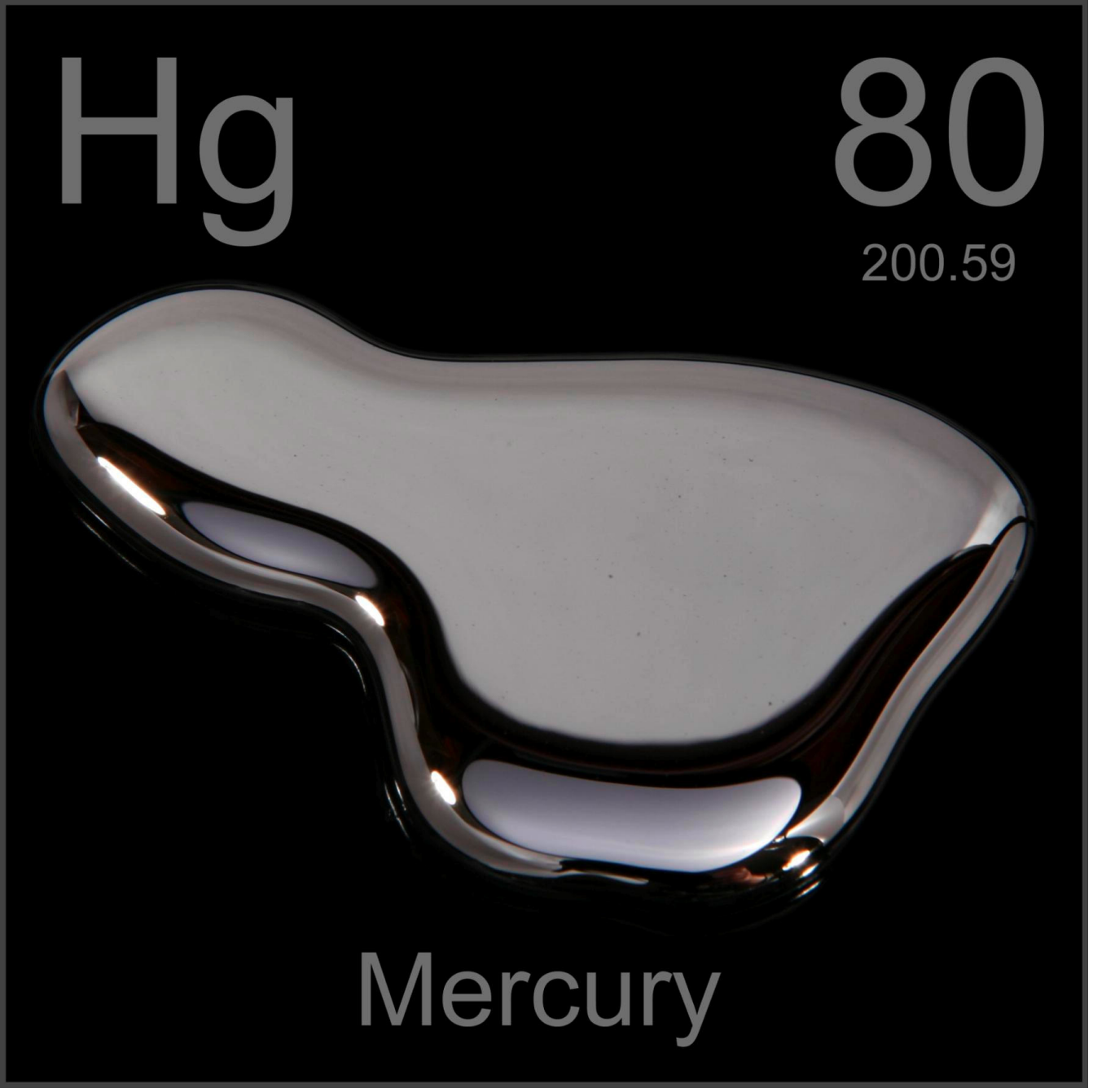


http://www.theodoregray.com/periodictable/Samples/080.14/index.s15.html

http://www.theodoregray.com/periodictable/Samples/080.20/index.s15.html

http://www.theodoregray.com/periodictable/Samples/080.22/index.s15.html

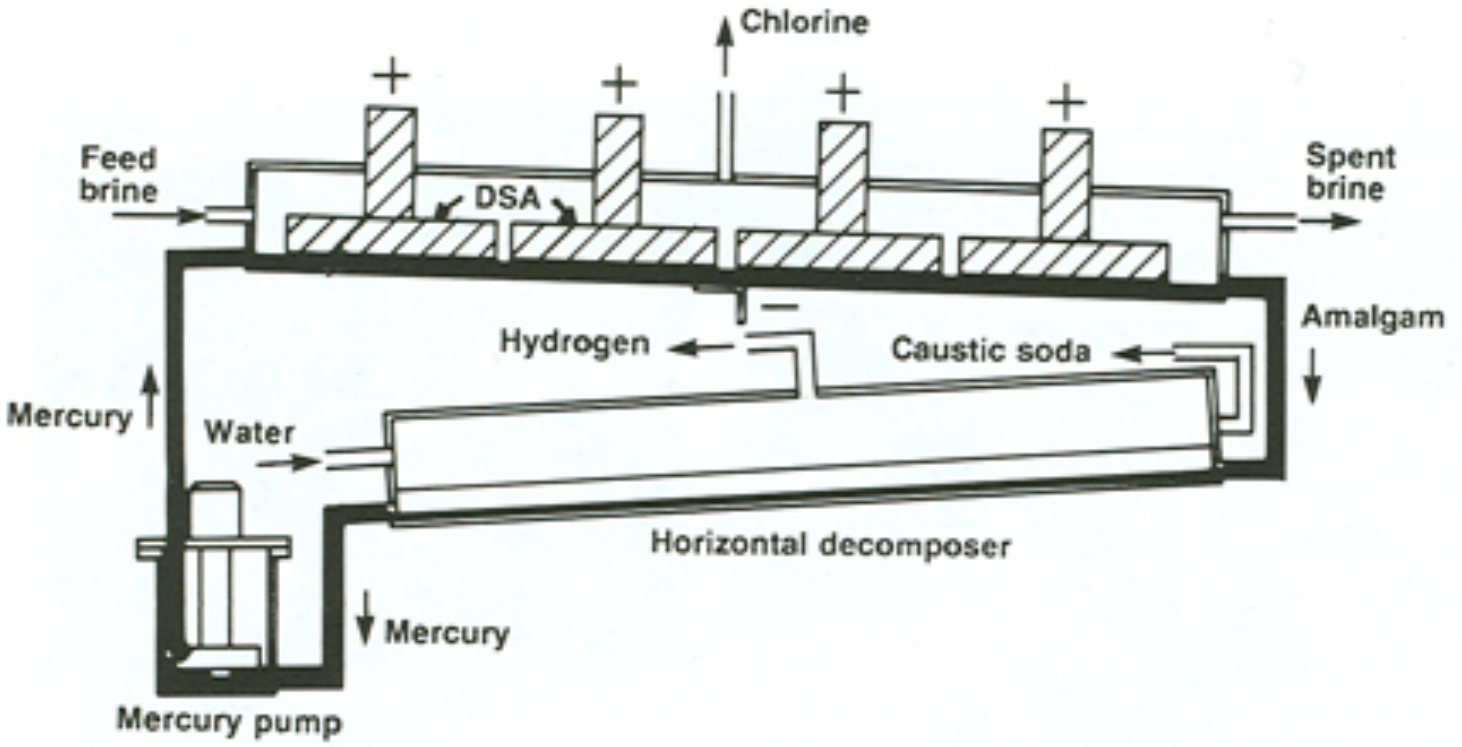
http://www.theodoregray.com/periodictable/Samples/080.23/index.s15.html

http://www.theodoregray.com/periodictable/Samples/080.28/index.s15.html

http://www.theodoregray.com/periodictable/Samples/080.29/index.s15.html

http://www.laboratoryequipment.com/sites/laboratoryequipment.com/files/legacyimages/032113_mercury.jpg

http://www.unep.org/hazardoussubstances/portals/9/images/Miner%20Burkina%20Faso%20-%20Kevin%20Telmer.png



