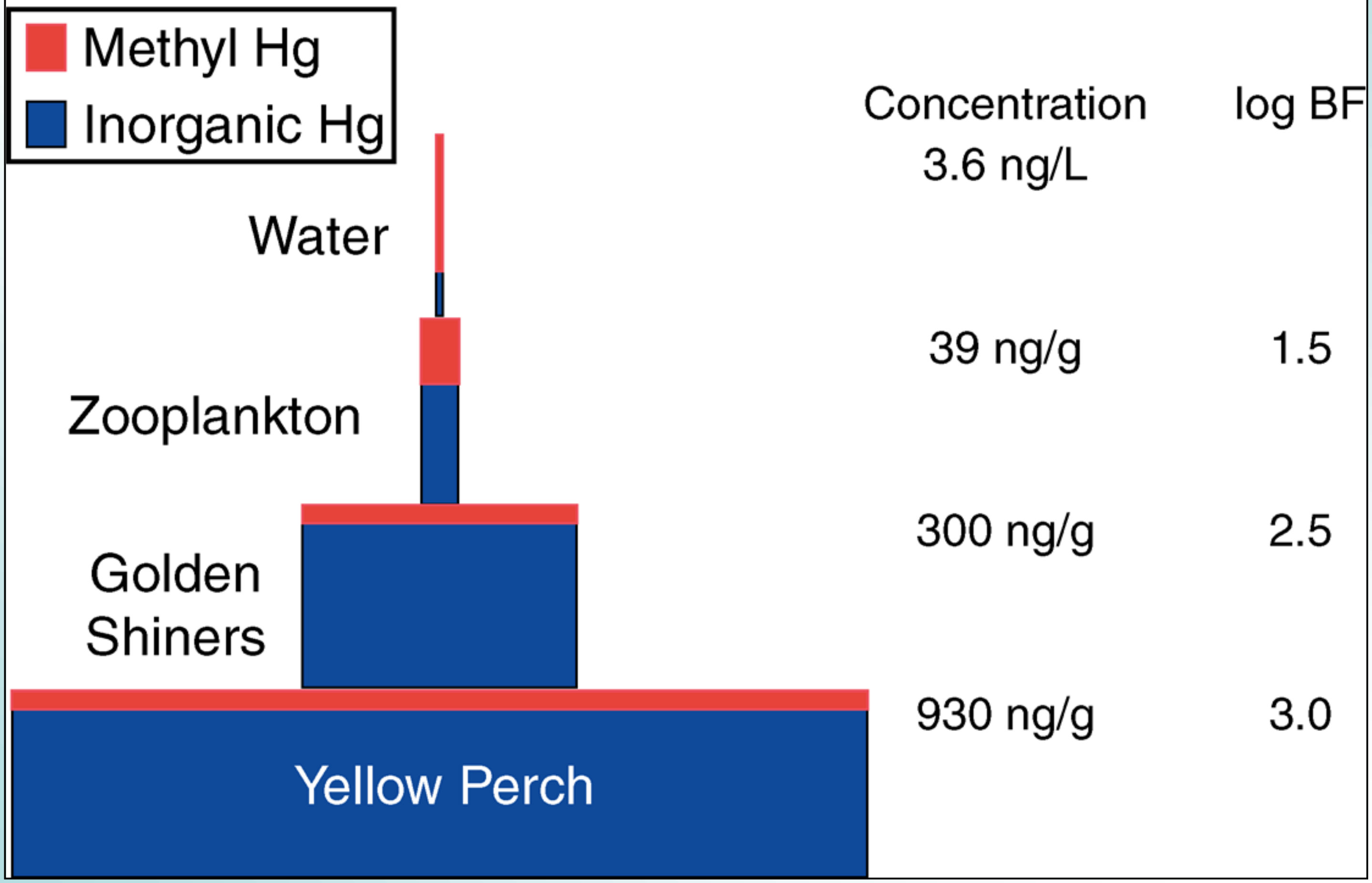


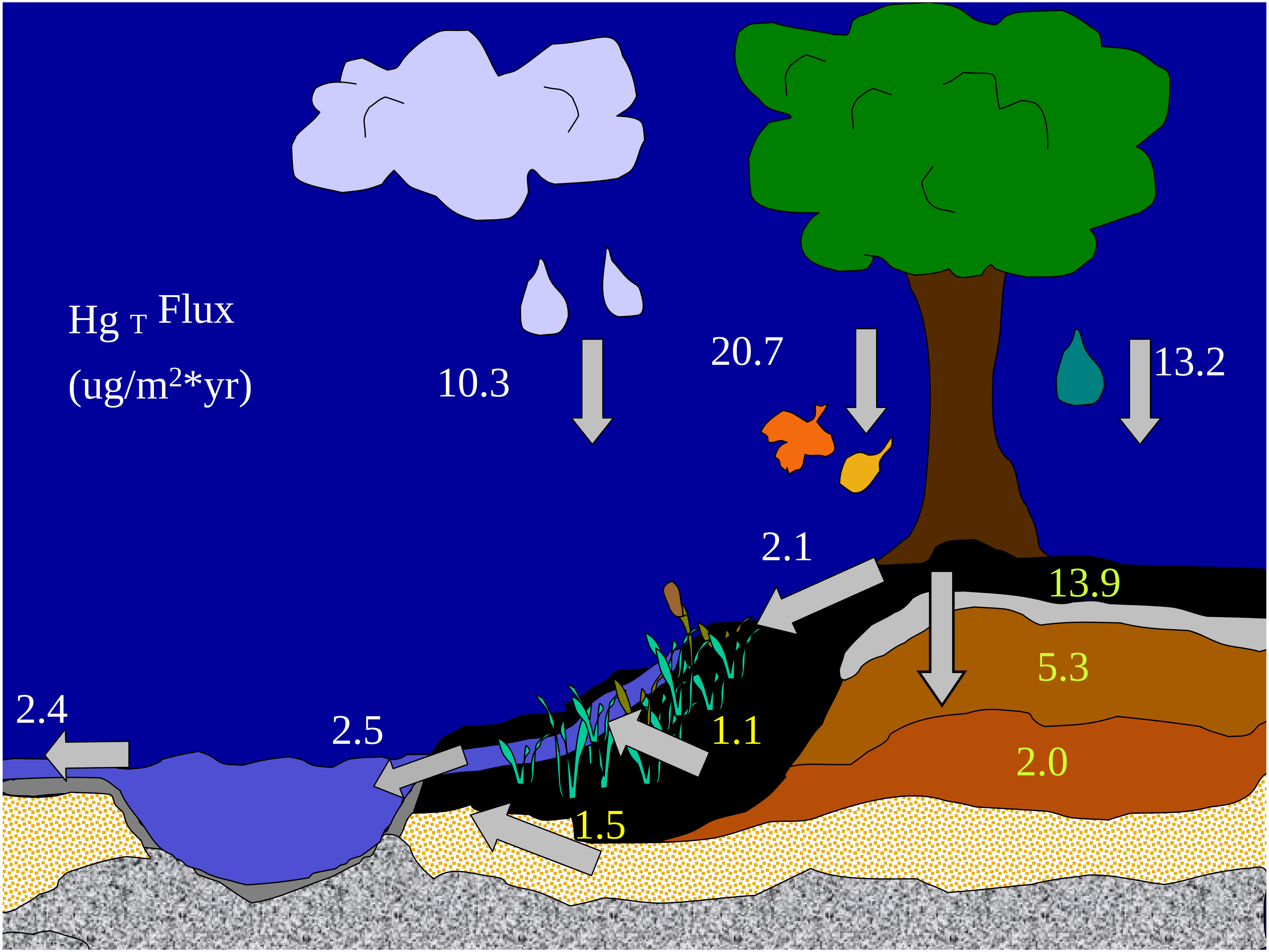
Hg_T (ng/L)
CH_3Hg^+ (ng/L)
DOC (mg C/L)
Riparian Wetland
Shallow Peat
Deep Peat
Site

