Global Cycles of Metal Elements

Introduction (Heavy metals)

Human activities and cycling of metals

Mechanisms of mobilization and immobilization

The Global Mercury Cycling

s-block

New Designation
Original Designation

Non-Metals (groups 13–17) · *p-block* (groups 13–18) · *d-block* / ***Transition Metals*** (groups 3–12) · s-block (groups 1–2, and 18)

Atomic #
Symbol
Atomic Mass

Period	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 H 1.0094																	2 He 4.00260
2	3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
3	11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
4	19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	57 to 71	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226.03	89 to 103	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (262)	108 Uno (265)	109 Une (266)	110 Uun (267)								

Metals

(Mass Numbers in Parentheses are from the most stable of common isotopes.)

Phases
Solid
Liquid
Gas

Rare Earth Elements — *d-block* (La, Ac) · *f-block* (Ce–Lu, Th–Lr)

Lanthanide Series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide Series	89 Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

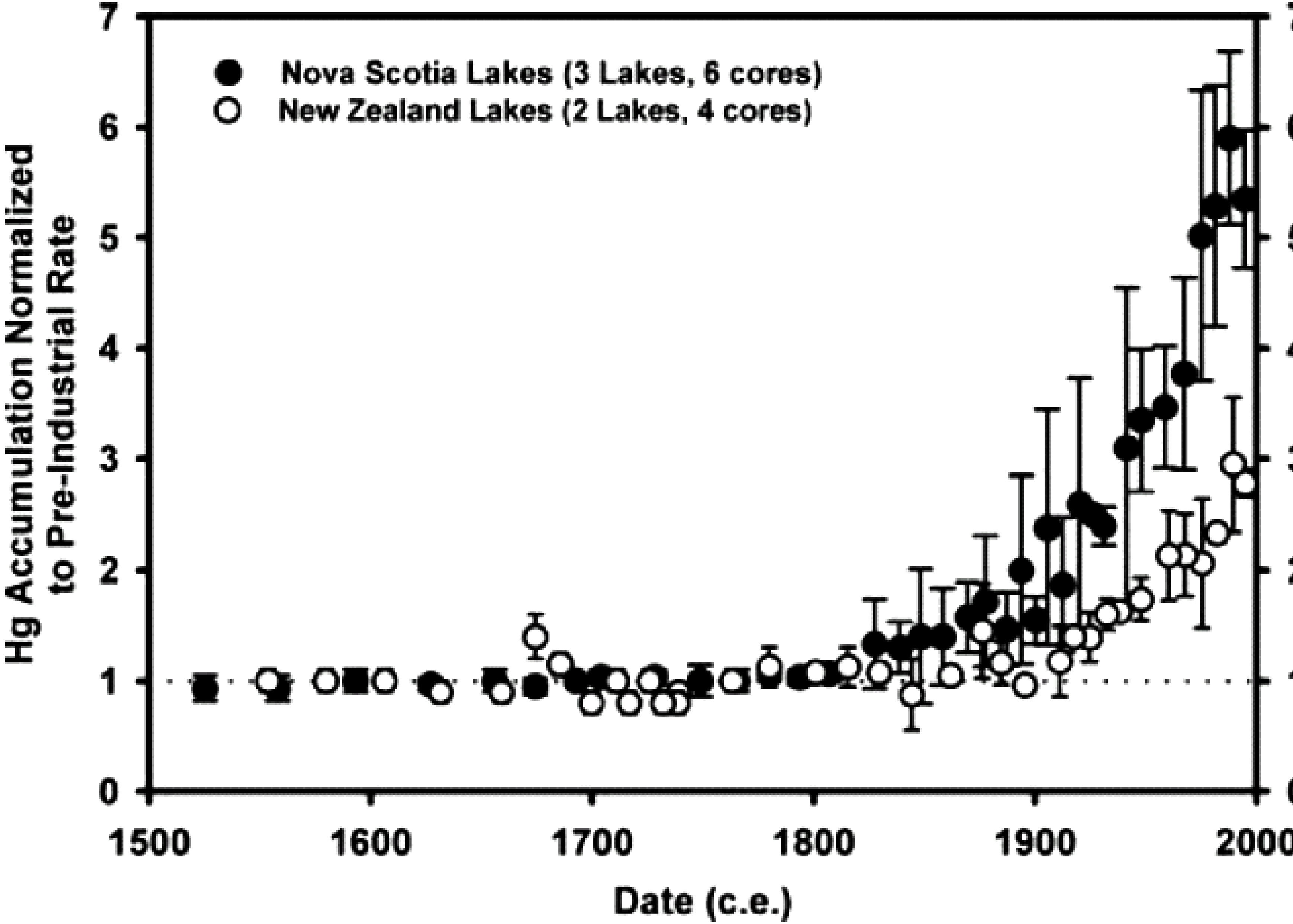
Human activities and cycling of metals

Table 15-2 Comparison between artificial and natural rates (10^3 tonnes/yr) of global metal injection into the oceans and atmosphere[a]

	Input from industrial world's municipal waste water	Input from combustion[b]	Natural weathering[c]
Cd	3	—	36
Cr	55	1.5	50
Cu	42	2.1	250
Fe	440	1400	24 000
Pb	15	3.6	110
Mn	7.4	7.0	250
Ni	17	3.7	11
Ag	2.3	0.07	11
Zn	100	7	720