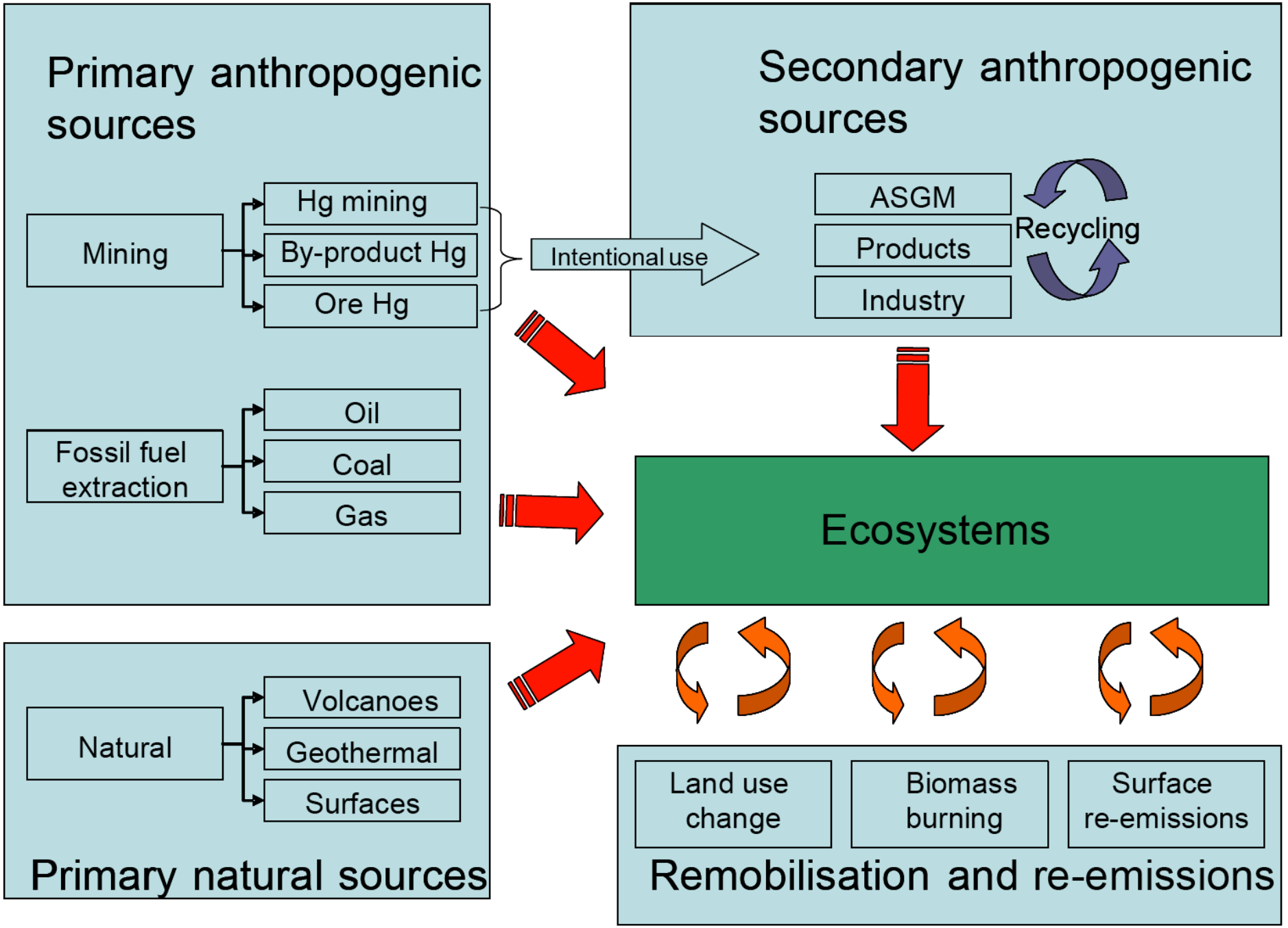
http://www.ec.gc.ca/lcpe-cepa/E7E0E329-7A23-4F30-84C9-99B0F7B89A0C/f4-eng.jpg

Sugestão de Leitura

- Technical Background Report to the Global Atmospheric Mercury Assessment (UNEP);
- The Mercury Study Report to Congress (U.S. EPA)

Fontes de Hg

- Combustão de combustíveis fósseis (carvão principalmente);
- Produção de aço;
- Produção de cimento;
- Produção de cloro e soda cáustica;
- Lixiviação de minérios (especialmente HgS);
- Mineração de ouro;
- Atividade vulcânica.