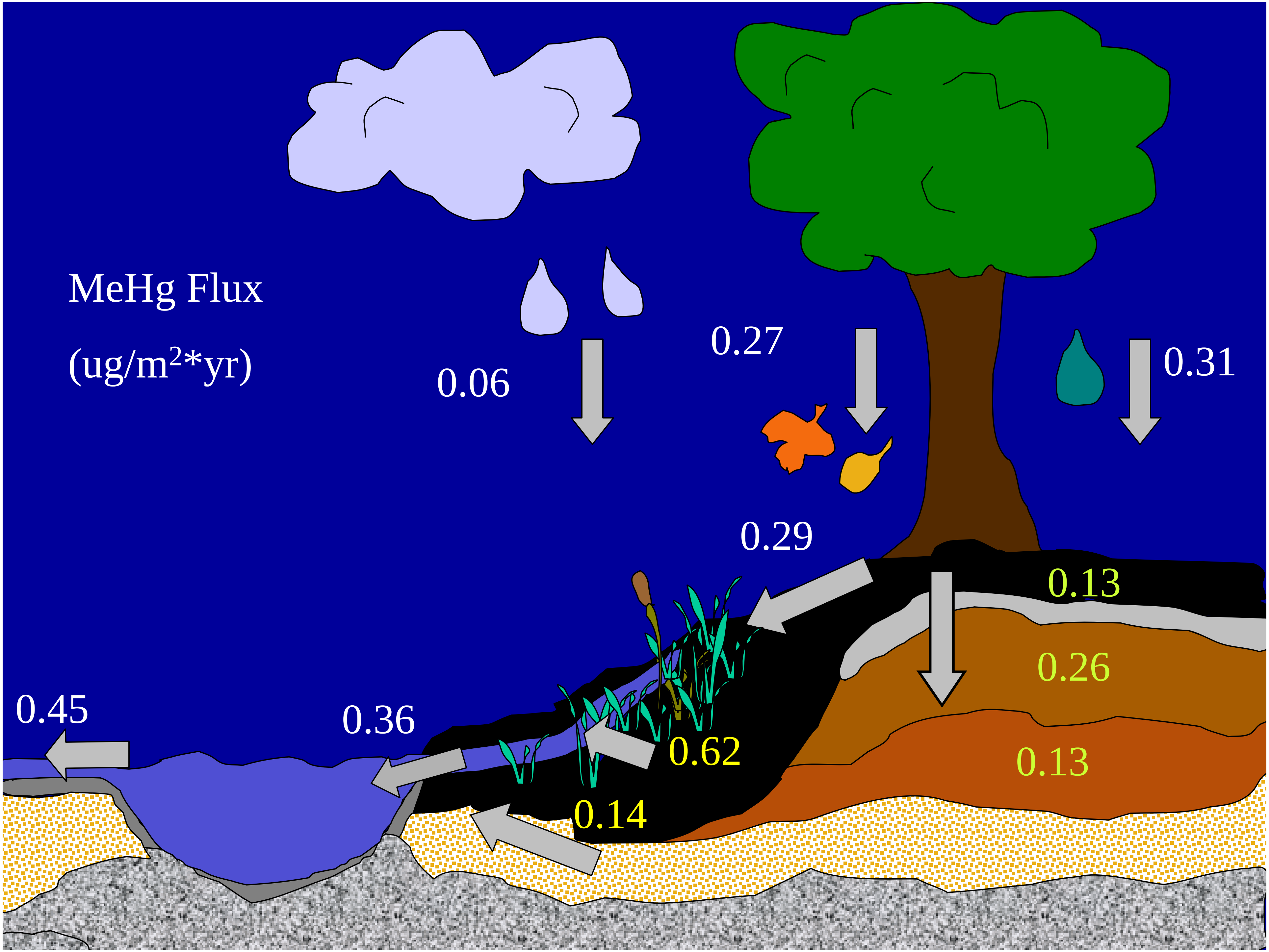


Sunday Pond Inlet
HgT (ng/L)
CH3Hg+ (ng/L)
% HgT as CH3Hg+
DOC (mg C/L)
SO42- (µmol/L)
Jul-99
Oct-99
Jan-00
Apr-00
Jul-00
Oct-00
Jan-01
Apr-01
Jul-01
Oct-01
Jan-02
Apr-02
Jul-02
Oct-02