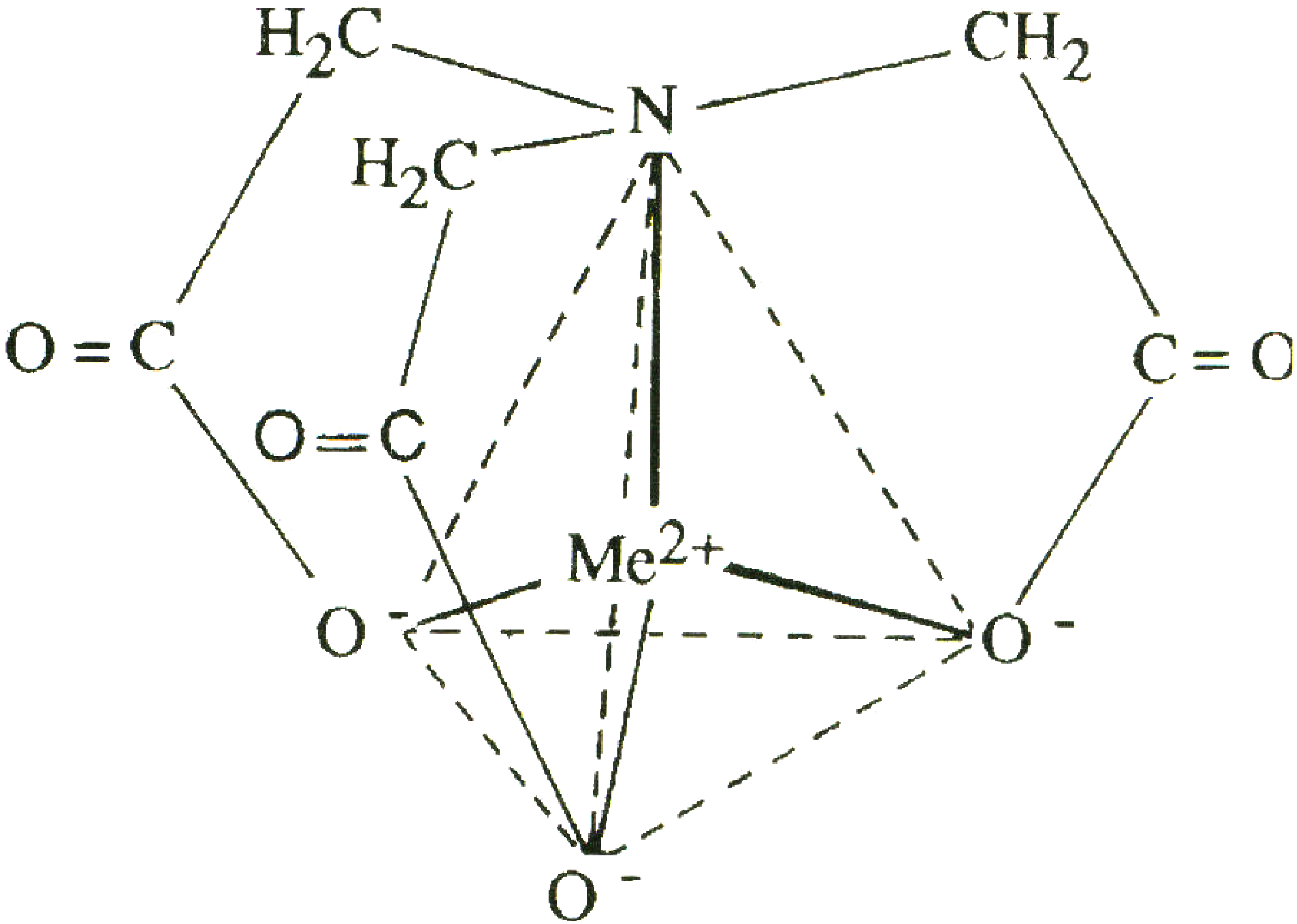
[a] Galloway (1979).
[b] Bertine and Goldberg (1971).
[c] Turekian (1971).

From: Jacobson, Charlson, Rodhe & Orians 2000



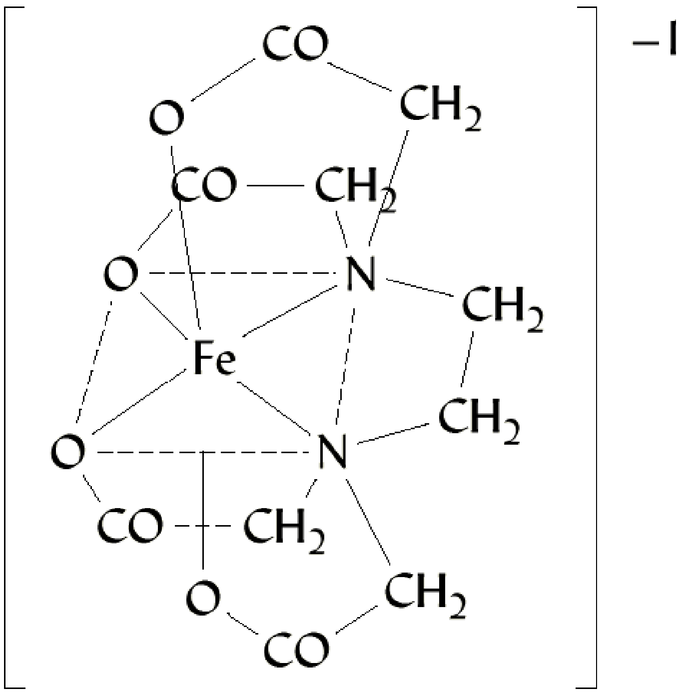
From: Lamborg et al. GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 16, NO. 4, 1104-1115.

Mechanisms of mobilization and immobilization



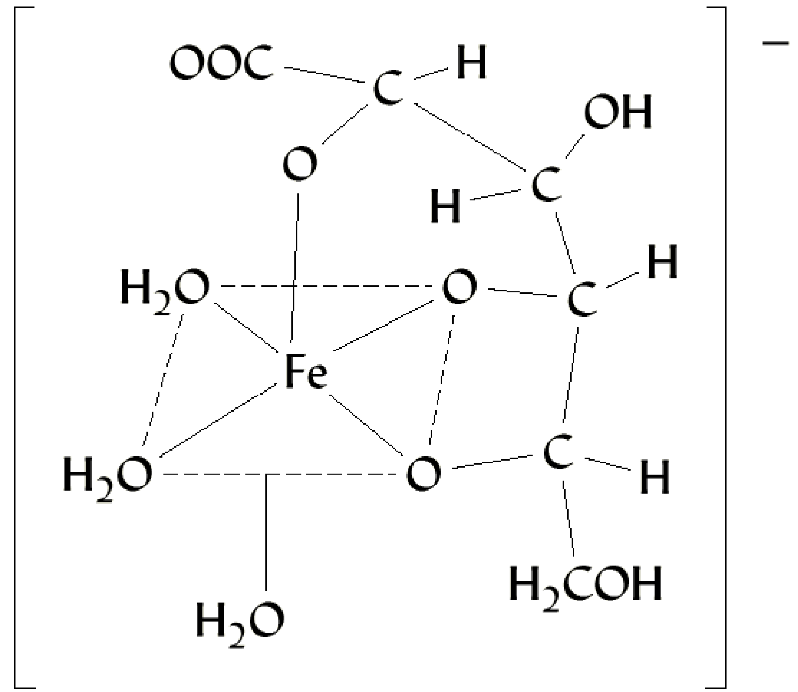
Nitrilotriacetate chelate of a divalent metal ion in a tetrahedral form. EDTA and nitrilotriacetate are **ligands (any compound, often organic ones, capable of forming chelate)**.

Metal ions react with certain organic molecules to form organometallic complexes called **chelates,** therefore, increasing their mobility and availability to biological uses.



