NATURAL pH OF RAIN

- Equilibrium with natural CO_2 (280 ppmv) results in a rain pH of 5.7:

$$CO_2(g) \underset{}{\overset{H_2O}{\rightleftharpoons}} CO_2 \bullet H_2O \qquad K_H = 3\times10^{-2} \text{ M atm}^{-1}$$

$$CO_2 \bullet H_2O \rightleftharpoons HCO_3^- + H^+ \qquad K_1 = 9\times10^{-7} \text{ M}$$

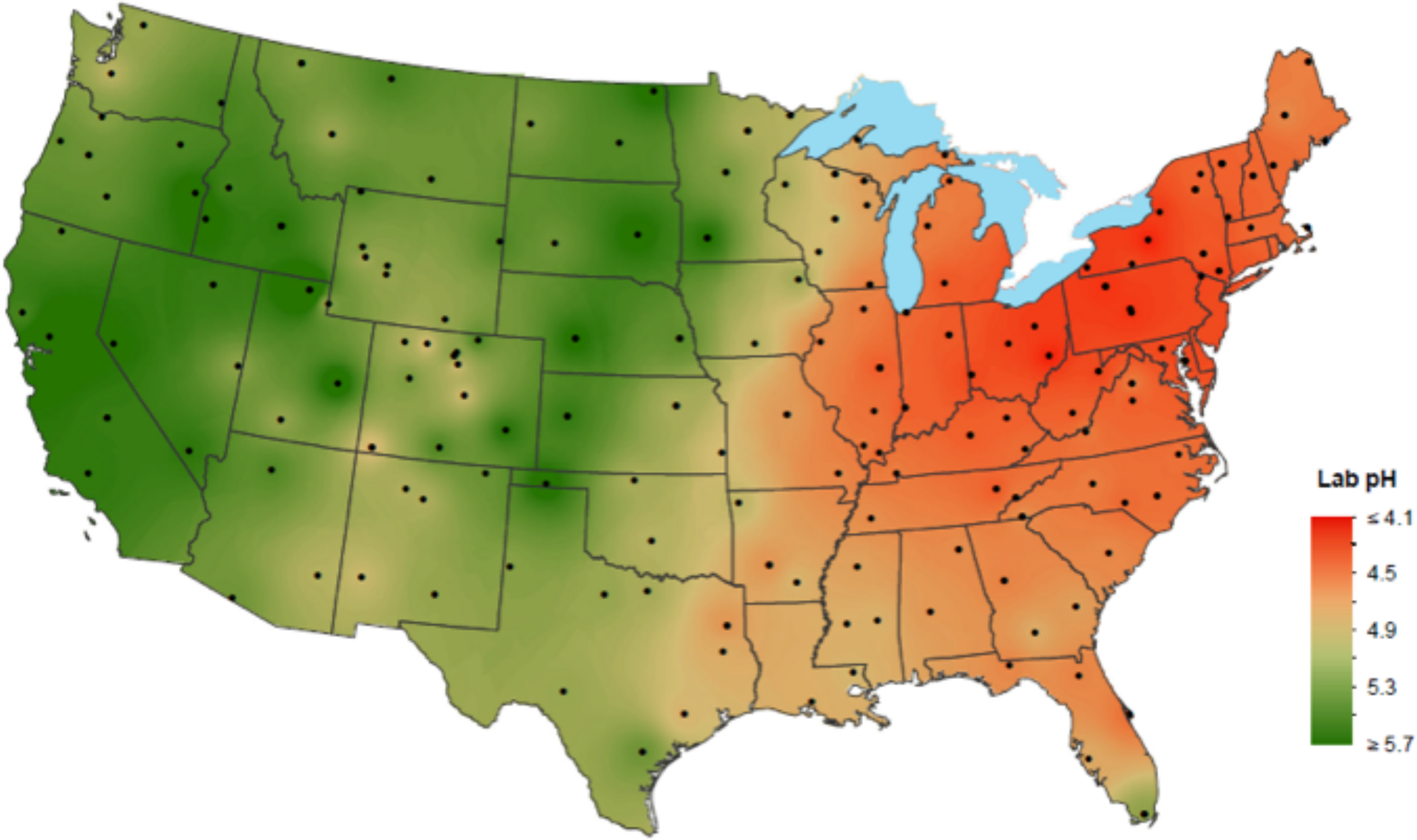
$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \qquad K_2 = 7\times10^{-10} \text{ M}$$

$$\Rightarrow [H^+] = (K_1 K_H P_{CO_2})^{1/2}$$

- This pH can be modified by natural acids (H_2SO_4, HNO_3, RCOOH…) and bases (NH_3, $CaCO_3$) ⇨ natural rain has a pH in range 5-7

"Acid rain" refers to rain with pH < 5 ⇨ damage to ecosystems

Mean pH of precipitation, 1990



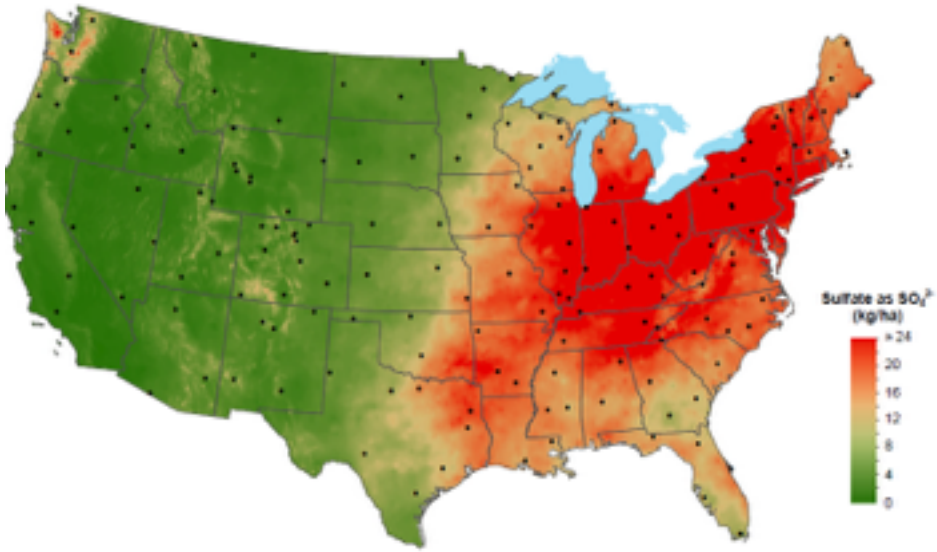
National Acid Deposition Program

Ionic composition of precipitation (late 1980s)

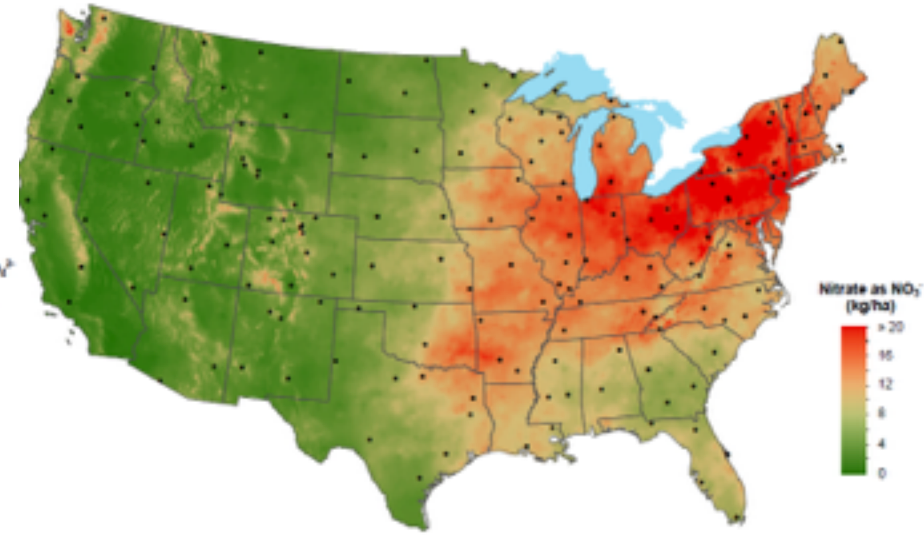
Table 13-1 Median Concentrations of Ions (μeq l^{-1}) in Precipitation at Two Typical Sites in the United States

Ion	*Rural New York State*	*Southwest Minnesota*
SO_4^{2-}	45	46
NO_3^-	25	24
Cl^-	4	4
HCO_3^-	0.1	10
Sum anions	74	84
H^+ (pH)	46 (4.34)	0.5 (6.31)
NH_4^+	8.3	38
Ca^{2+}	7	29
Mg^{2+}	1.9	6
K^+	0.4	2.0
Na^+	5	14
Sum cations	68	89