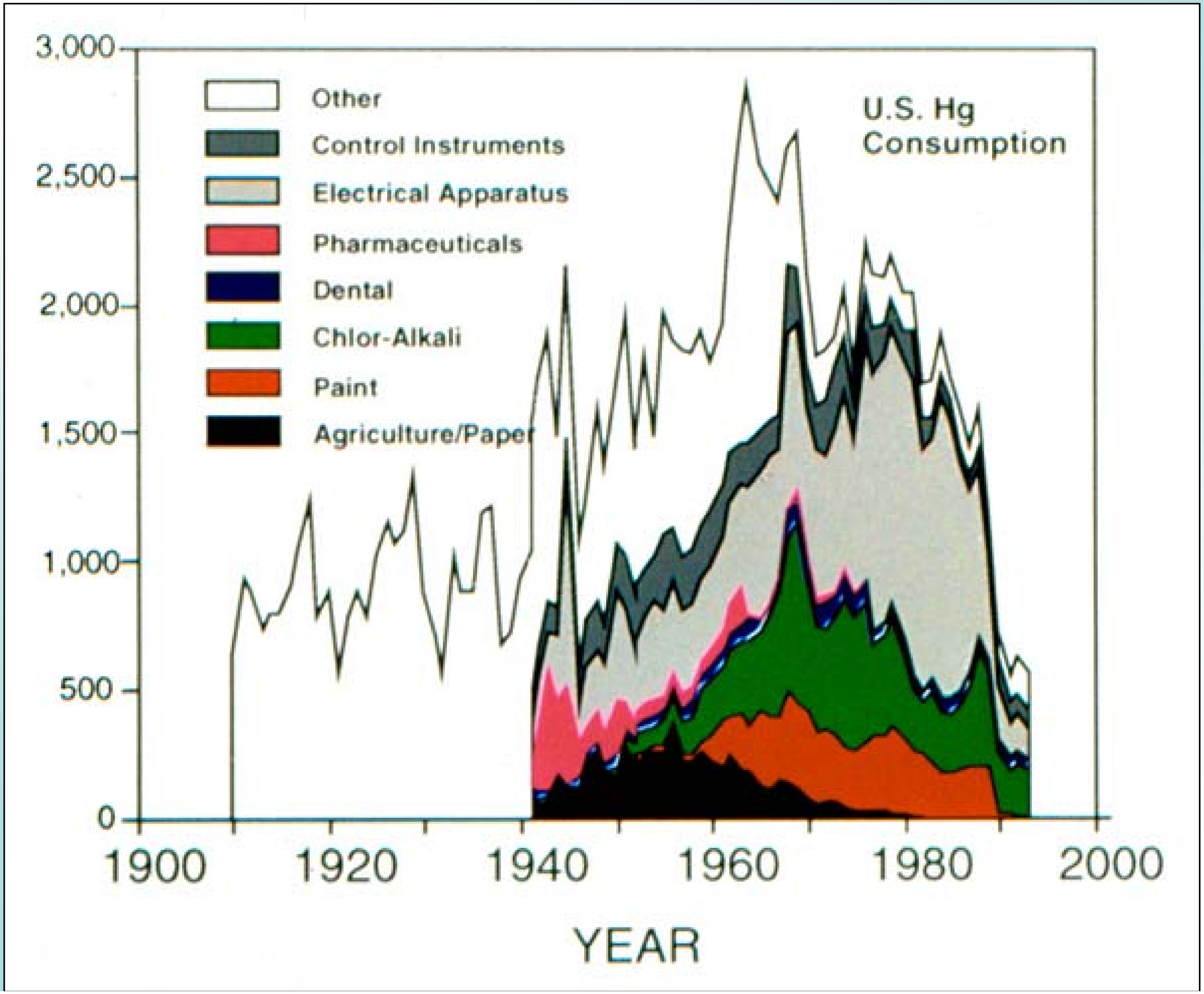
Biocomplexity of Mercury in Sunday Lake

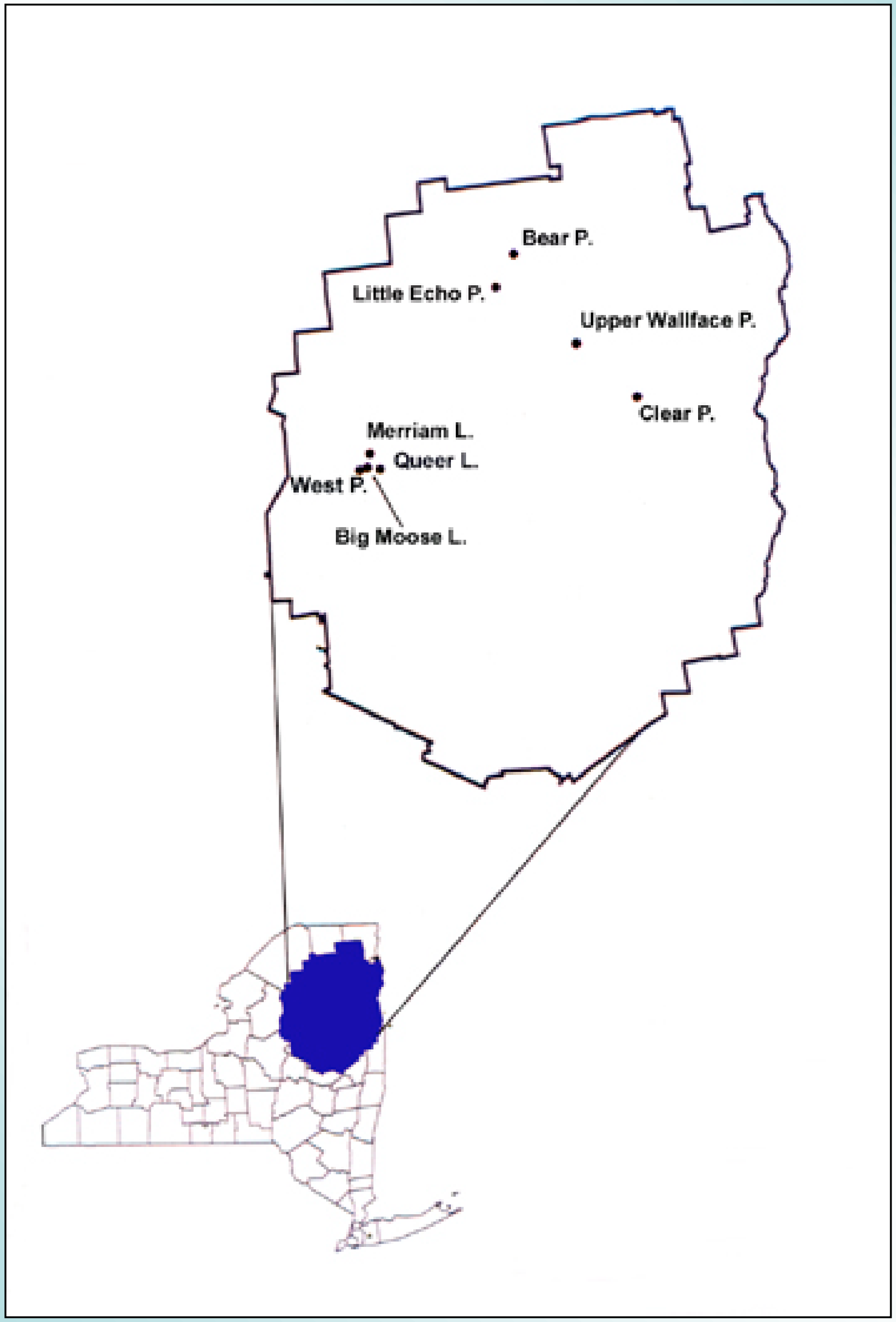


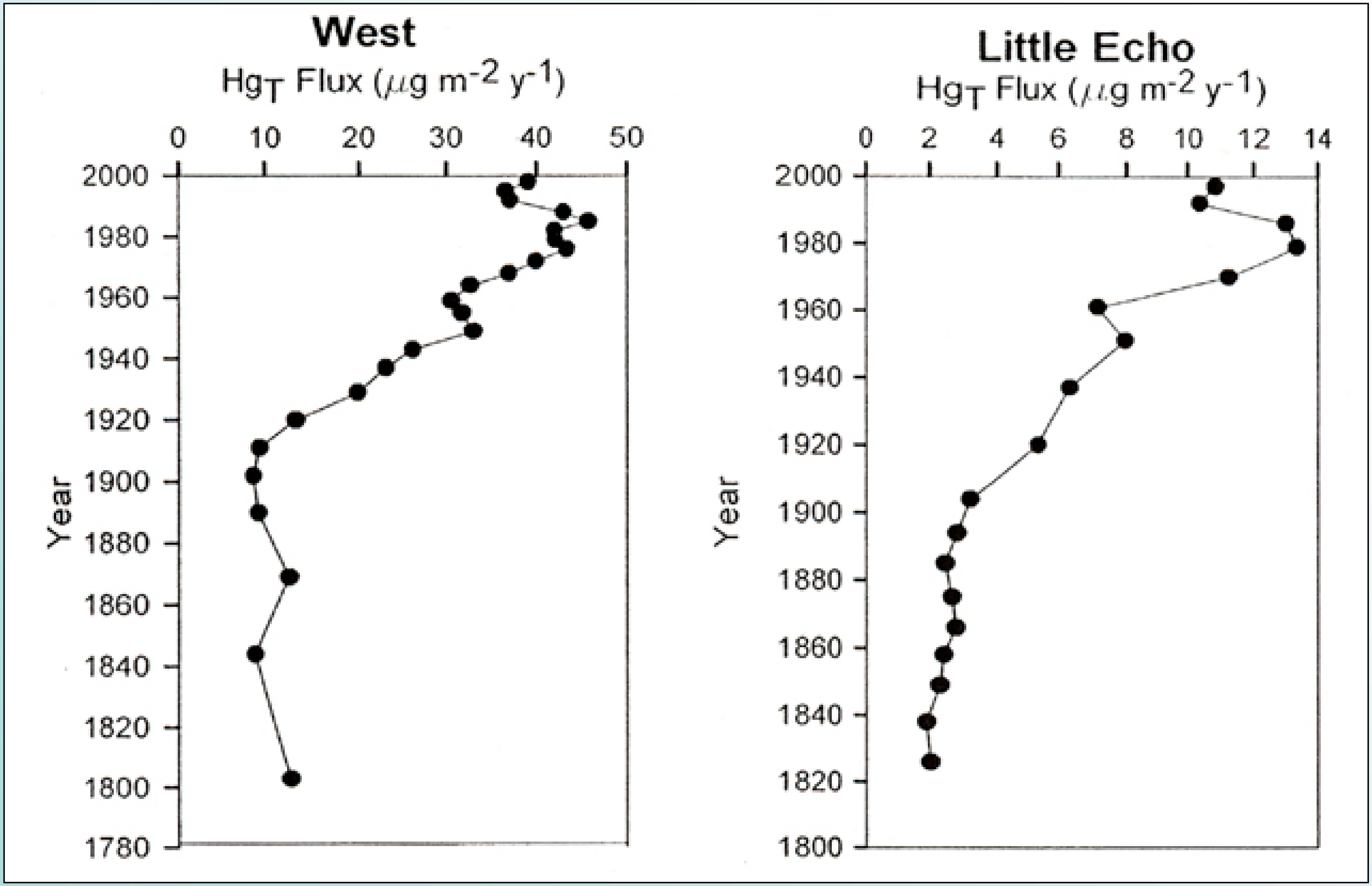

Hg T Flux
(ug/m2*yr)
10.3
20.7
13.2
2.1
13.9
5.3
2.0
1.1
1.5
2.5
2.4


MeHg Flux
(ug/m2*yr)
0.06
0.27
0.31
0.29
0.13
0.26
0.13
0.45
0.36
0.62
0.14

Historical Patterns of Hg Deposition




Bear P.
Little Echo P.
Upper Wallface P.
Clear P.
Merriam L.
Queer L.
West P.
Big Moose L.