http://www.chem.unep.ch/mercury/Atmospheric_Emissions/Technical_background_report.pdf

Fontes de Hg: Antropogênicas vs. Naturais

- 1,6 ng/m3 (pré-industrial = 0,5 ng/m3);
- antropogênico:natural = 1,4:1;
- Antropogênico = 2.900 ton/ano;
- Natural = 2.100 ton/ano;
- 200.000 ton emitidas desde 1890 (95% disso imobilizada em solo ou oceanos)

http://www.mercvt.org/facts/global.htm

Table 1.1. Environmental mercury fluxes from Global Mercury Models.

Hg Fluxes (kton/yr)	**Lamborg et al., 2002b**	**Mason and Sheu, 2002**	**Selin et al., 2007**	**Mason, 2008**	**Friedl et al., 2008**
Natural emissions from land	1.0	0.81	0.5		
Re-emissions from land		0.79	1.5		
Emissions from biomass burning					0.675
(A) Total emissions from land	1.0	1.6	2.0	1.85[a]	
Natural emissions from ocean	0.4	1.3	0.4		
Re-emissions from ocean	0.4	1.3	2.4		
(B) Total oceanic emissions	0.8	2.6	2.8	2.6	
(C) Primary anthropogenic emissions	2.6	2.4	2.2		
Total sources (A+B+C)	**4.4**	**6.6**	**7.0**		
(D) Deposition to land	2.2	3.52			
(E) Deposition to ocean	2.0	3.08			
Total deposition (D+E)	**4.2**	**6.6**	**7.0**	**6.4**	
Net load to land	1.2	1.72 [b]			
Net load to ocean (burial in sediments)	1.2 (0.4)	0.68 (0.2)			
Total net load (land + ocean)	**2.4**	**2.4**	**2.2**		
Other parameters					
Mercury burden in the troposphere (kton)	5.22	5.00	5.36		
GEM lifetime (y)	1.3	0.76	0.79		

[a] Including Hg^0 emissions (0.2 kton/yr) in response to Atmospheric Mercury Depletion Events (AMDEs) in polar regions. Biomass burning is not included in the emissions from land in this Table.

[b] Value includes taking account of estimated flux from land to water via rivers (0.2).

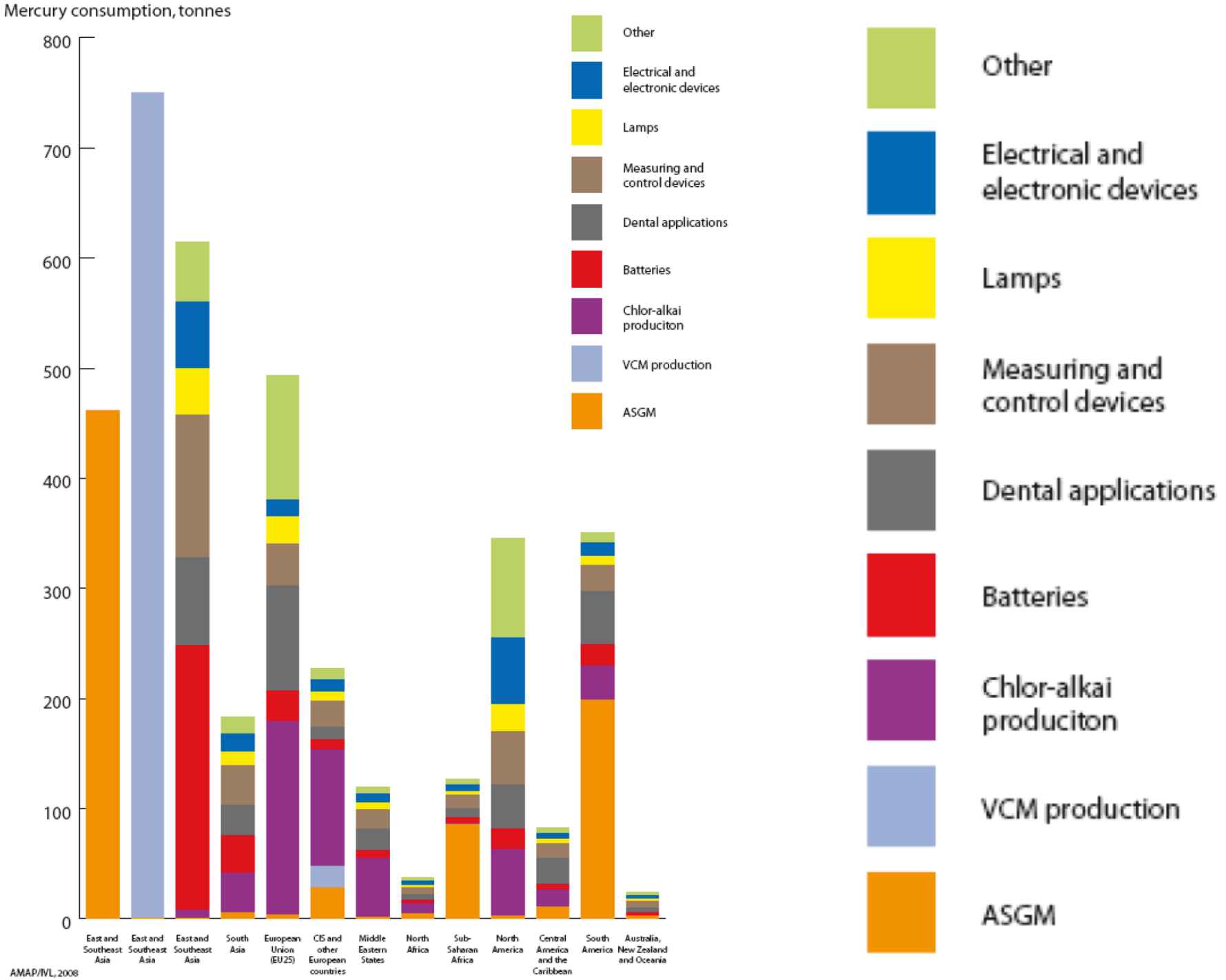
http://www.chem.unep.ch/mercury/Atmospheric_Emissions/Technical_background_report.pdf