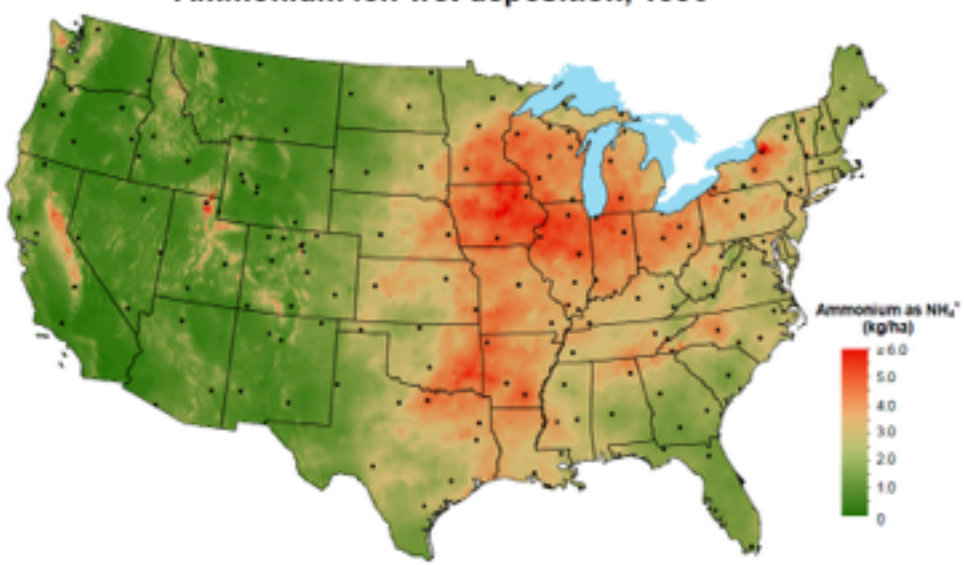
Sulfate ion wet deposition, 1990



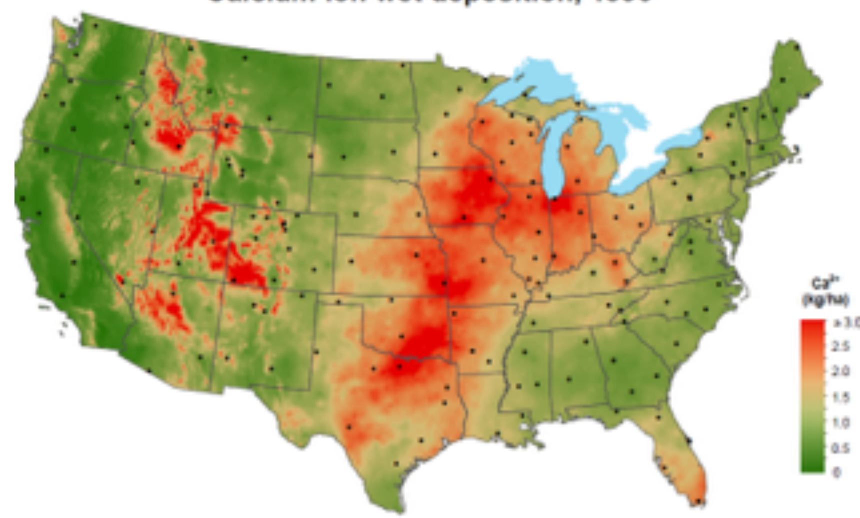
Nitrate ion wet deposition, 1990



Ammonium ion wet deposition, 1990

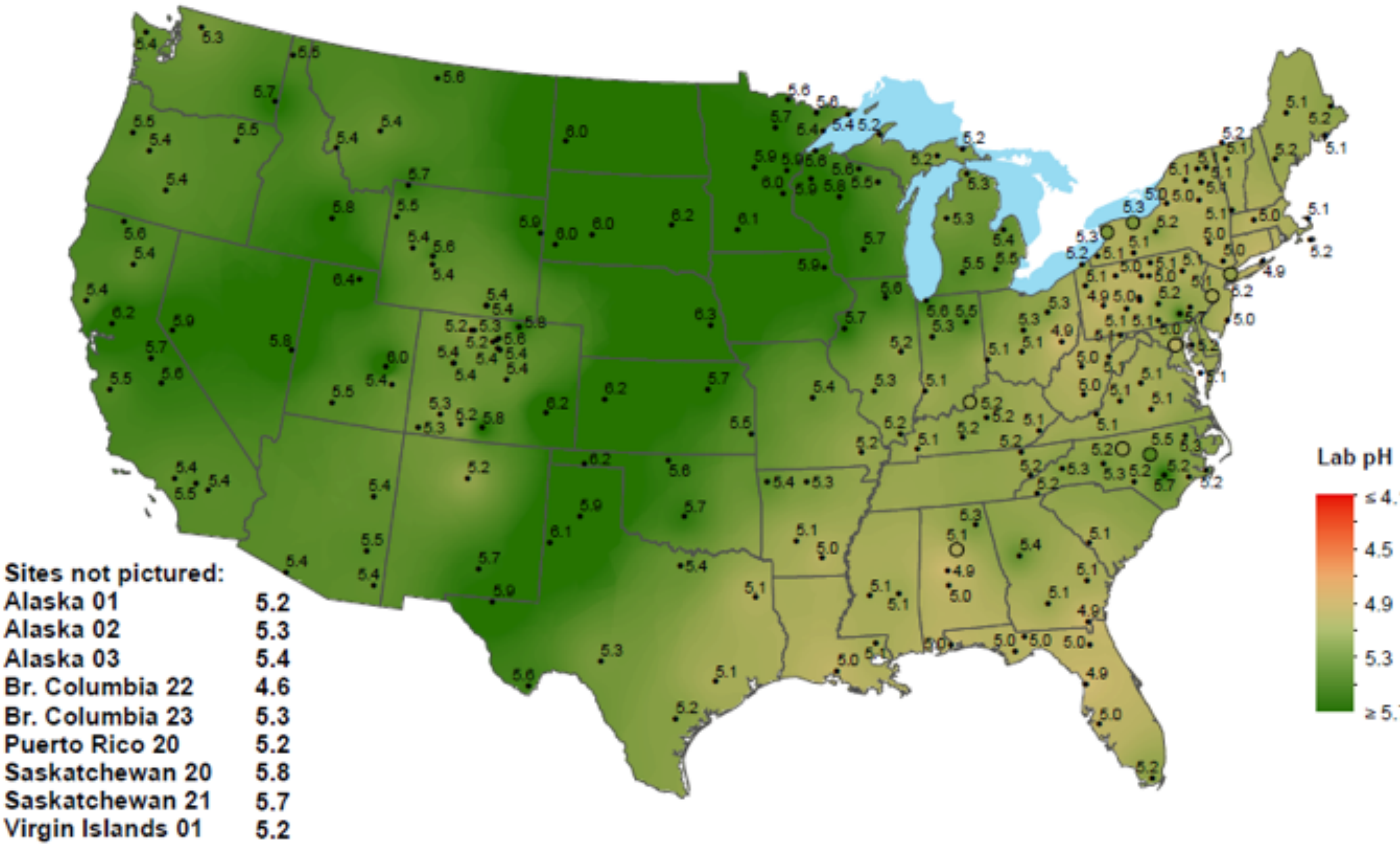


Calcium ion wet deposition, 1990

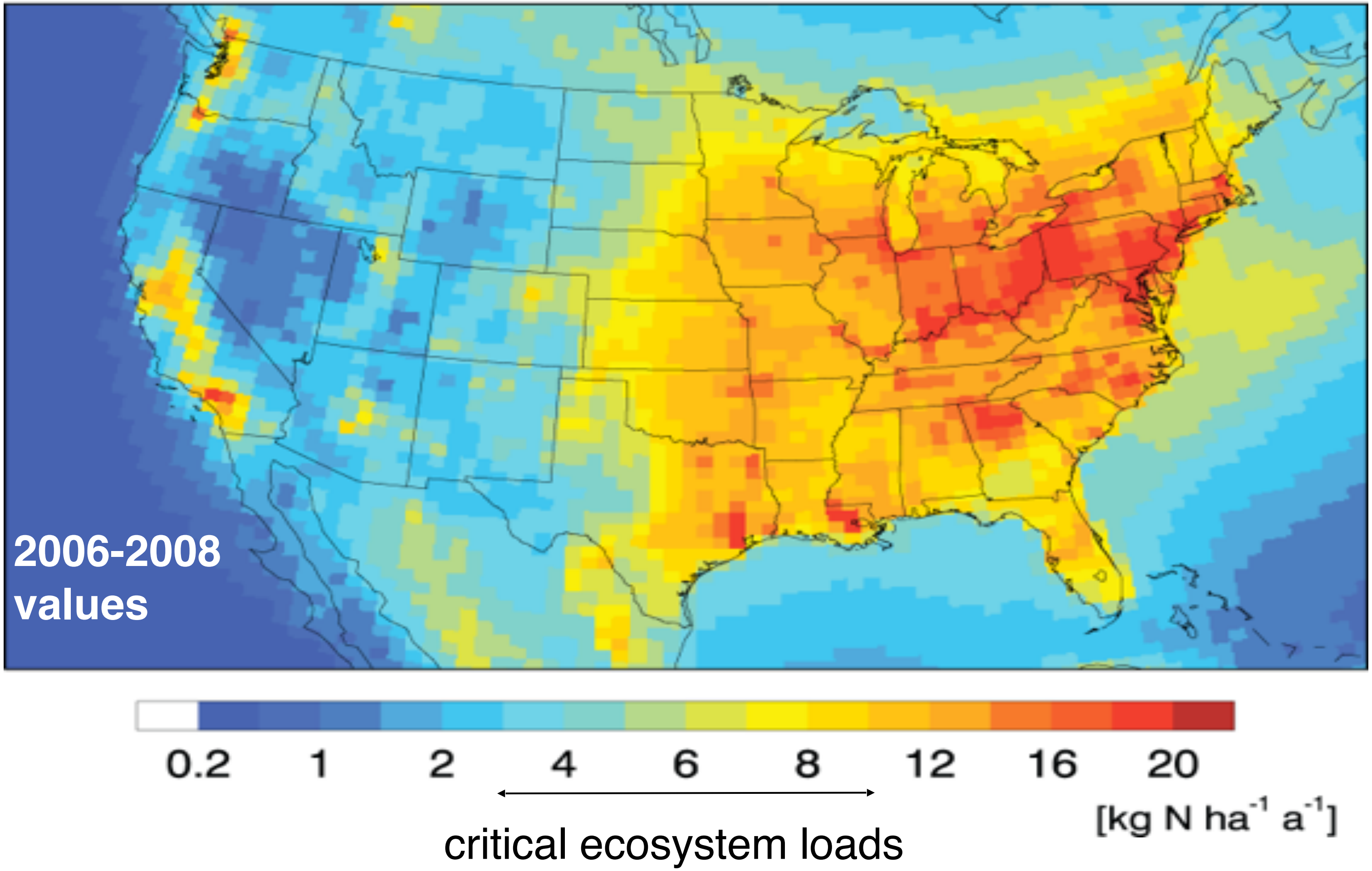


Mean pH of precipitation, 2015

5



Total nitrogen deposition (nitrate and ammonium)



- Nitrogen deposition exceeds critical loads in much of the country
- About half is nitrate, half is ammonium
- NO_x emissions are decreasing but ammonia emissions are not

Zhang et al. [2012], Ellis et al. [2013]

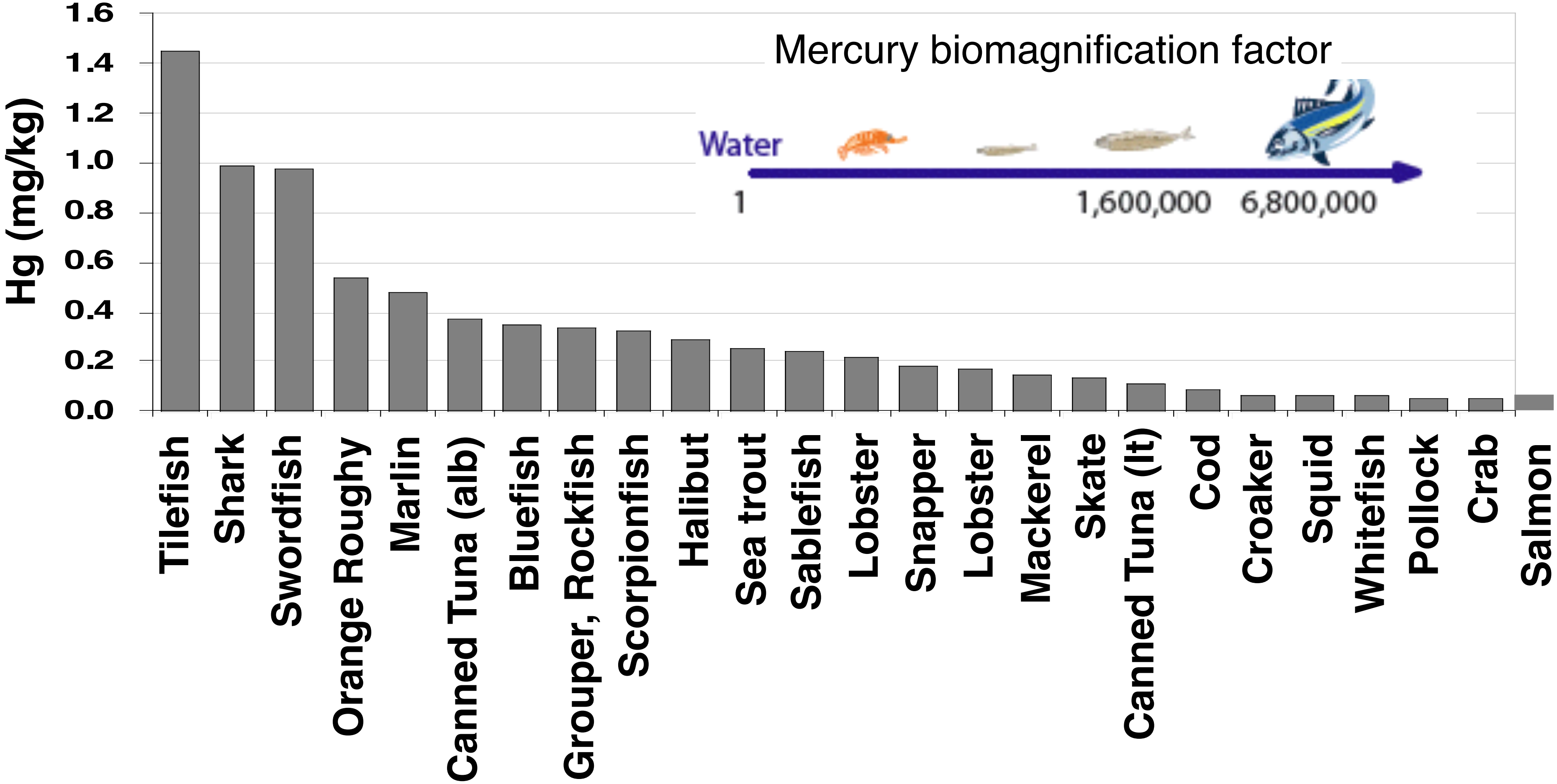
Environmental mercury and the role of the atmosphere

Mercury from fish consumption: a global environmental issue

EPA reference dose (RfD): 0.1 µg kg^{-1} d^{-1} (about 2 fish meals per week)

Children IQ deficits (fetal exposure)
Well-established
$8 billion per year cost in US

Adult cardiovascular, fertility effects
Suspected



Electronic structure of mercury

Group #	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
* Lanthanides (Lanthanoids)			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
** Actinides (Actinoids)			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Mass number = 80: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2$

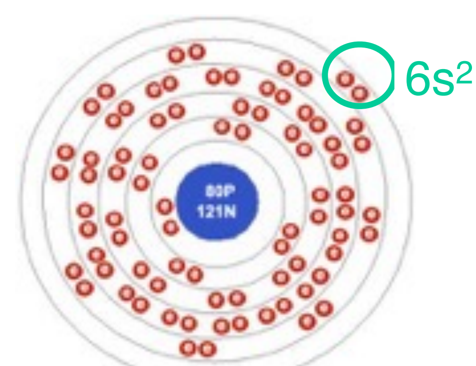
- Filling of subshells makes elemental Hg(0) stable, liquid, volatile
- Mercury can also shed its two outer electrons ($6s^2$) and be present as Hg(II) (mercuric) compounds