Fe (III) EDTA

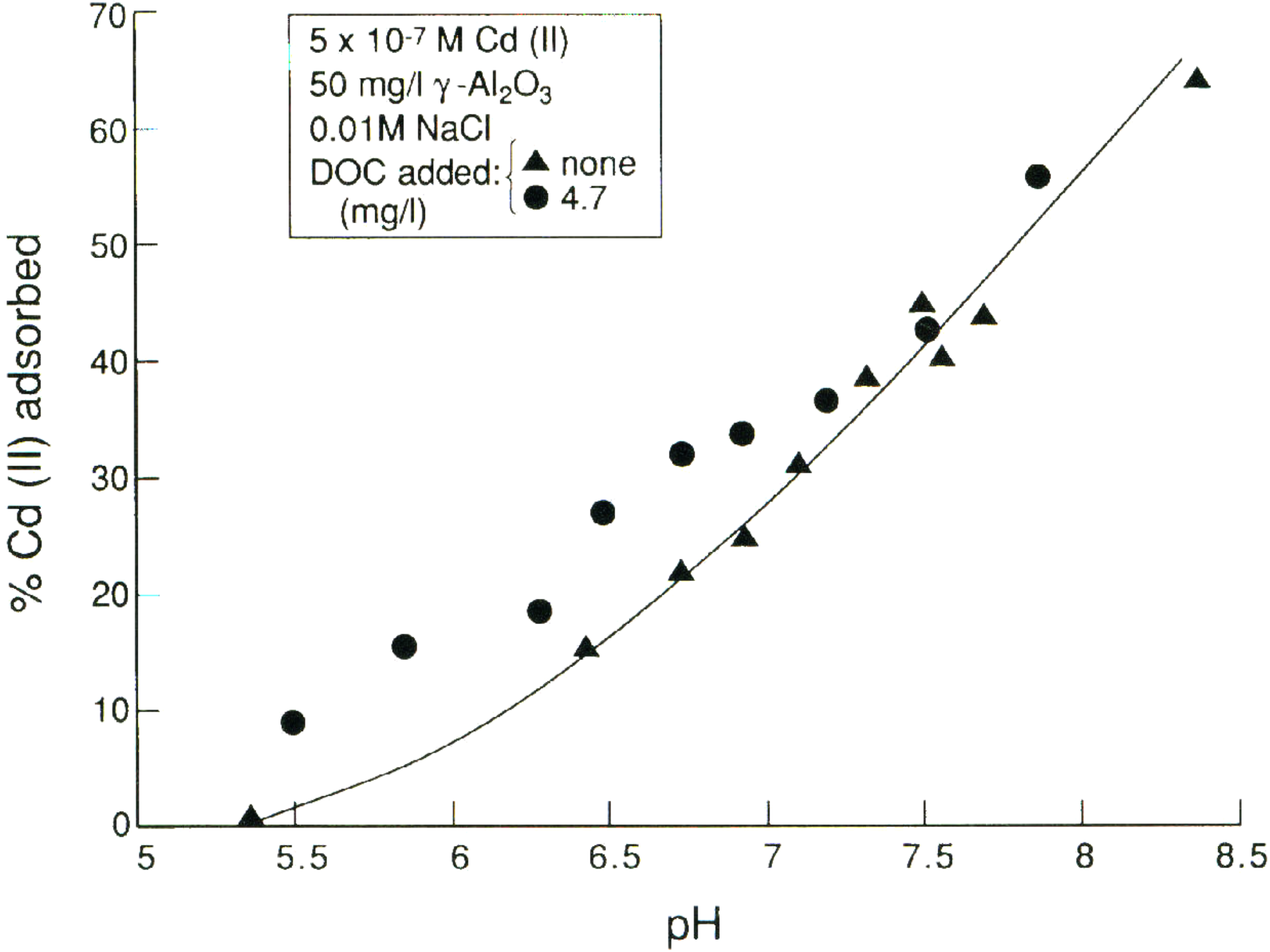
(*a*)



Fe(III) gluconate

(*b*)

EDTA: ethylene-diamine-tetra-acetate



5 x 10-7 M Cd (II)
50 mg/l γ -Al2O3
0.01M NaCl
DOC added:
(mg/l)
none
4.7
% Cd (II) adsorbed
pH
0
10
20
30
40
50
60
70
5
5.5
6
6.5
7
7.5
8
8.5

The Global Mercury Cycling

Health effects of mercury:

Mercury exposure at high levels can harm the brain, heart, kidneys, lungs, and immune system of people of all ages. Research shows that most people's fish consumption does not cause a health concern. However, it has been demonstrated that high levels of methylmercury in the bloodstream of unborn babies and young children may harm the developing nervous system, making the child less able to think and learn.

For official information on mercury please see http://www.epa.gov/mercury/index.html

Ecological effects of mercury:

Birds and mammals that eat fish are more exposed to mercury than other animals in water ecosystems. Similarly, predators that eat fish-eating animals may be highly exposed. At high levels of exposure, methylmercury's harmful effects on these animals include death, reduced reproduction, slower growth and development, and abnormal behavior.

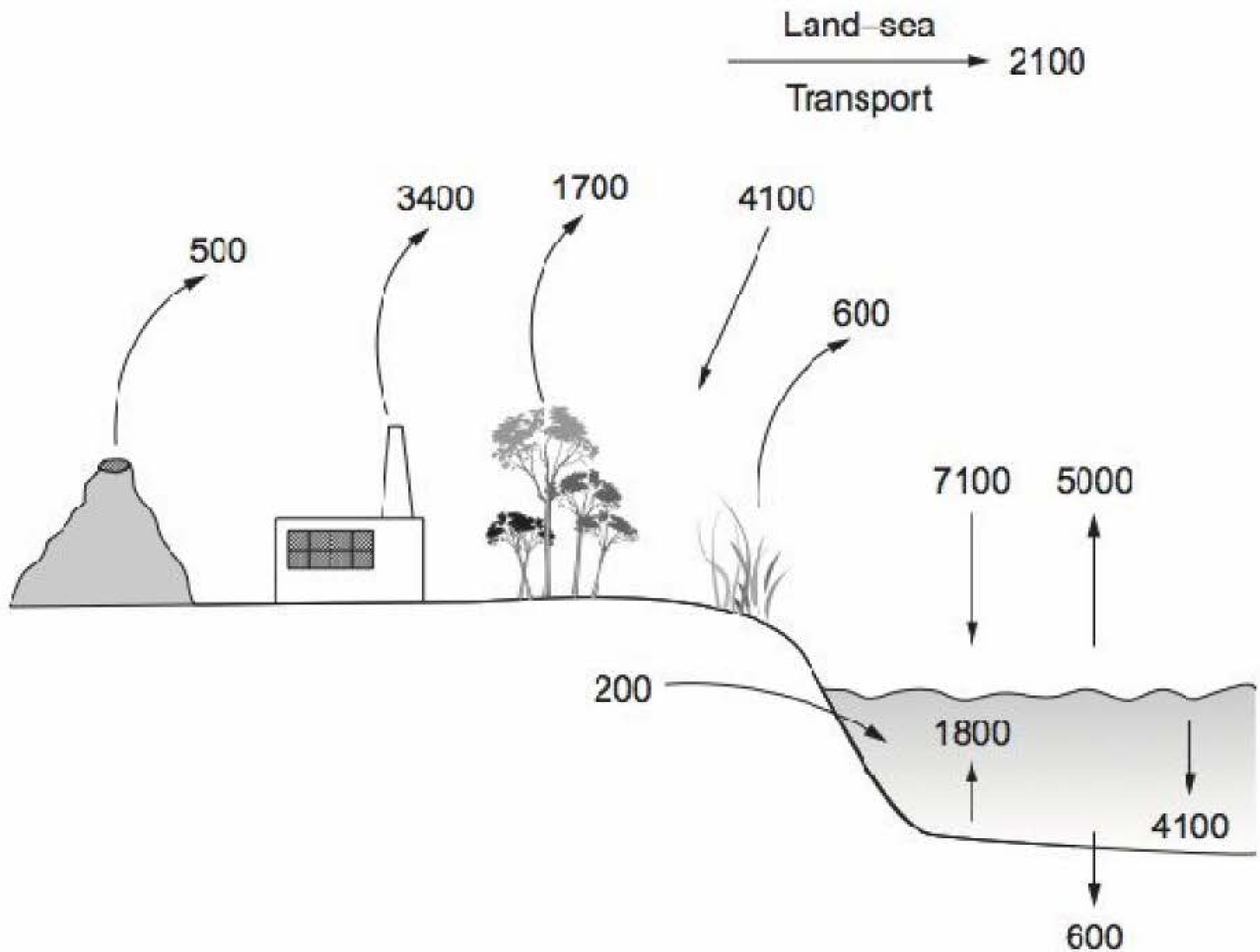


FIGURE 13.6 The global mercury cycle of the modern world. All values are 10^6 g Hg/yr. *Source: From Selin (2009).*