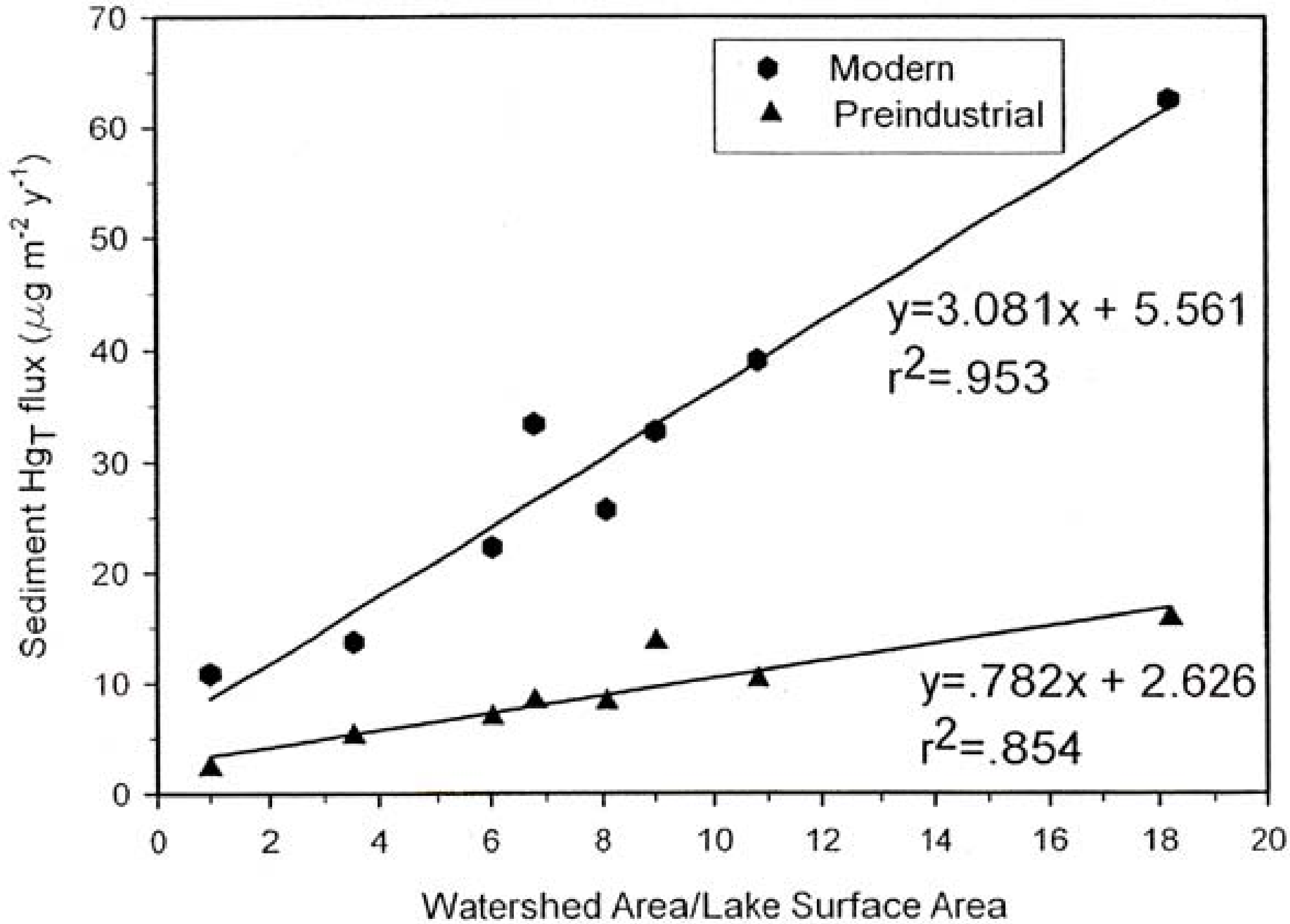


West
HgT Flux (μg m-2 y-1)
0 10 20 30 40 50
2000 1980 1960 1940 1920 1900 1880 1860 1840 1820 1800 1780
Year
Little Echo
HgT Flux (μg m-2 y-1)
0 2 4 6 8 10 12 14
2000 1980 1960 1940 1920 1900 1880 1860 1840 1820 1800
Year

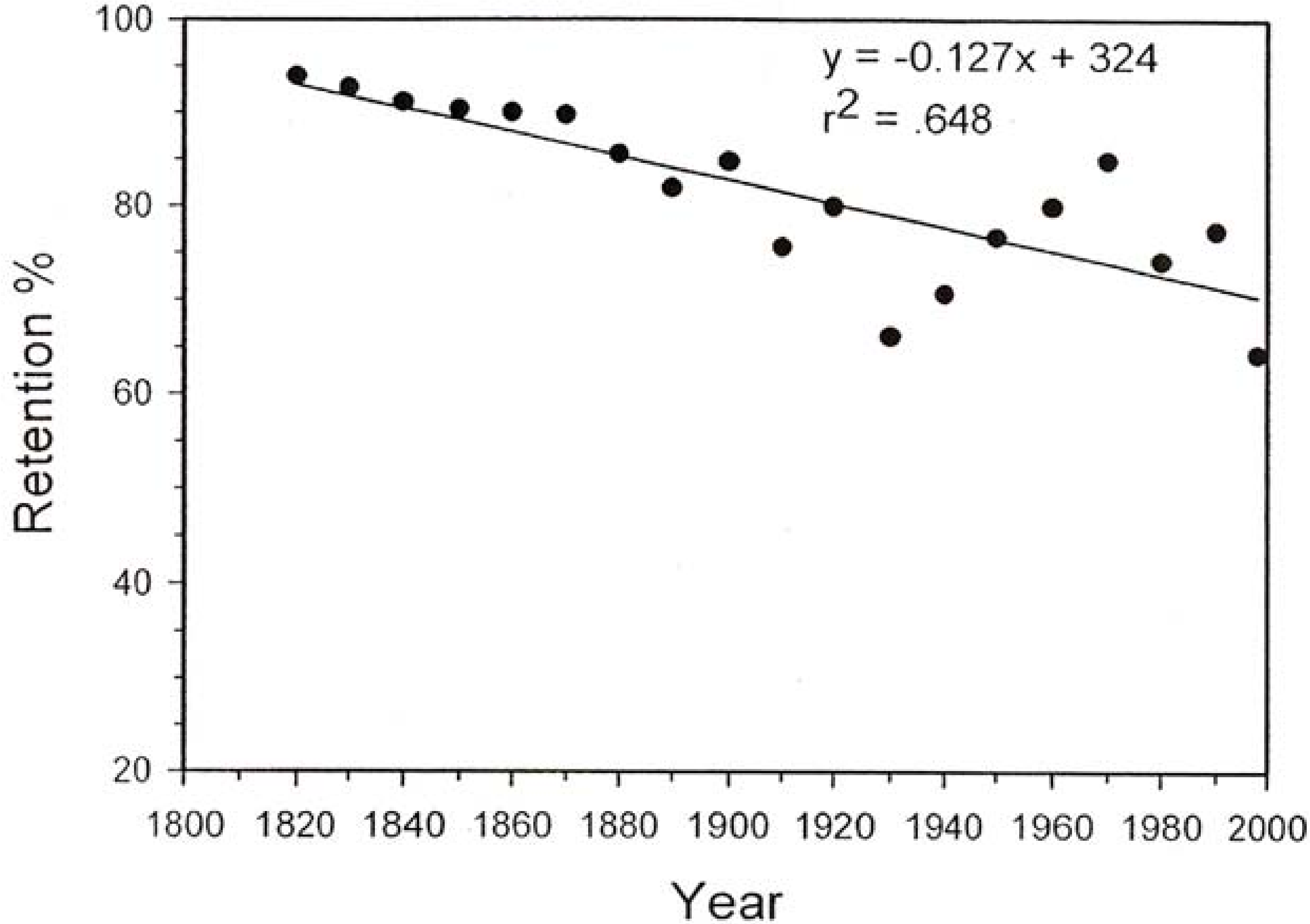
Sediment Hg_T Fluxes

Preindustrial, maximum, and modern Hg_T fluxes (µg/m^2-yr; 1998 values) of the Adirondack study lakes, along with the ratios obtained relative to background values