oxidation

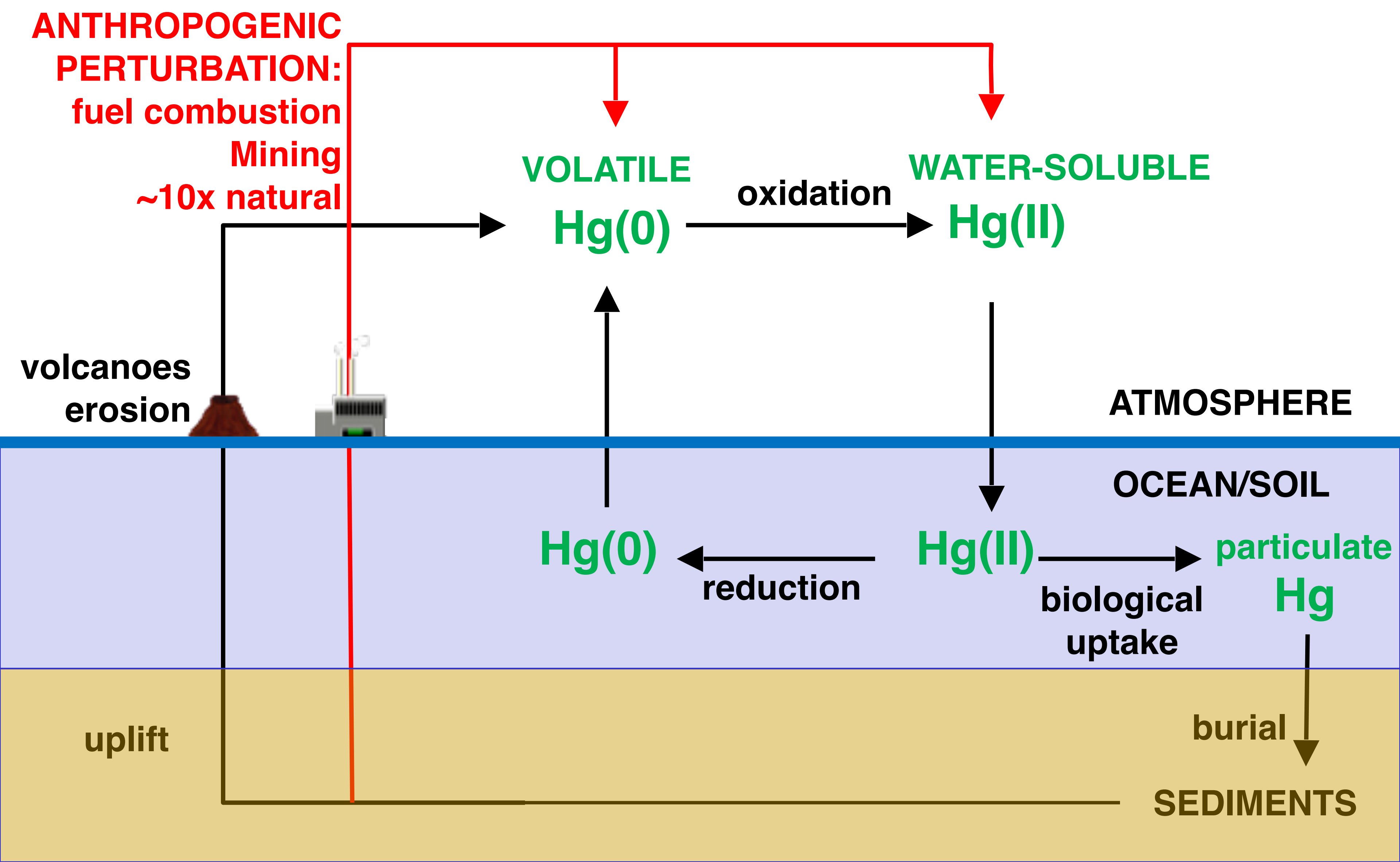
Hg(0) ⇄ Hg(II)

reduction

elemental mercury — mercuric compounds

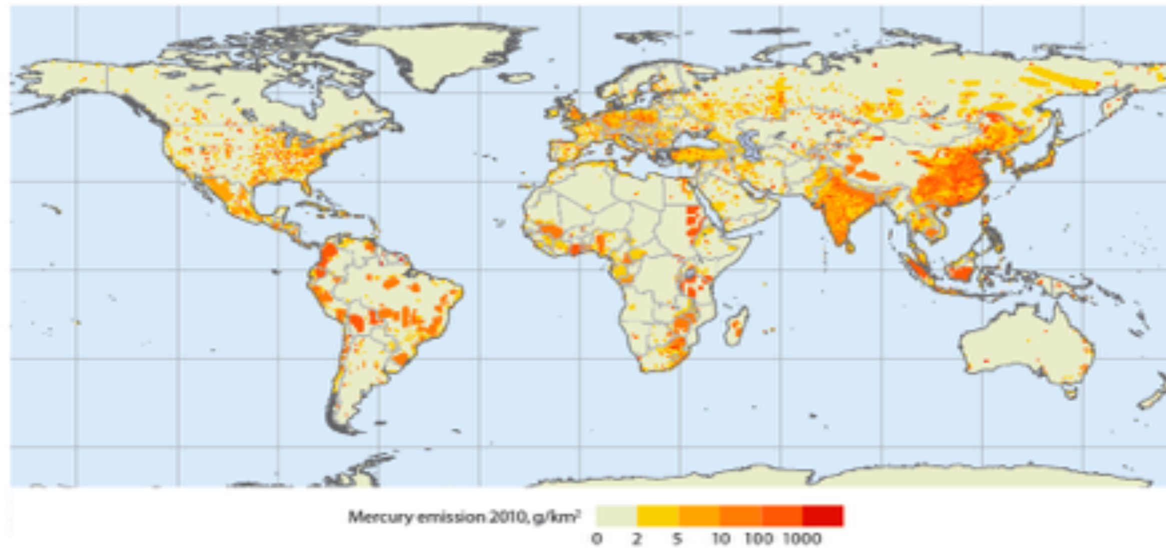


Biogeochemical cycle of mercury



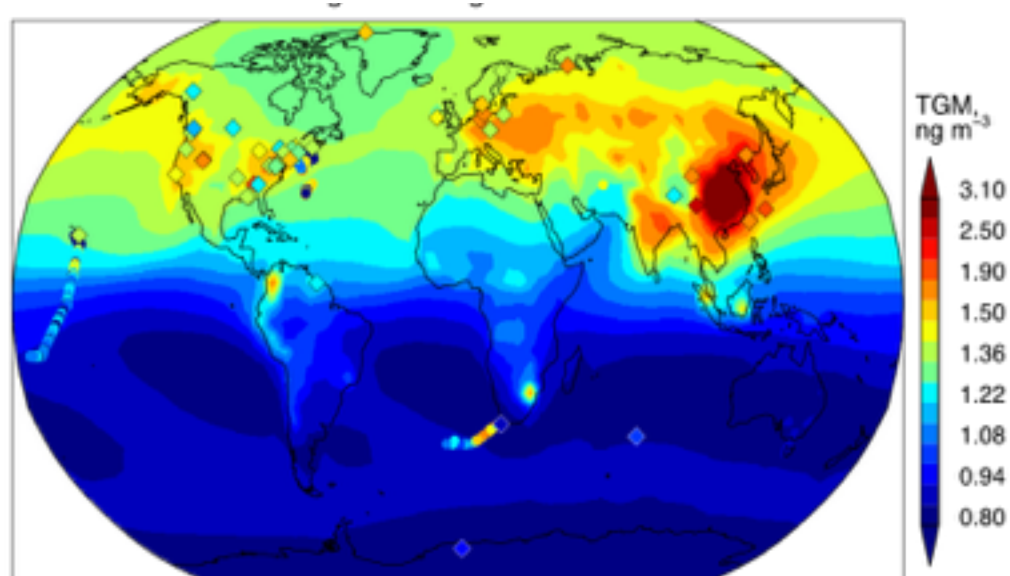
Global transport of mercury through the atmosphere

Present-day emission of mercury to atmosphere from coal and mining



Atmospheric concentrations

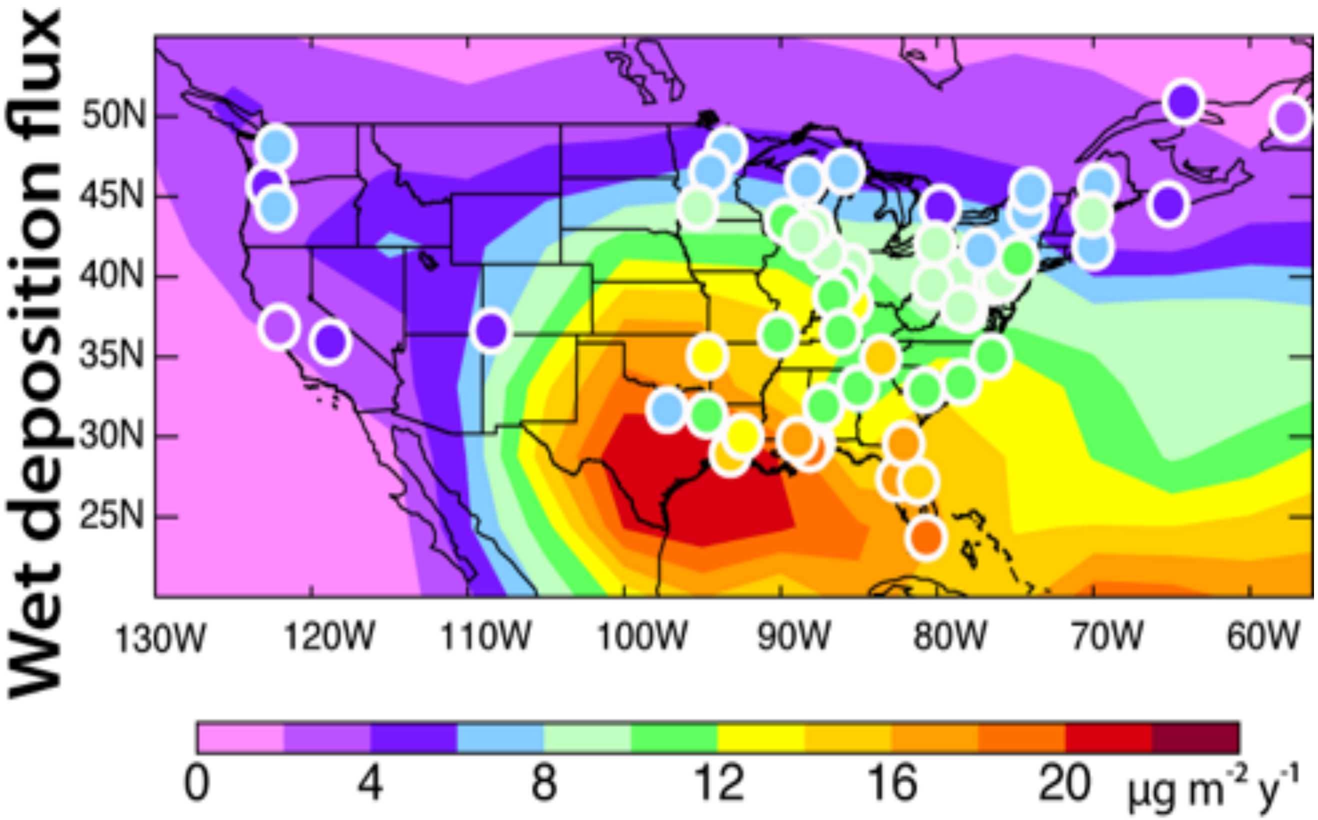
Observed variability of atmospheric Hg implies an atmospheric lifetime against deposition of about 0.5 years