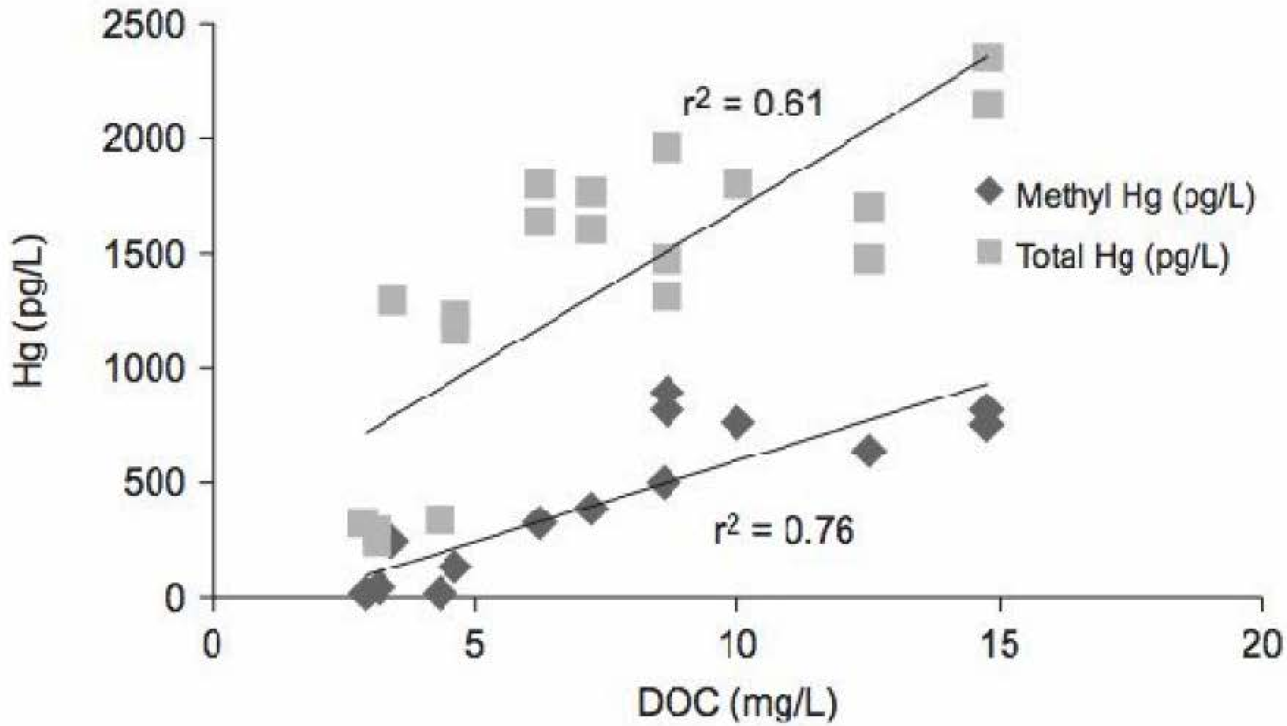
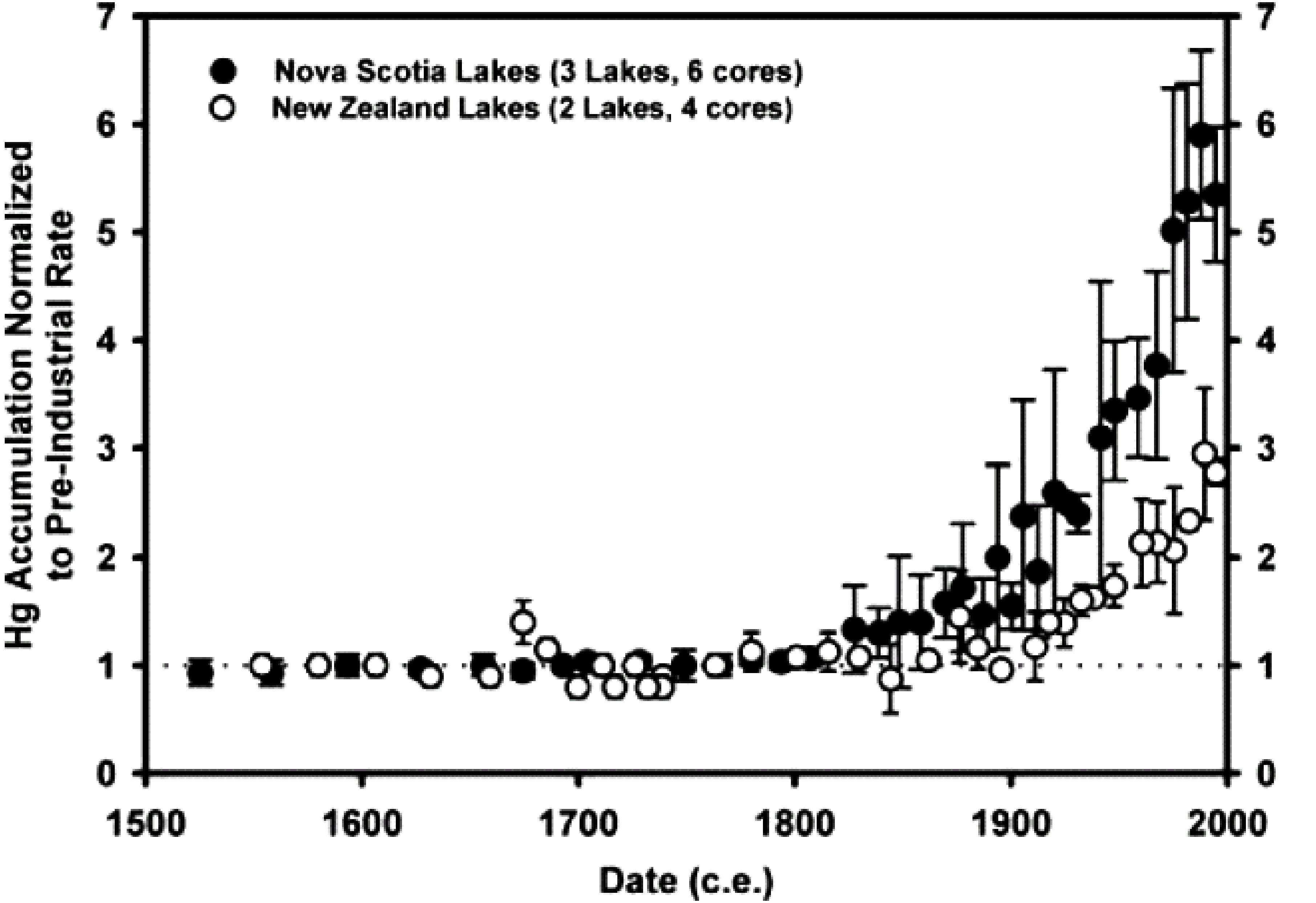
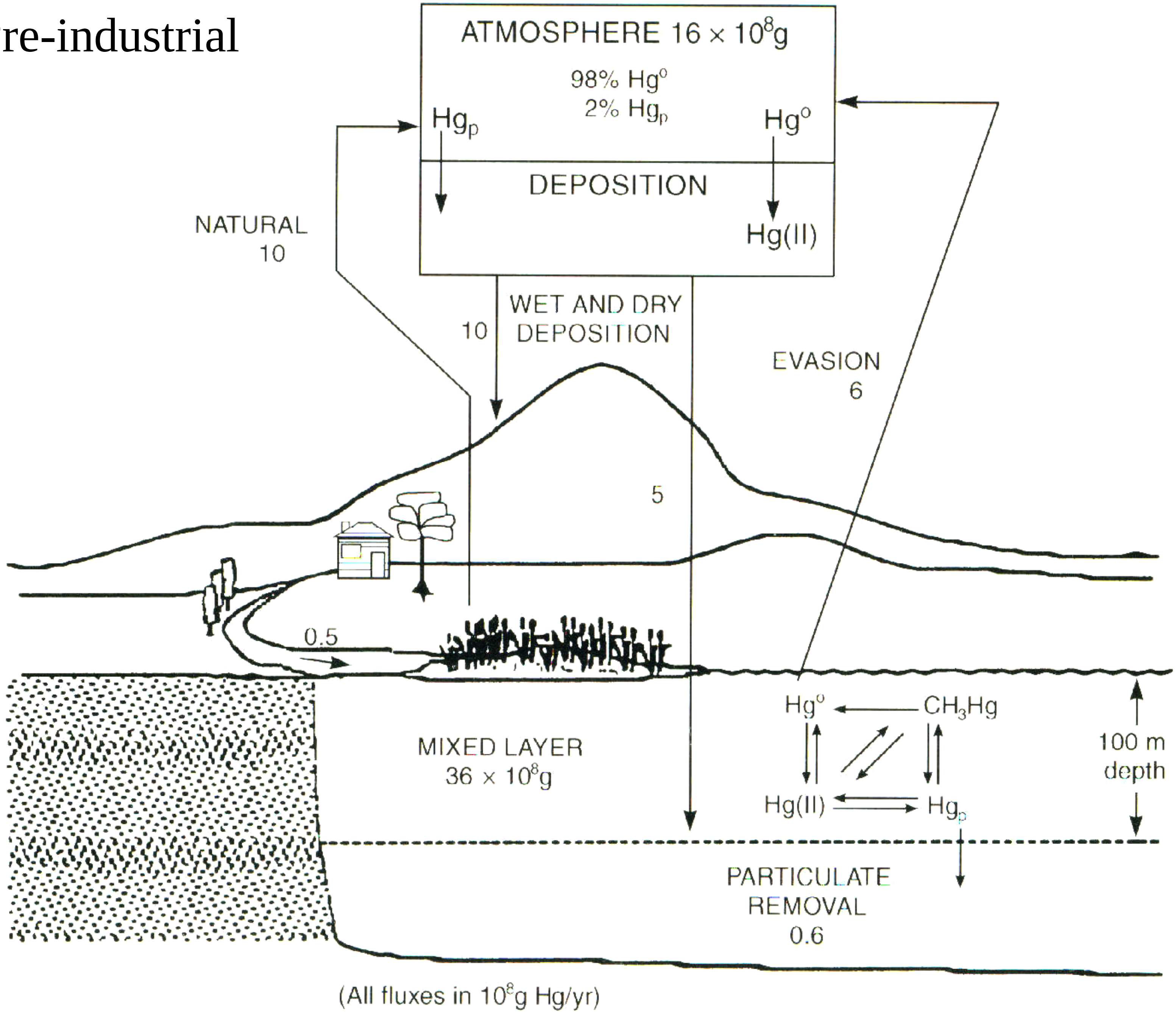