Table 3.4. Total mercury consumed[1] worldwide by region and by major application.

Elemental mercury 2005 (tonnes)	**Artisanal gold mining**			**VCM production**			**Chlor-alkali production**			**Batteries**		
	min	*max*	*ave*	*min*	*max*	*ave*	*min*	*max*	*ave*	*min*	*max*	*ave*
East & Southeast Asia	408	514	461	700	800	750	5	11	8	180	300	240
South Asia	2	10	6	0	0	0	32	40	36	20	45	33
European Union (EU25)	3	5	4	0	0	0	155	195	175	20	35	28
CIS & other European countries	18	38	28	15	25	20	95	115	105	8	12	10
Middle Eastern States	1	3	2	0	0	0	48	58	53	5	8	7
North Africa	0	10	5	0	0	0	7	11	9	2	3	3
Sub-Saharan Africa	59	112	86	0	0	0	1	2	1	4	6	5
North America	2	4	3	0	0	0	55	65	60	17	20	19
Central America & the Caribbean	7	14	11	0	0	0	12	18	15	4	6	5
South America	141	256	199	0	0	0	25	35	30	15	25	20
Australia, New Zealand & Oceania	0	5	3	0	0	0	0	0	0	2	3	3
Total per application	**641**	**971**	**806**	**715**	**825**	**770**	**435**	**550**	**492**	**277**	**463**	**370**

Elemental mercury 2005 (tonnes)	**Dental applications**			**Measuring and control devices**			**Lamps**		
	min	*max*	*ave*	*min*	*max*	*ave*	*min*	*max*	*ave*
East & Southeast Asia	72	88	80	122	136	129	38	45	42
South Asia	23	32	28	34	38	36	11	12	12
European Union (EU25)	85	105	95	30	45	38	20	30	25
CIS & other European countries	10	12	11	22	25	24	7	9	8
Middle Eastern States	15	25	20	15	18	17	5	6	6
North Africa	4	6	5	6	6	6	2	2	2
Sub-Saharan Africa	6	9	8	11	13	12	3	4	4
North America	35	45	40	40	55	48	21	28	25
Central America & the Caribbean	20	28	24	12	13	13	4	4	4
South America	40	56	48	23	25	24	7	8	8
Australia, New Zealand & Oceania	3	5	4	5	6	6	2	2	2
Total per application	**313**	**411**	**362**	**320**	**380**	**350**	**120**	**150**	**135**