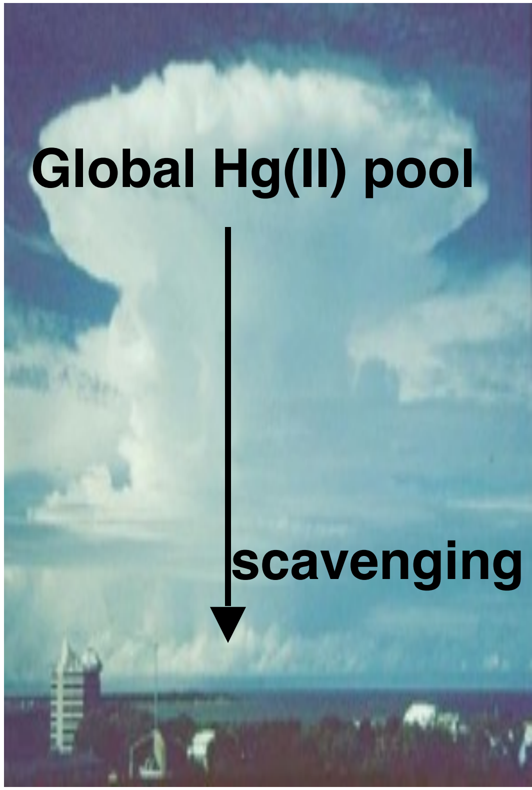
UNEP [2013]; Horowitz et al. [2017]

Mercury wet deposition is controlled by global transport

EPA deposition data (circles), model (background)



Florida T-storm



Highest mercury deposition in US is along the Gulf Coast,
where thunderstorms scavenge globally transported mercury from high altitudes

Selin and Jacob [2008]

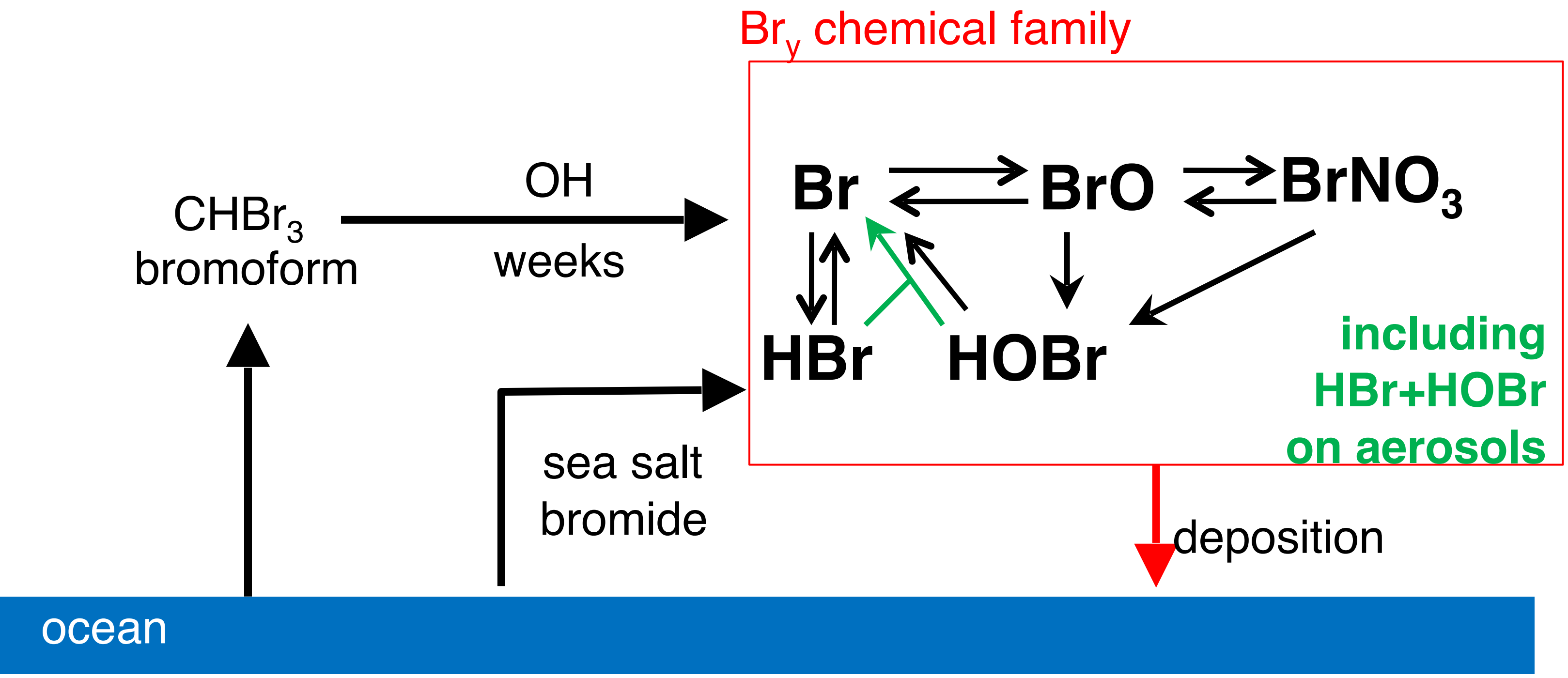
Atmospheric redox chemistry of mercury: driver of mercury deposition

$$Hg(0) \underset{hv}{\overset{Br}{\rightleftharpoons}} Hg(II)$$

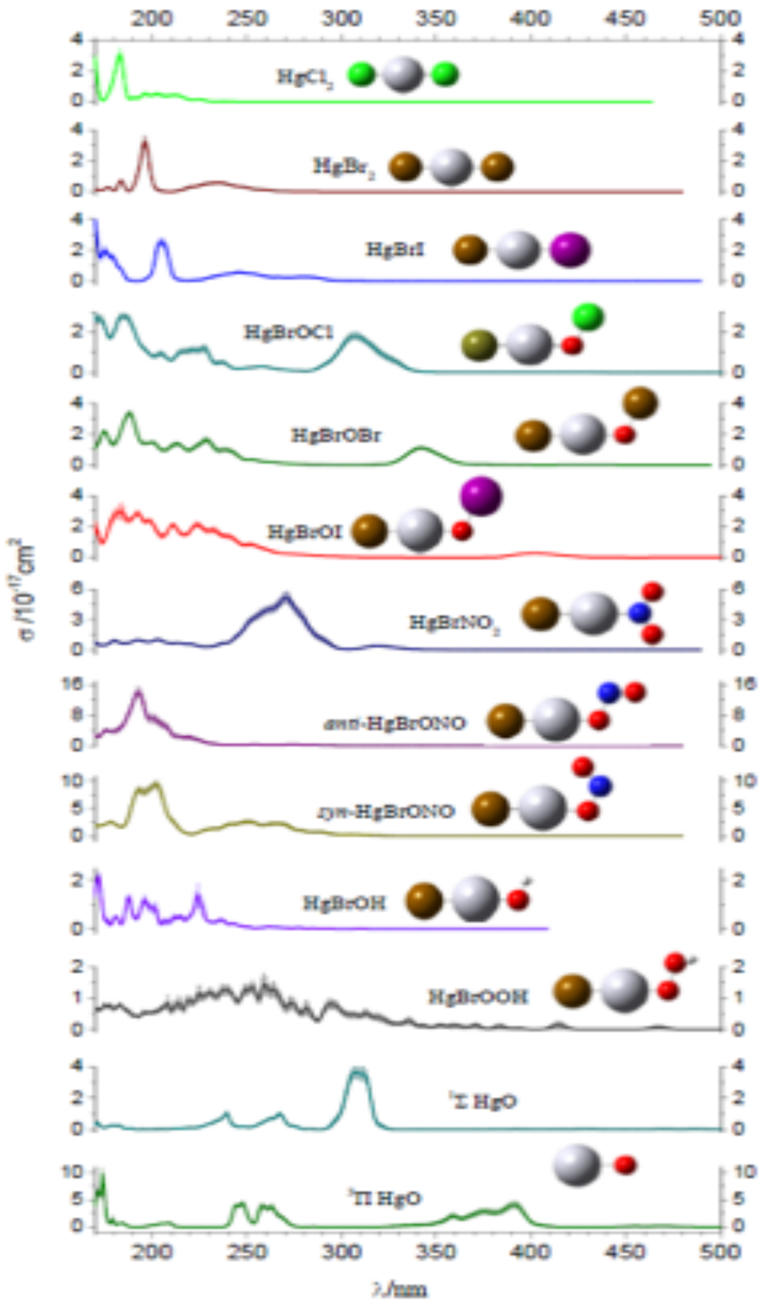
- Oxidation of Hg(0) by OH is too slow
- Oxidation by Br atoms is currently thought to dominate