FIGURE 13.7 Concentration of total and methylmercury in stream waters draining into Lake Sunapee, New Hampshire as a function of the concentration of dissolved organic carbon. *Source: From Kathleen Weathers et al., unpublished.*

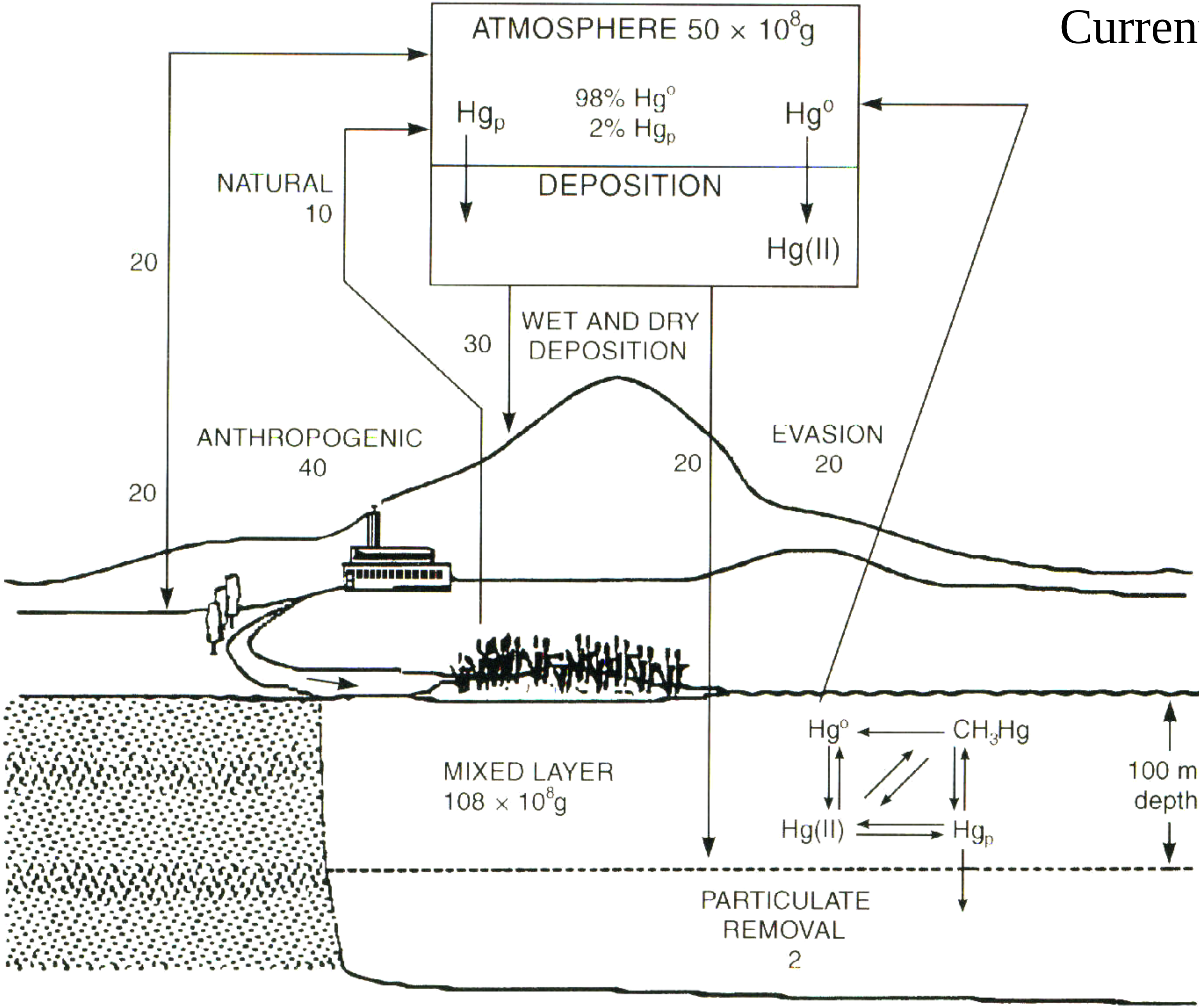


From: Lamborg et al. 2002. GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 16, NO. 4, 1104-1115.