Elemental mercury 2005 (tonnes)	**Electrical and electronic devices**			**Other[2]**			**Regional totals**		
	min	*max*	*ave*	*min*	*max*	*ave*	*min*	*max*	*ave*
East & Southeast Asia	56	66	61	45	63	54	1626	2023	1825
South Asia	16	18	17	12	18	15	150	213	182
European Union (EU25)	10	20	15	75	150	113	398	585	492
CIS & other European countries	10	12	11	8	12	10	193	260	227
Middle Eastern States	7	8	8	5	8	7	101	134	118
North Africa	3	4	4	2	3	3	26	45	36
Sub-Saharan Africa	5	6	6	4	5	5	93	157	125
North America	55	65	60	60	120	90	285	402	344
Central America & the Caribbean	5	6	6	4	6	5	68	95	82
South America	11	12	12	8	12	10	270	429	350
Australia, New Zealand & Oceania	2	3	3	2	3	3	16	27	22
Total per application	**180**	**220**	**200**	**225**	**400**	**313**	**3226**	**4370**	**3798**


Mercury consumption, tonnes
800
700
600
500
400
300
200
100
0
Other
Electrical and electronic devices
Lamps
Measuring and control devices
Dental applications
Batteries
Chlor-alkai produciton
VCM production
ASGM
East and Southeast Asia
East and Southeast Asia
East and Southeast Asia
South Asia
European Union (EU25)
CIS and other European countries
Middle Eastern States
North Africa
Sub-Saharan Africa
North America
Central America and the Caribbean
South America
Australia, New Zealand and Oceania
AMAP/IVL, 2008
Other
Electrical and electronic devices
Lamps
Measuring and control devices
Dental applications
Batteries
Chlor-alkai produciton
VCM production
ASGM