$$Hg + Br + M \rightleftharpoons HgBr + M$$

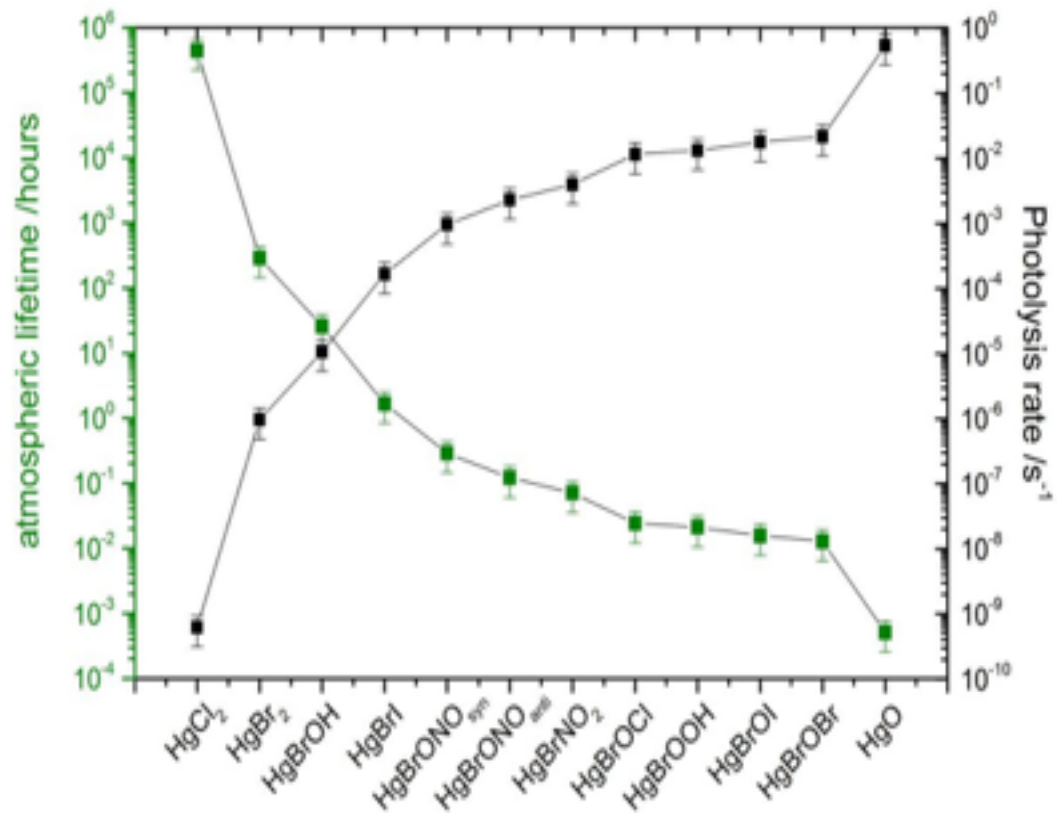
$$HgBr + X + M \rightarrow HgBrX + M \qquad X \equiv OH, Br, Cl, NO_2, HO_2$$



Hg(II) likely photolyzes but speciation is uncertain

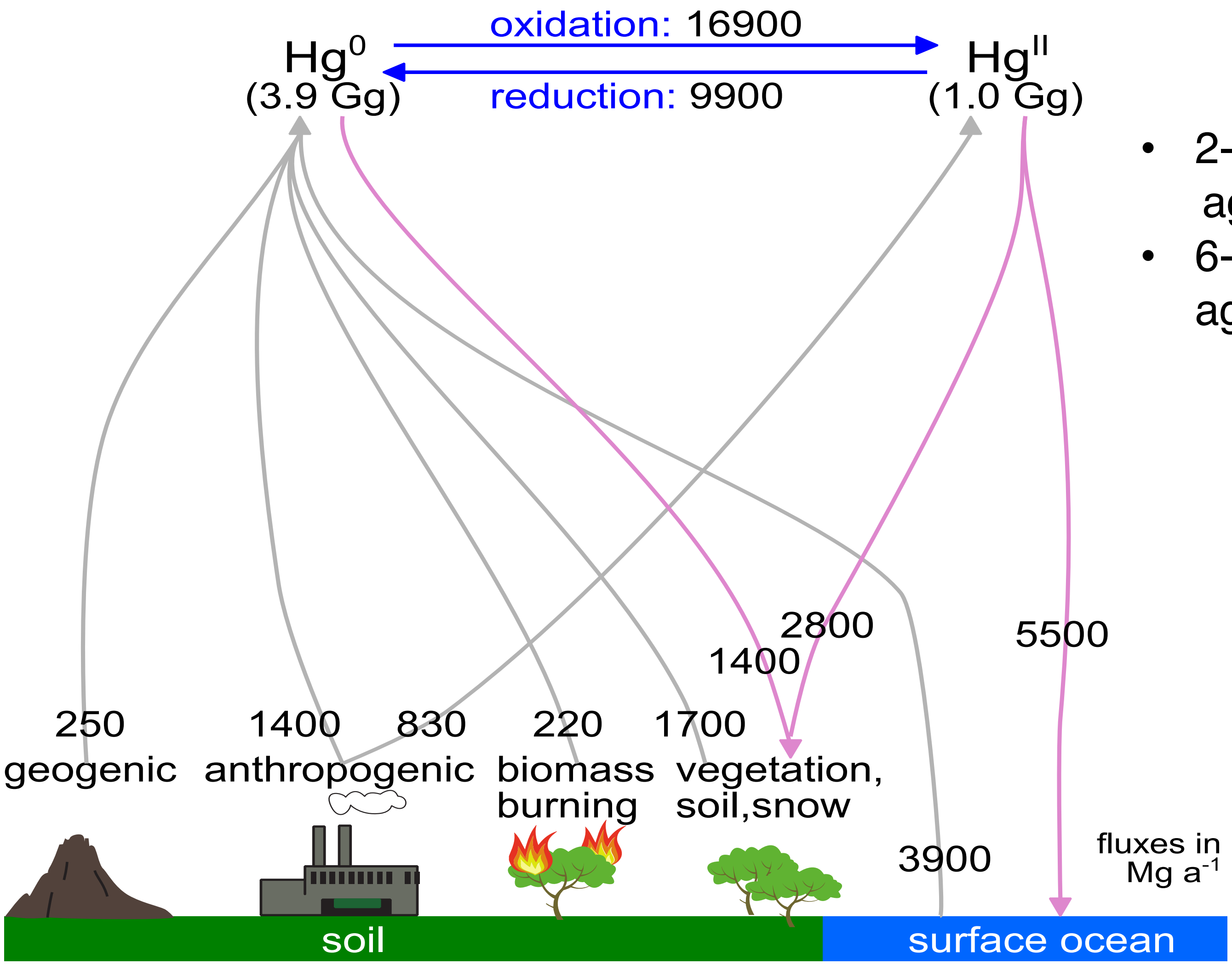


Speciation may change by cycling through aerosols and clouds, formation of Hg(II)-organic complexes has been proposed



Saiz-Lopez et al., submitted

Current view of atmospheric Hg budget



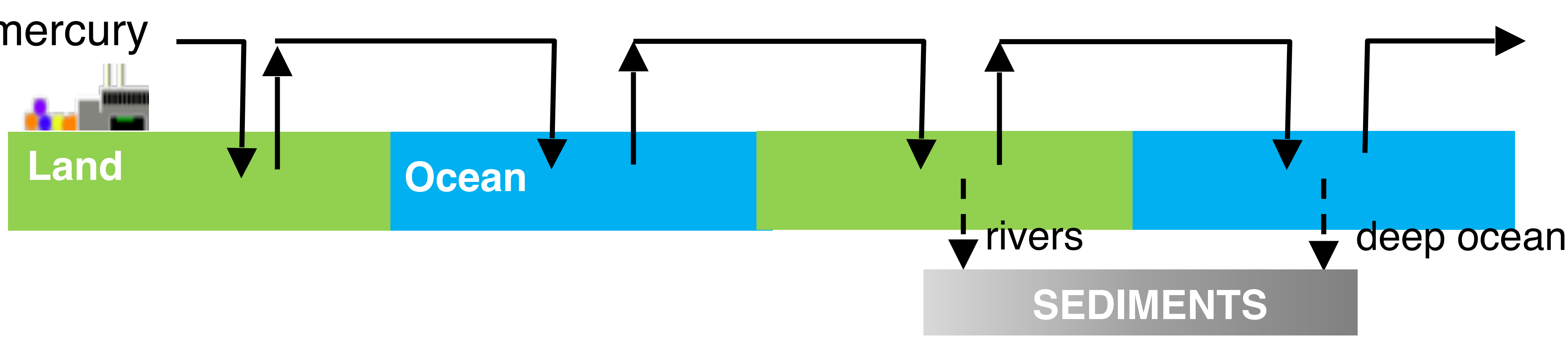
- 2-month lifetime of Hg^0 against oxidation
- 6-month lifetime of atm Hg against deposition