Pre-industrial

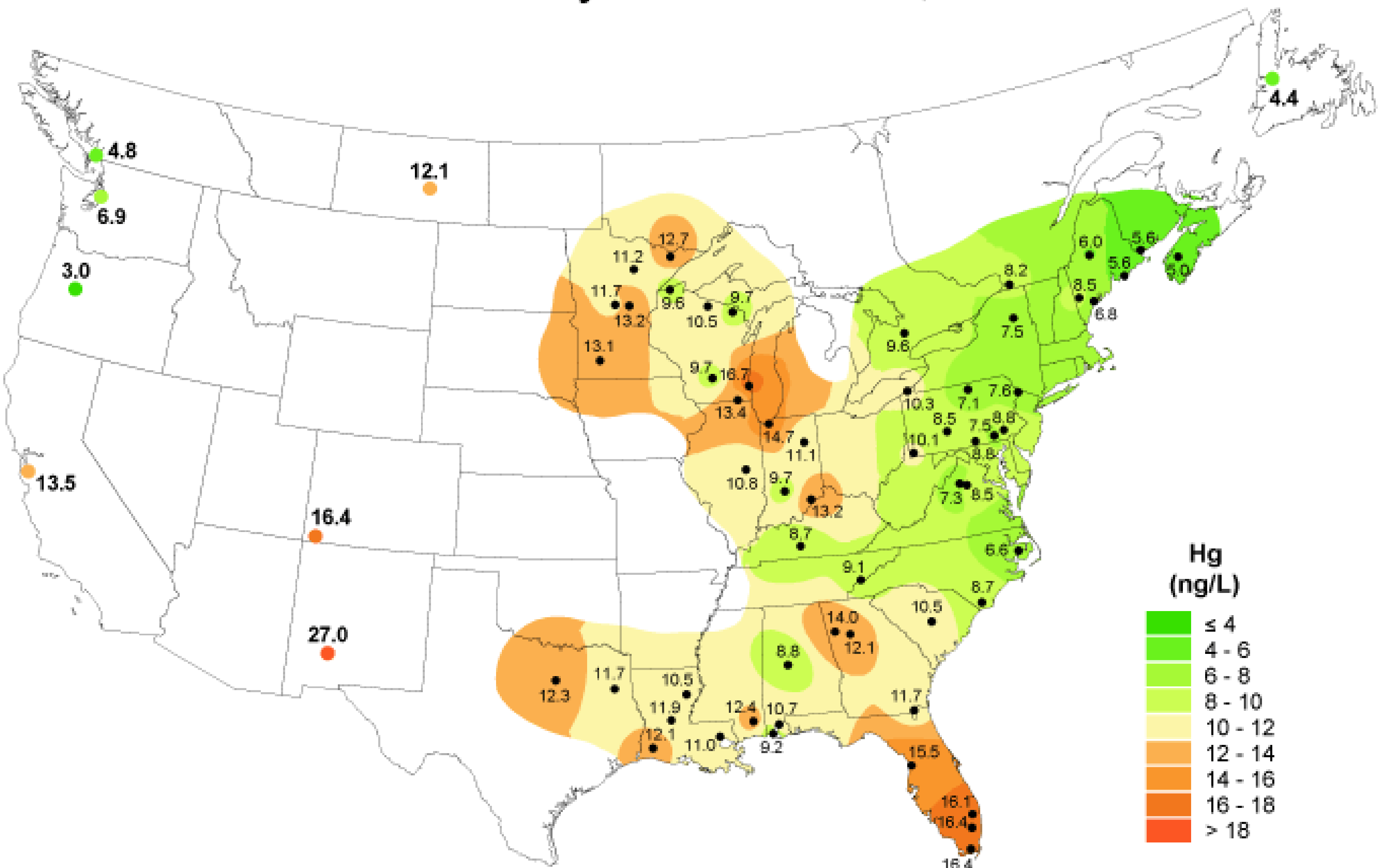


Current (1990's)



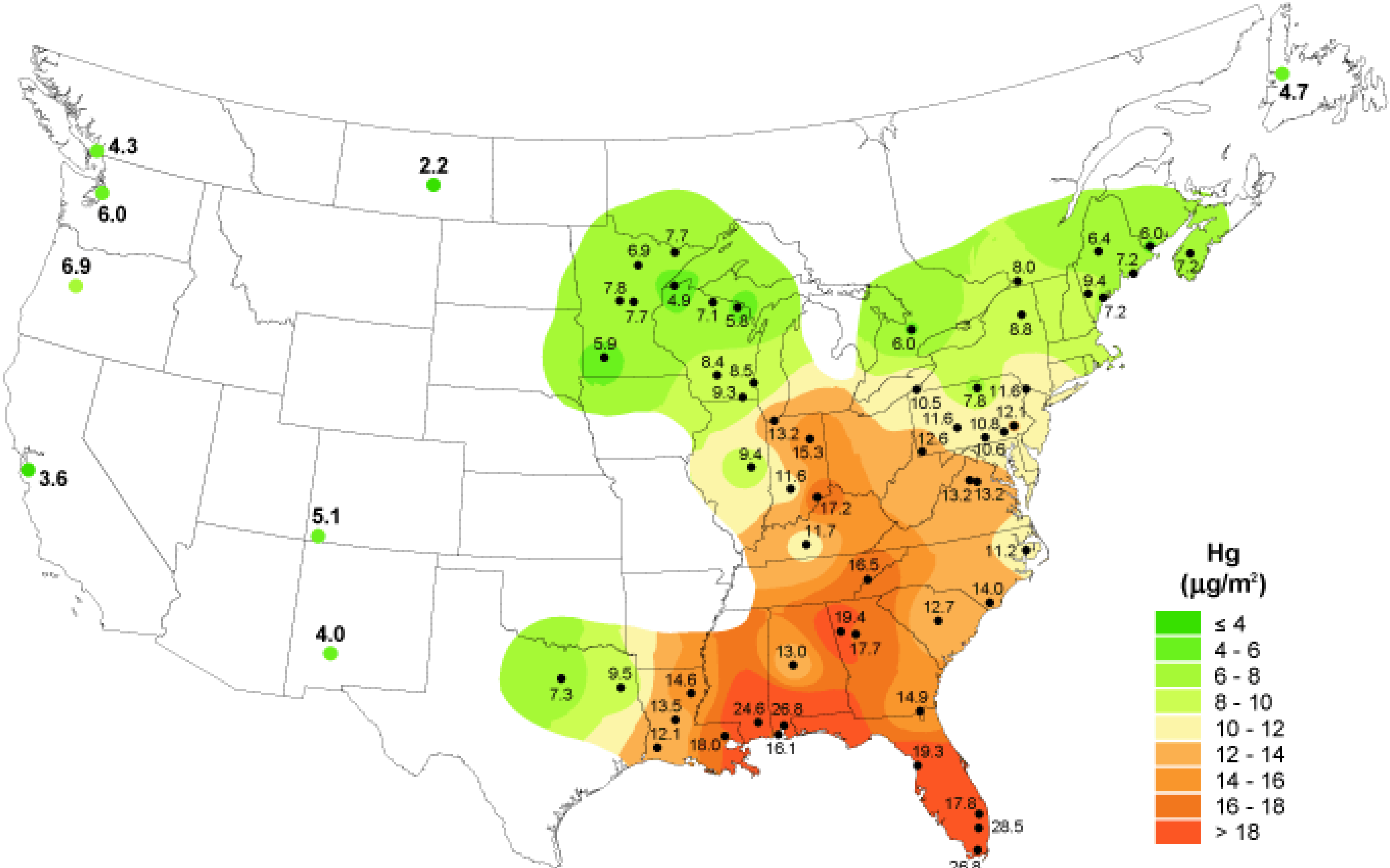
(All fluxes in 10^8g Hg /yr)