Lake	**Preindustrial Flux (years averaged)**	**Maximum Flux (year)**	**Maximum Flux Ratio**	**Modern Flux (year)**	**Modern Flux Ratio**
Big Moose	16.0	90 (1973)	5.7	62	4.0
Little Echo	2.3	13 (1979)	5.8	11	4.7
Merriam	6.9	27 (1990)	3.9	22	3.2
West	10.0	46 (1985)	4.5	39	3.8
Bear	5.2	36 (1985)	6.9	14	2.6
Queer	8.3	116 (1983)	14.0	33	4.0
Upper Wallface	14.0	38 (1980)	2.8	33	2.4
Clear	8.2	26 (1995)	3.1	26	3.1
		Avg =	**5.8**	**Avg =**	**3.5**



Modern
Preindustrial
y=3.081x + 5.561
r2=.953
y=.782x + 2.626
r2=.854
Sediment HgT flux (μg m-2 y-1)
Watershed Area/Lake Surface Area
0
10
20
30
40
50
60
70
0
2
4
6
8
10
12
14
16
18
20



y = -0.127x + 324
r^2 = .648
Retention %
100
80
60
40
20
1800
1820
1840
1860
1880
1900
1920
1940
1960
1980
2000
Year

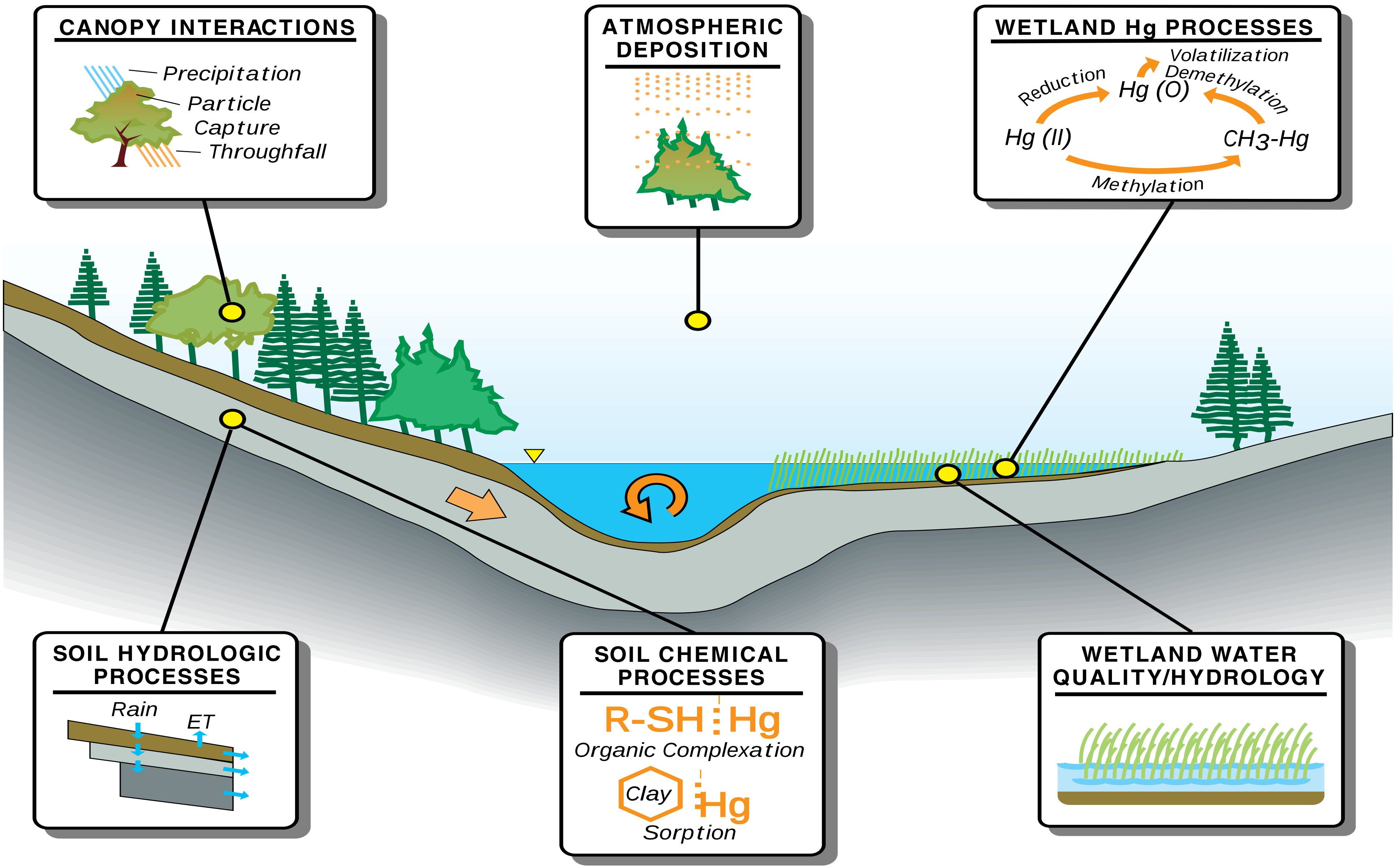
Utility Emission Controls

Policy or Proposal	Hg Emissions	Compliance Date	Emissions Trading among Plants?	Comments
1990 Clean Air Act	~48 T	N/A	N/A	
Jeffords Bill S.556 (as amended)	~ 5T 90% reduction	2007	No	5 ton cap
Smith Bill S.2815 (Clear Skies)	~15 T 70% reduction	2018	Yes	26 tons per yr by 2010 15 tons per yr by 2018
Clinton Bill S.588	No Control	N/A	N/A	

Utility MACT

Proposed 15 December 2003
Finalized late 2004
Compliance late 2007

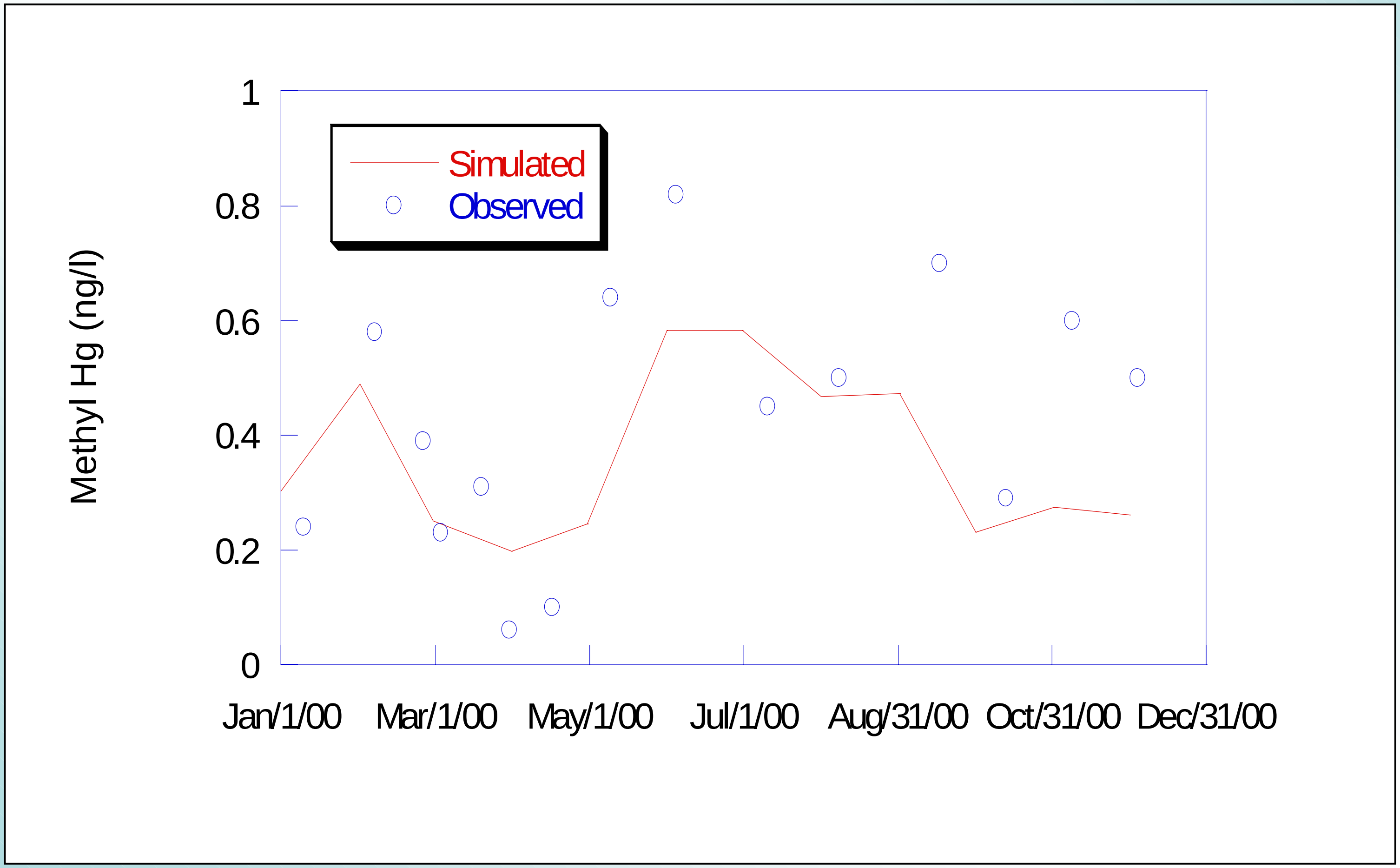
Mercury in Adirondack Wetlands, Lakes, and Terrestrial Systems (MAWLTS) Model