Horowitz et al., 2017

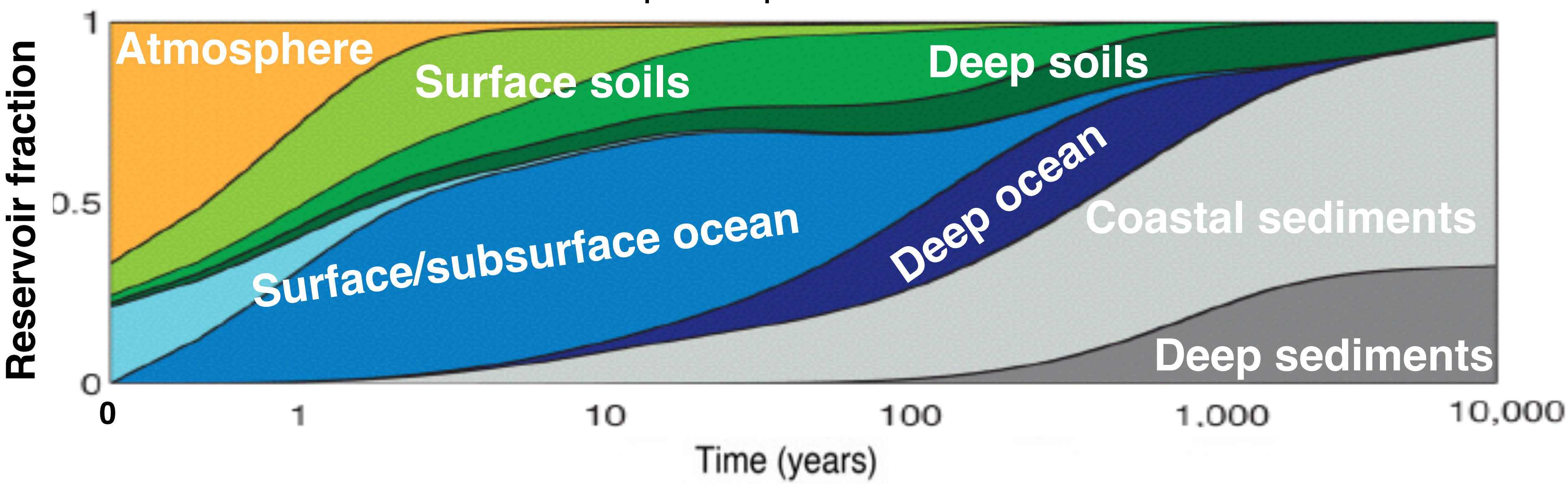
UNEP Minimata Convention on Mercury (2013)

- Requires best available technology for coal-fired power plants
- Mercury mining to be banned in 15 years
- Regulation of mercury use in artisanal gold mining

“Grasshopper effect” keeps mercury in environment for decades



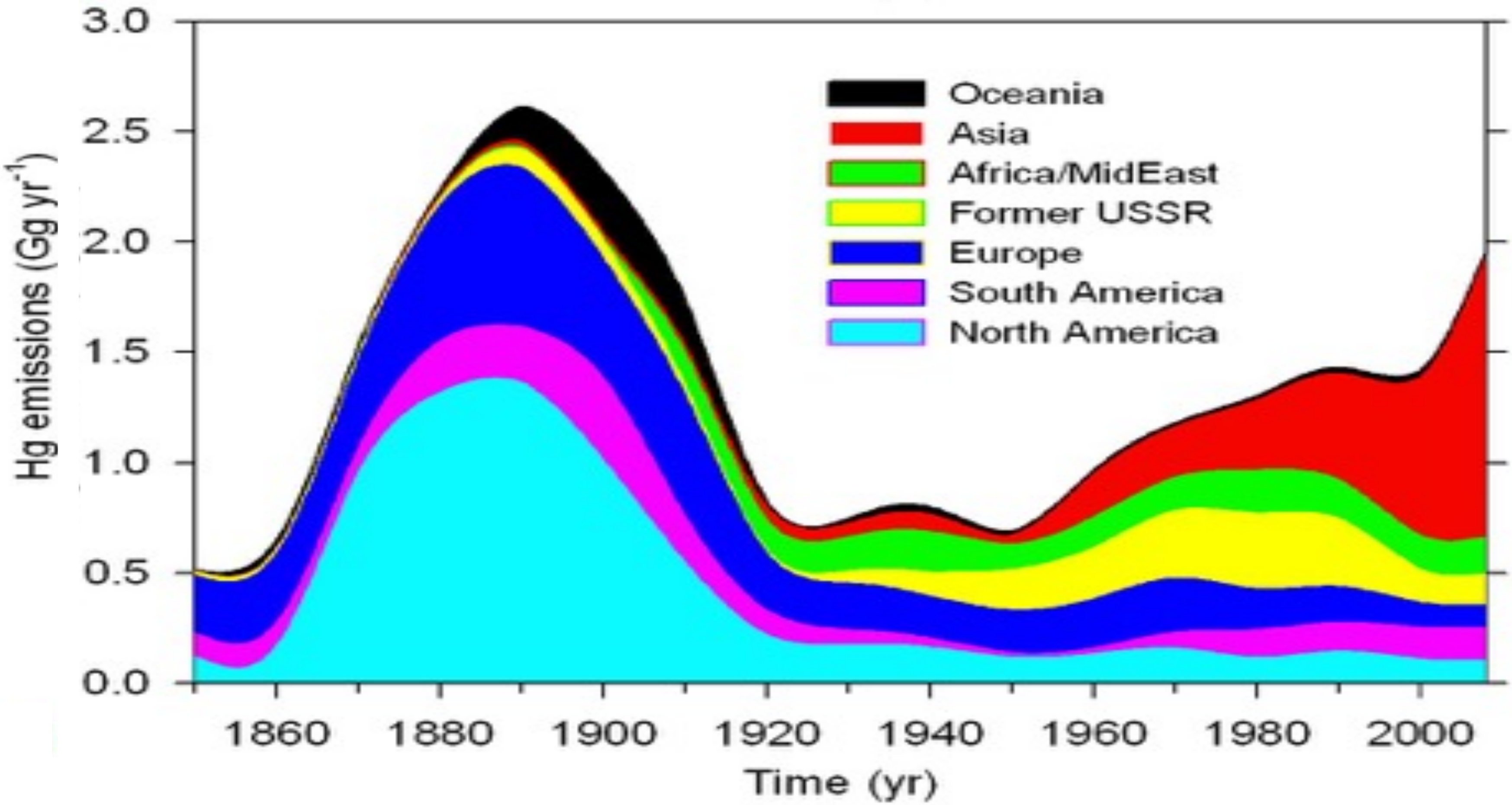
Fate of an atmospheric pulse emitted at time zero:



Amos et al. [2014]