Total Mercury Concentration, 2003

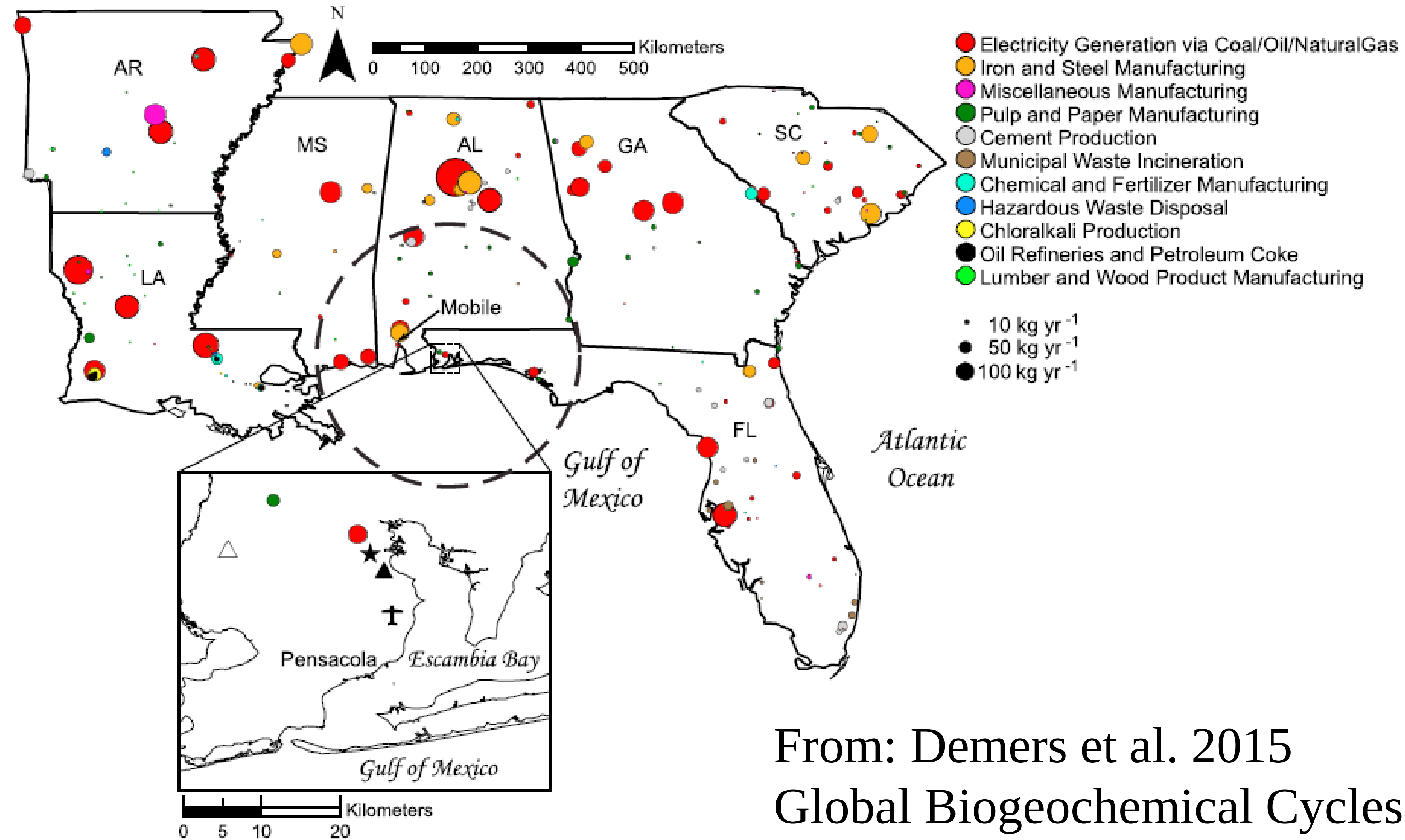


National Atmospheric Deposition Program/Mercury Deposition Network

Total Mercury Wet Deposition, 2003

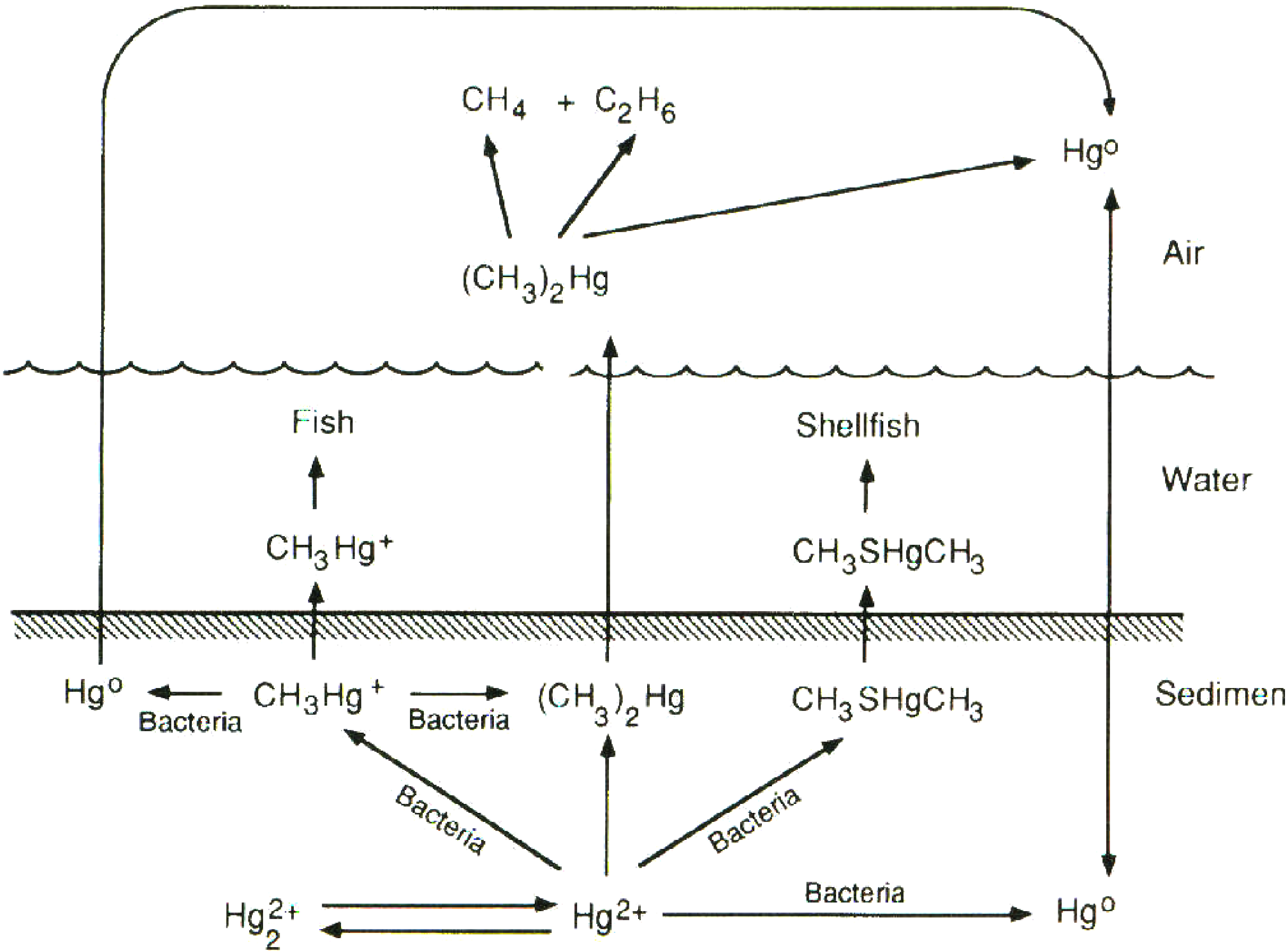


National Atmospheric Deposition Program/Mercury Deposition Network



From: Demers et al. 2015
Global Biogeochemical Cycles

Figure 1. Map of sampling location for ambient atmospheric mercury (total gaseous mercury, TGM) in a coastal urban-industrial region near a coal-fired power plant in Pensacola, Florida, and emissions of total mercury (THg; kg yr^{-1}) in the southeastern region of the United States, including Arkansas (AR), Louisiana (LA), Mississippi (MS), Alabama (AL), Georgia (GA), South Carolina (SC), and Florida (FL) [*U.S. Environmental Protection Agency (USEPA)*, 2011b]. Mercury emissions source categories are differentiated by color; circles are scaled by radius to represent the magnitude of annual emissions from each source. The dashed circle centered in Pensacola shows the region within 250 km of the TGM sampling site. The inset



CH4 + C2H6
Hgo
Air
(CH3)2Hg
Fish
Shellfish
Water
CH3Hg+
CH3SHgCH3
Hgo
Bacteria
CH3Hg+
Bacteria
(CH3)2Hg
CH3SHgCH3
Sediment
Bacteria
Bacteria
Hg2 2+
Hg2+
Bacteria
Hgo

Some important points of the mercury cycle:

(1) The exchange rate between atmosphere and Earth's surface is much faster than transport rate from land to ocean.

(2) Human activity has increased mercury in the atmosphere three times of the pre-industrial level, and also has increased the flux rate from land to ocean three times.

(3) Average residence times for mercury in the atmosphere, soils, oceans, and oceanic sediments are approximately: 1 year, 1000 years, 3200 years, and 250 million years, respectively.

Redfield Ratio--Synthesis of Biogeochemical Cycles

In 1958, Albert C. Redfield published a paper (The biological control of chemical factors in the environment. American Scientist 46:205-221), in which he noted that the organic debris falling to the deep ocean contained N and P in a fairly constant atom ratio to the content of carbon: C:N:P = 80:15:1.

Later, Broecker (1974), recalculated Redfield ratio to include $CaCO_3$. His modified ratio of falling particles: **C:N:P:Ca = 120:15:1:40**, and for upwelling sea water: **C:N:P:Ca = 80:15:1:3200.**

This relatively constant ratio represents the proportionality of most biological processes which link biogeochemical cycles at many levels in the ecological hierarchy from the cell level to the biosphere level. **All biological elements cycle together, not alone.**

This point can also be inferred from the average elemental composition of most living cells.