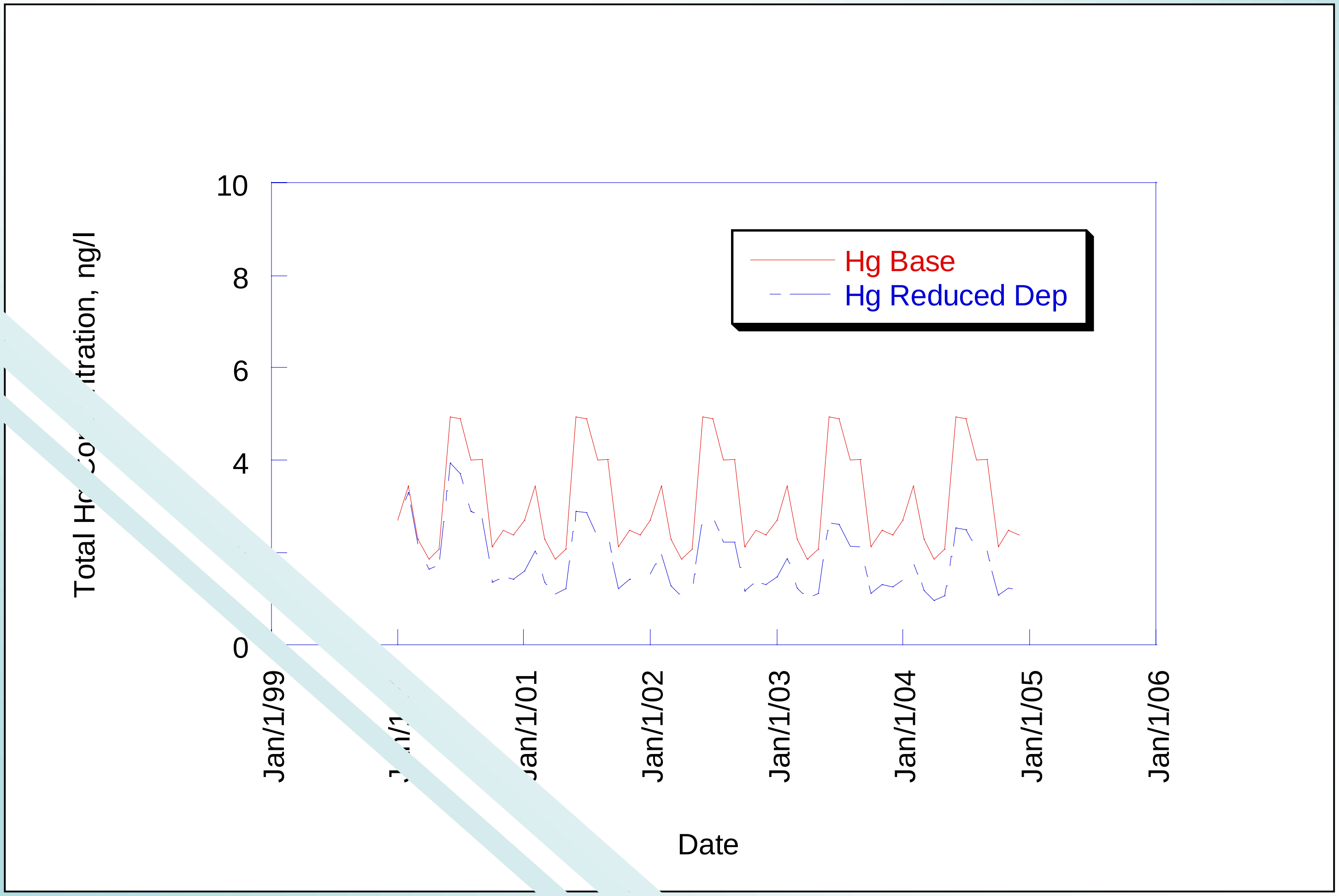
Model Hg Forms and Compartments

- Hg forms:
  - Inorganic Hg(II)
  - Methylmercury
  - Elemental mercury
- Compartments:
  - Surface Water
  - Up to 5 sediment layers