Thus mercury pollution is in large part a legacy problem

Historical global emissions from coal combustion, mining, and industry

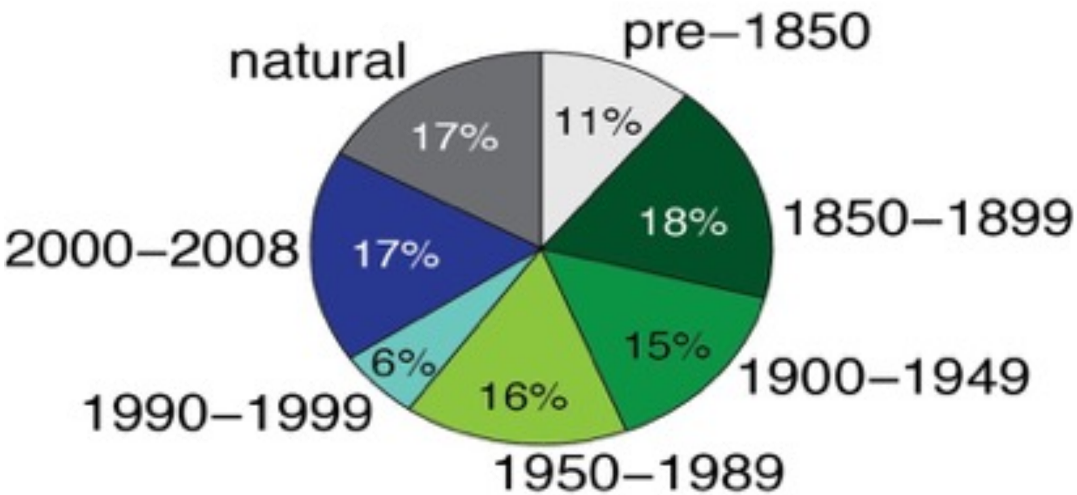


The dominance of Asian emissions is a recent development

Streets et al. , 2011

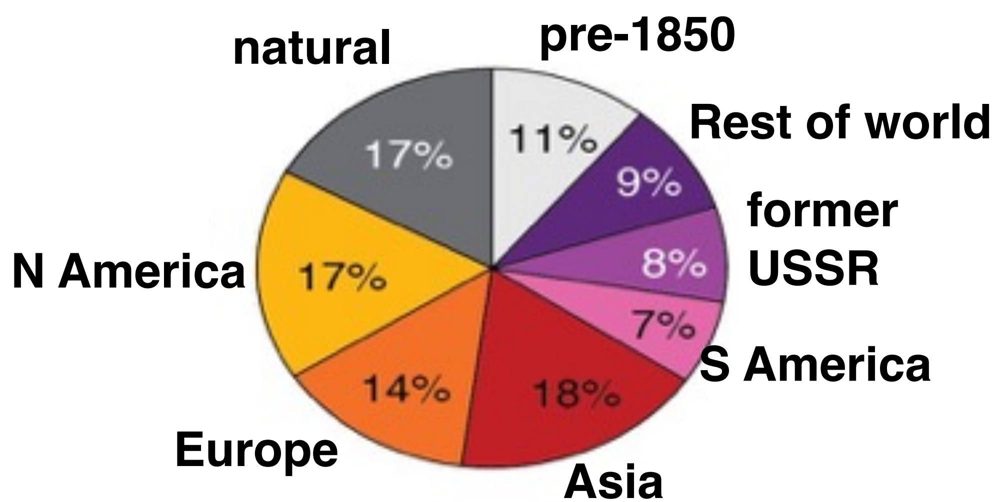
Who is responsible for mercury in the present-day ocean?

by time of initial emission:



Half of human-derived mercury presently in the ocean was emitted before 1950

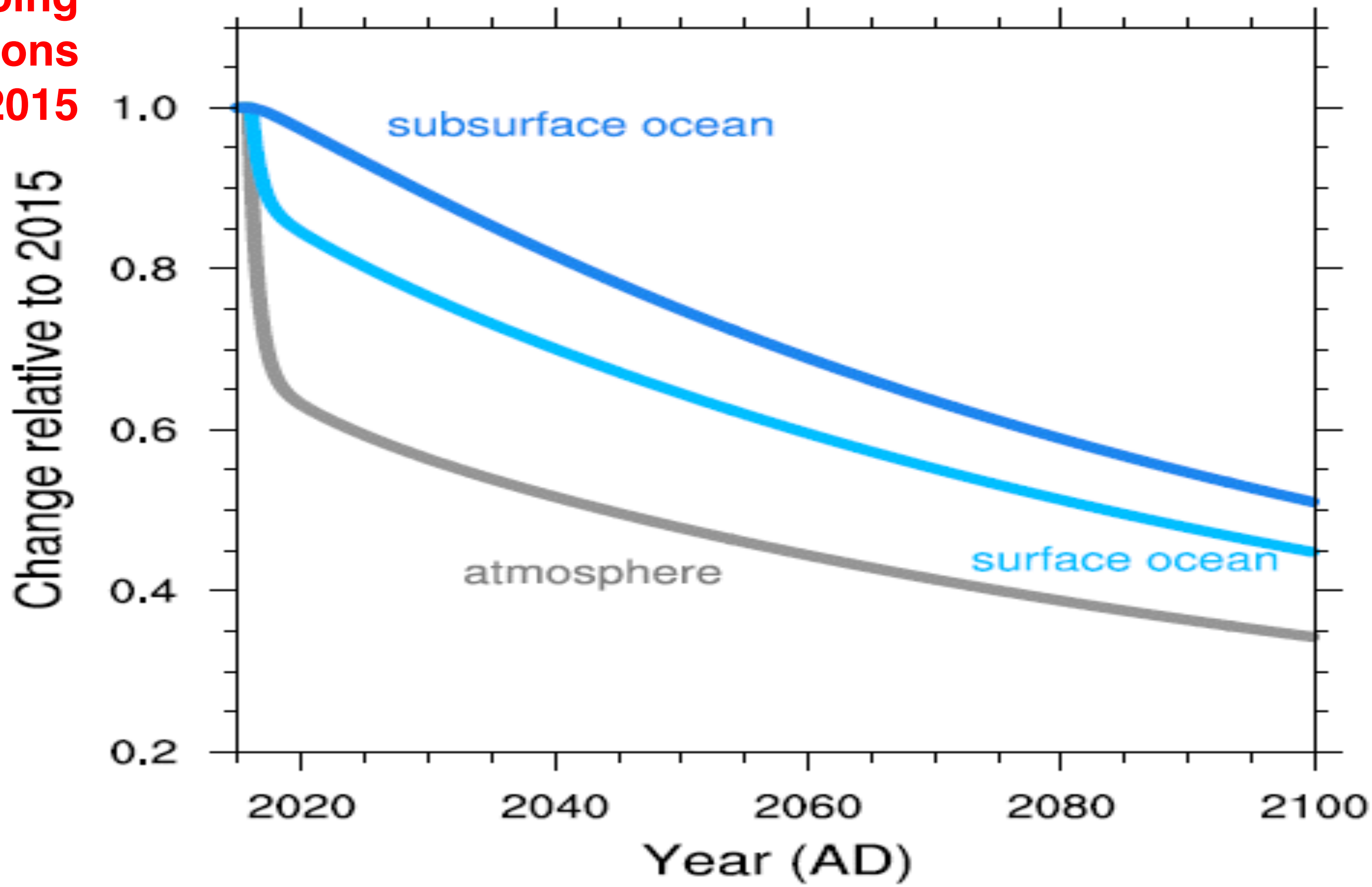
by source continent:



Amos et al. [2013]

What can we hope from the Minimata Convention?

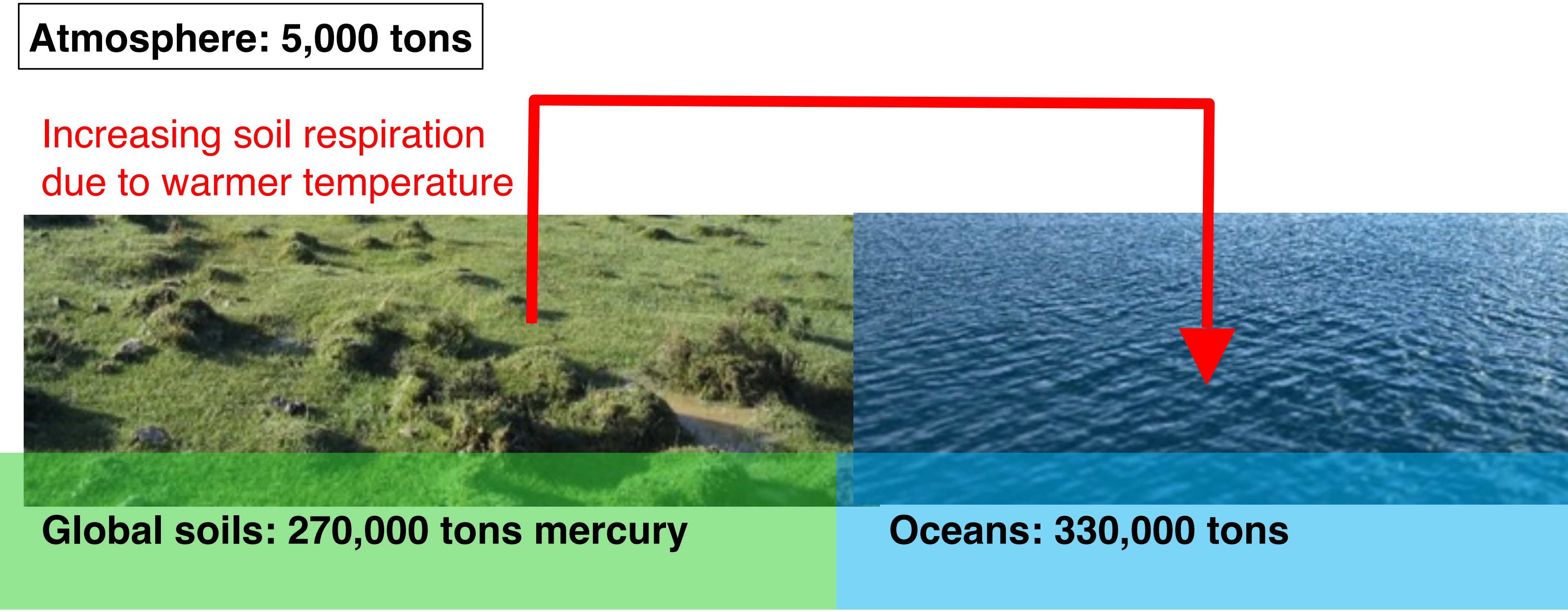
Effect of zeroing all human emissions by 2015



Zeroing human emissions right now would decrease ocean mercury by 50% by 2100, whil
keeping emissions constant would increase it by 40%

Amos et al. [2013, 2014]

The wild card of climate change: potential mobilization of the large soil mercury pool



Climate change may be as important as emission controls
for the future of environmental mercury in the century ahead.