This relative constant proportionality is some time called the stoichiometric principle.

Cell Elemental Composition

Element	Dry Weight, %
Carbon	50
Oxygen	20
Nitrogen	14
Hydrogen	8
Phosphorus	3
Sulfur	1
Potassium	1
Sodium	1
Calcium	0.5
Magnesium	0.5
Chlorine	0.5
Iron	0.2
All others	0.3

Source: Stanier et al 1976. The Microbial World. 4th ed. Prentice Hall. These numbers vary depending on species and conditions, such as granules (phosphorus, sulfur, etc.), but the ratio of C, O, H, N is much stable. Porges et al. 1956 determined that the ratio of a heterogeneous microbial population: C:H:N:O =5:7:1:2.

TABLE 14.1 Estimates of the Global Flux in the Biogeochemical Cycles of Certain Elements, Illustrating the Human Impact

Element	Juvenile flux[a] (1)	Chemical weathering (2)	Natural cycle[b] (3)	Biospheric recycling ratio[c] 3/(1+2)	Human mobilization[d] (4)	Human enhancement 4/(1+2)	Reference for global cycle
B	0.02	0.19	8.8	42	0.58	2.8	Park and Schlesinger (2002)
C	30	210	107,000	446	8700	36.3	Chapter 11
N	5	20[e]	9200[f]	368	221	8.8	Chapter 12
P	~0	2	1000	500	25	12.5	Chapter 12
S	10	70	450	5.6	130	1.6	Chapter 13
Cl	2	260	120	0.46	170	0.65	Figure 3.16
Ca	120	500	2300	3.7	65	0.10	Milliman et al. (1999), Caro et al. (2010)
Fe	6	1.5	40	5.3	1.1[g]	0.14	Muller et al. (2006)
Cu	0.05	0.056	2.5	23.6	1.5[g]	14.2	Rauch and Graedel (2007)
Hg	0.0005	0.0002	0.003	4.3	0.0023	3.3	Selin (2009)

Note: All data 10^{12} g/yr.

[a] *Degassing from the Earth's crust and mantle; sum of volcanic emissions to the atmosphere (subaerial) and net hydrothermal flux to the sea (Elderfield and Schultz 1996) and for N, fixation by lightning (Chapter 12).*

Summary

These metal elements have many similar properties, but each also has special properties that make it unique.

To a large degree, human activities have altered biogeochemical cycles of many metal elements.

Transportation, speciation, mobilization and immobilization are the three type of mechanisms that control biogeochemical cycles of metal elements.

The global mercury cycle is characterized by: (1) the exchange rate between the atmosphere and the Earth's surface is much faster than the transport rate from land to ocean; (2) recent human activity has increased mercury in the atmosphere by three folds since industrialization; and (3) average residence times for mercury in the atmosphere, soils, oceans, and oceanic sediments are approximately: 1 year, 1000 years, 3200 years, and 250 million years, respectively.

All biogeochemical cycles are linked together as shown by Redfield ratio and the elemental composition of living cells.