Preliminary Calibration: Methyl Hg



Simulated Response of Total Hg: 50% Decrease in Atmospheric Deposition

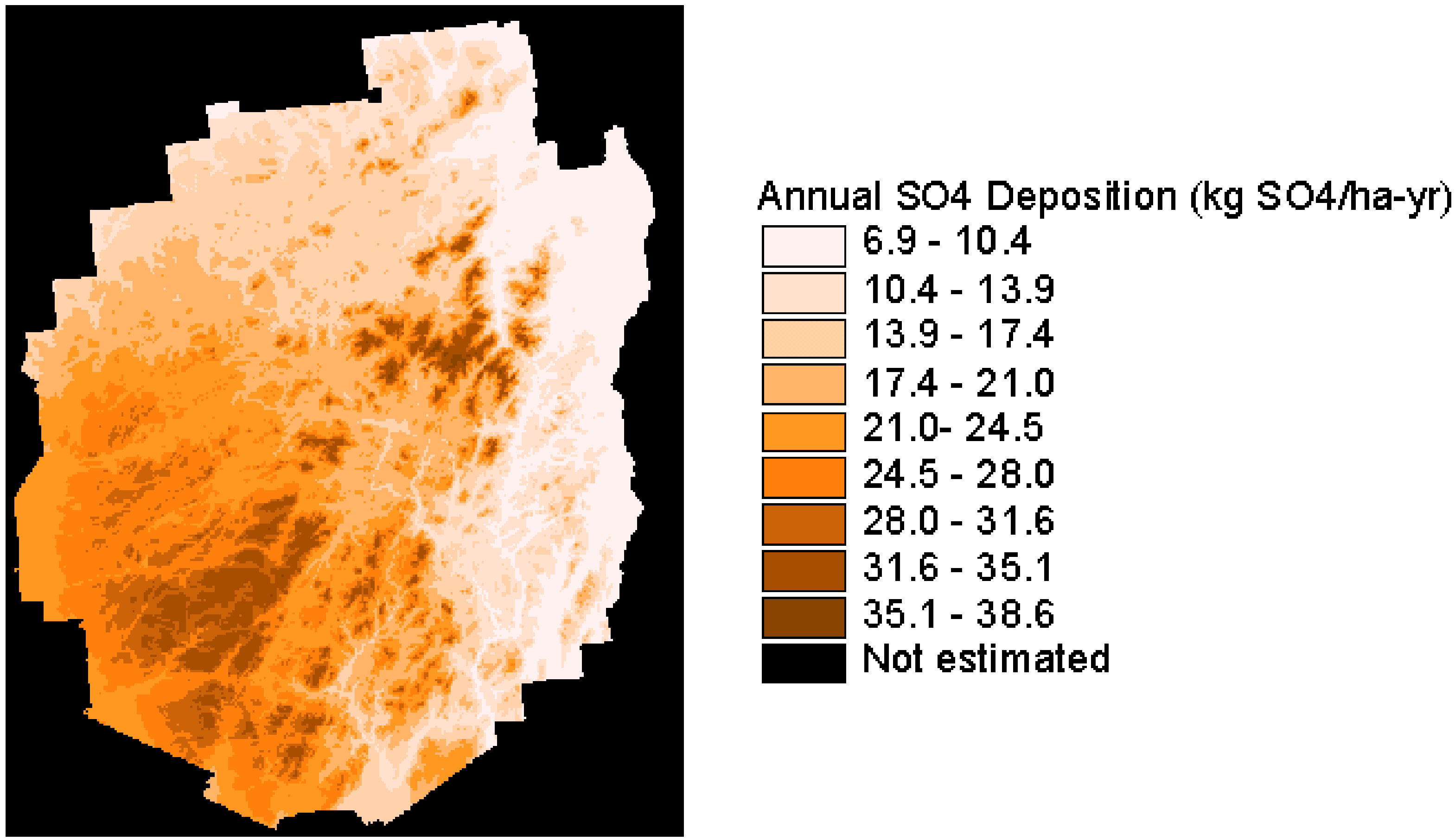


Conclusions

- Mercury is a global contaminant.
- Mercury emissions largely occur from electric utilities, non-utility boilers and incinerators.
- Mercury emitted as Hg0 is globally dispersed. Mercury emitted as Hg (II) is deposited near the source.
- Methyl Hg bioconcentrates up the aquatic food chain.
- Virtually every state has fish consumption advisories due to elevated Hg.

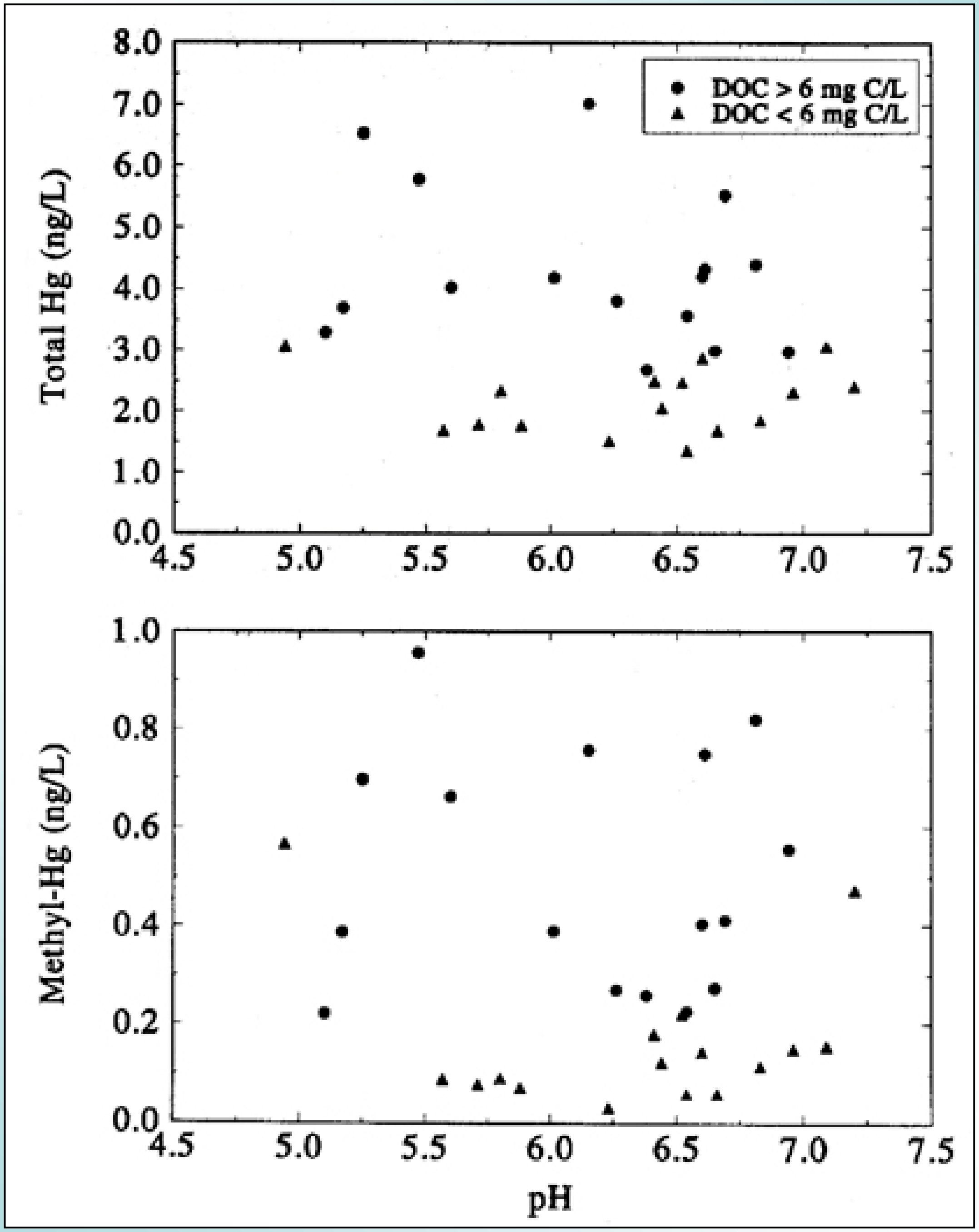
Conclusions (cont.)

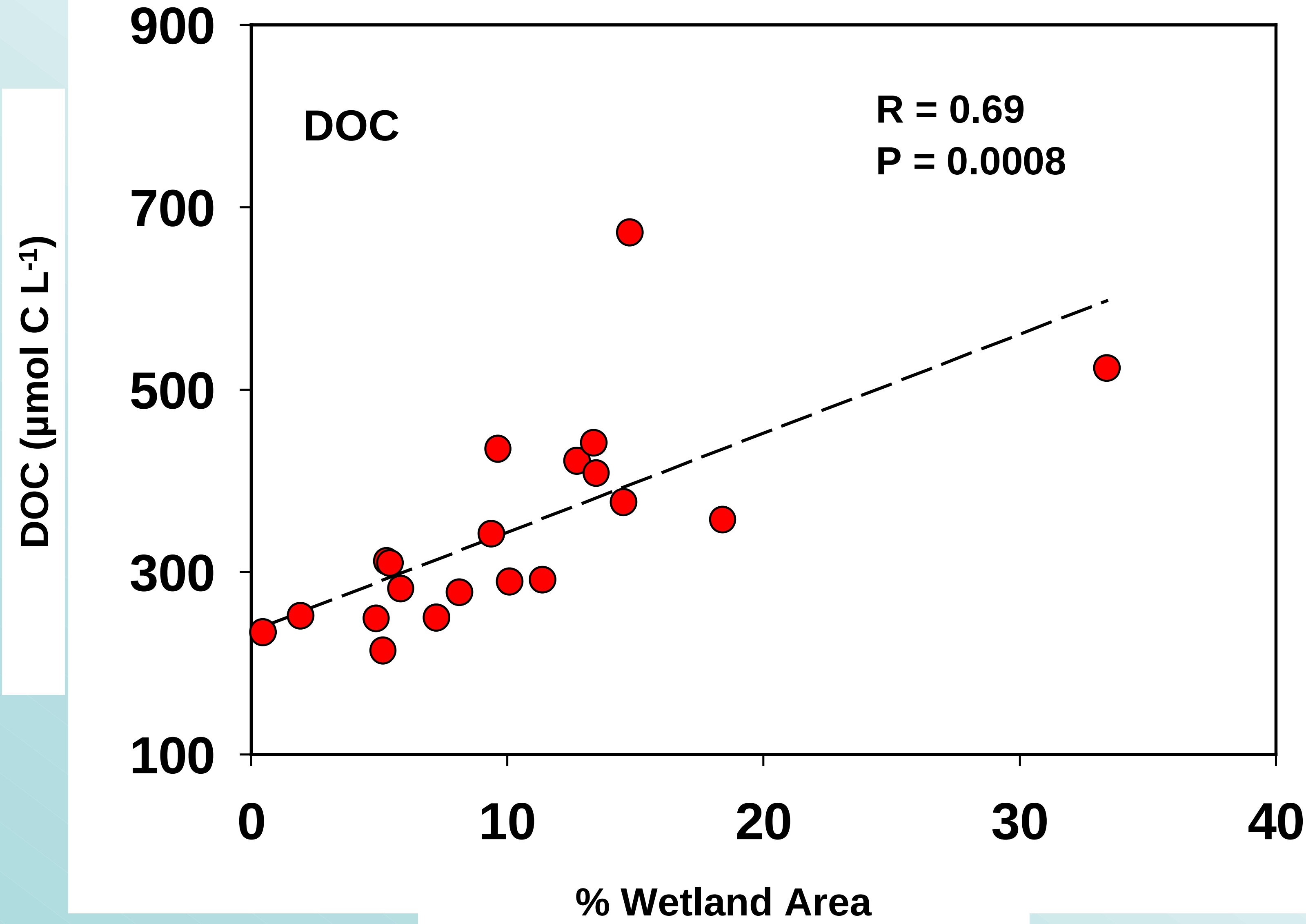
- The forest canopy greatly amplifies atmospheric Hg deposition.
- Wetlands are a critical controller of water and fish Hg.
- Mercury contamination has increased 5 fold over the last 150 years.
- Controls on Hg emissions from electric utilities are being proposed.


Annual SO4 Deposition (kg SO4/ha-yr)
6.9 - 10.4
10.4 - 13.9
13.9 - 17.4
17.4 - 21.0
21.0- 24.5
24.5 - 28.0
28.0 - 31.6
31.6 - 35.1
35.1 - 38.6
Not estimated

Summary (n=1469)

	No. of Lakes	(%)	Surface area (ha)	(%)
pH < 5.0	352	24	2,000	8.4
ANC < 0 μeq/L	388	26	2,650	11

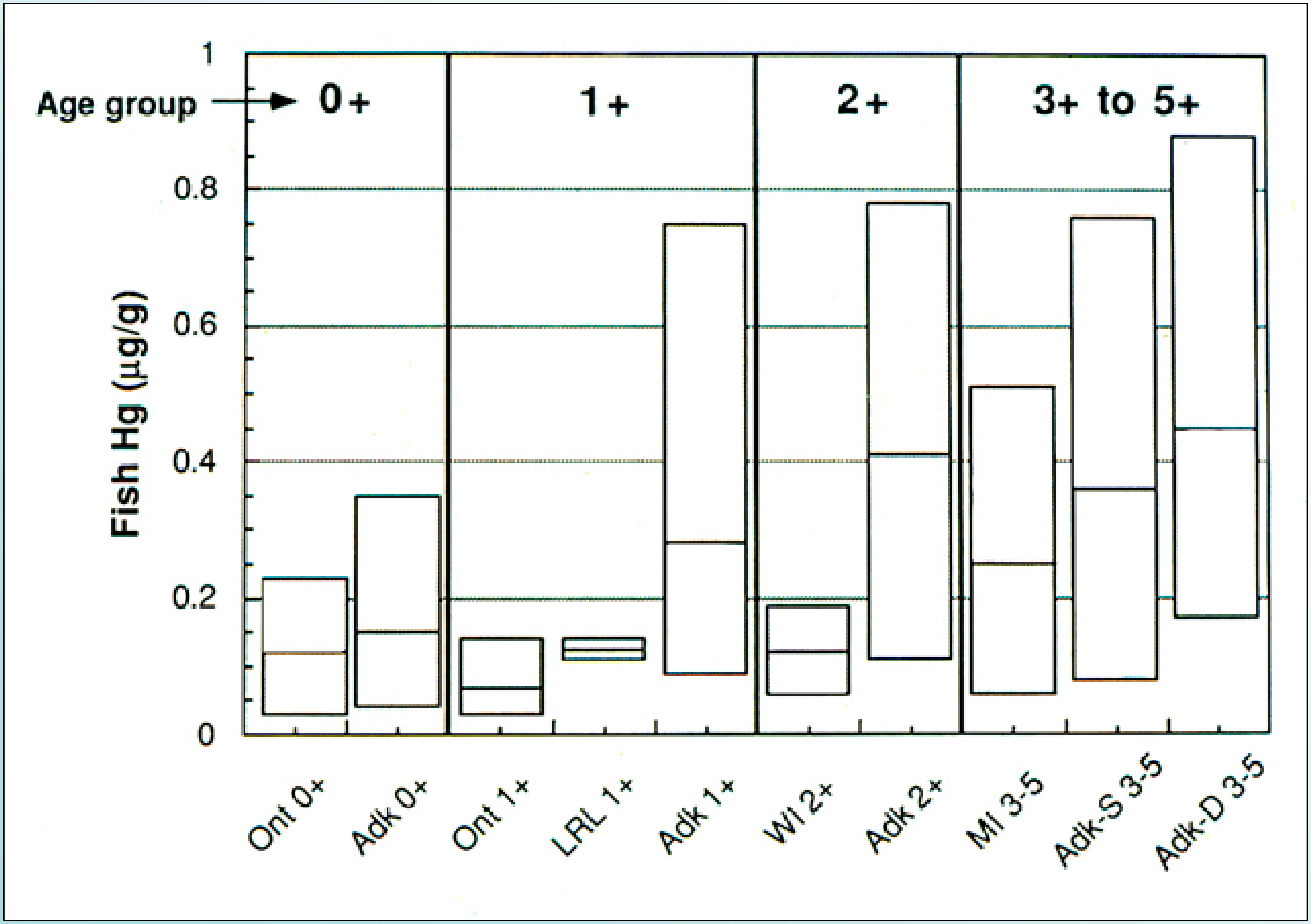

DOC > 6 mg C/L
DOC < 6 mg C/L
Total Hg (ng/L)
Methyl-Hg (ng/L)
pH
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
0.2
0.4
0.6
0.8
4.5
5.0
5.5
6.0
6.5
7.0
7.5



DOC
R = 0.69
P = 0.0008
900
700
500
300
100
0
10
20
30
40
DOC (µmol C L-1)
% Wetland Area

Typical Mercury Concentration in Freshwater (ng/L)

SITE	TOTAL Hg	REFERENCE
Remote Lakes - Wisconsin	0.9 – 1.9	Fitzgerald & Watras 1989
- Washington (state)	0.2	Bloom 1989
- California	0.6	Gill & Bruland 1990
- Manitoba	0.2 – 1.1	Bloom & Effler 1990
- Montana	0.35 - 2.8	Watras et al. 1995
- Sweden	1.4 - 15	Lee & Iverfeldt 1991
- Wisconsin	0.28 – 4.9	Watras et al. 1995
- Adirondacks	**0.8 – 6.1**	**This study**
Urban Lake - Washington (state)	1.7	Bloom & Watras 1989
Great Lakes - Erie	3.9	Gill & Bruland 1990
- Ontario	0.9	Gill & Bruland 1990
Mining Contaminated Lakes - Clear Lake	3.6 – 104	Gill & Bruland 1990
- Davis Creek Reservoir	5.2 – 6.4	Gill & Bruland 1990
Chlor-Alkali Contaminated Lakes - Onondaga Lake	7 – 19	Bloom & Effler 1990
- Clay Lake (Ontario)	5 – 80	Parks et al. 1989



Age group
0+
1+
2+
3+ to 5+
Fish Hg (µg/g)
1
0.8
0.6
0.4
0.2
0
Ont 0+
Adk 0+
Ont 1+
LRL 1+
Adk 1+
WI 2+
Adk 2+
MI 3-5
Adk-S 3-5
Adk-D 3-5