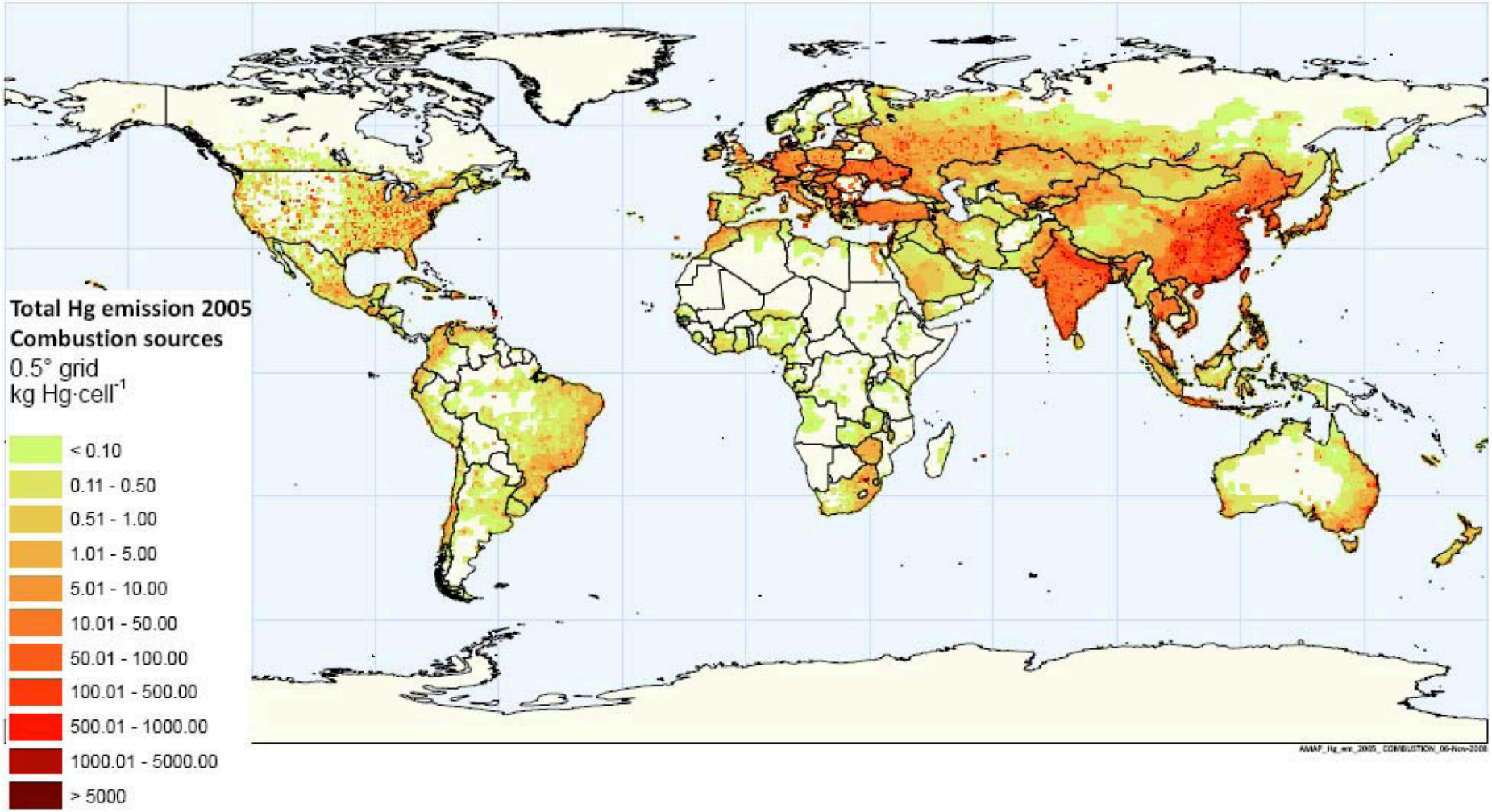


Figure 3.7. The gridded distribution of total mercury from (power plant and residential heating) combustion sources.

Table 3.7. Mercury by-product emissions from anthropogenic sources worldwide in 2005 (tonnes)(nb. values are rounded to 3 significant digits).

Region	Station-ary combust-ion	Non-ferrous metals product-ion	Pig iron and steel product-ion	Cement product-ion	Gold product-ion	Mercury product-ion (primary sources)	Waste incinerat-ion*	Caustic soda product-ion	Other sources	Total
Africa	37.3	2.1	1.6	10.9	8.9	0.0	0.6	0.1	0.0	61.6
Asia (excluding Russia)	622	90.0	24.1	138	58.9	8.8	5.7	28.7	0.6	977
Europe (excluding Russia)	76.6	18.7		18.8	0.0	0.0	10.1	6.3	14.7	145
North America	71.2	5.7	14.4	10.9	12.9	0.0	15.1	6.5	7.2	144
Oceania	19.0	6.1	0.8	0.4	10.1	0.0	0.0	0.2	0.0	36.6
Russia	46.0	5.2	2.6	3.9	4.3	0.0	3.5	2.8	1.5	69.8
South America	8.0	13.6	1.8	6.4	16.2	0.0	0.0	2.2	1.5	49.6
World	880	141	45.4	189	111	8.8	35.0	46.8	25.5	1480

Table 3.8. Concentrations of mercury in various fossil fuels.

Fuel	Concentration, g/tonne
Hard coals	
Europe	0.01–1.5
USA	0.01–1.5
Australia	0.03–0.4
South Africa	0.01–1.0
Russia	0.02–0.9
Brown coals	
Europe	0.02–1.5
USA	0.02–1.0
Crude oil	0.01–0.5

Table 3.12. Estimated emissions of mercury from artisanal gold mining.

Region	Hg emission, tonnes
Australia New Zealand and Oceania	0.2
Sub-Saharan Africa	8
Central America and the Caribbean	5
CIS and other European countries	4
East and Southeast Asia	233
Middle Eastern States	3
North America	6
South America	64
South Asia	28
Total	350

Table 3.13. Estimated global anthropogenic emissions of mercury to air in 2005 from various sectors (ni are rounded to 3 significant digits).

Sector	Emissions in 2005 (t)	Low-end estimate	High-end estimate	%
Power plants	*498*			
Residential heat	*375*			
Other Industrial/Residential/Commercial combustion	*5.2*			
Fossil fuel combustion for power and heating	878	595	1160	45.6
Pig iron and steel	*54.5*			
Non-ferrous metals	*132*			
Mercury production	*8.8*			
Secondary steel	*4*			
Metal production (ferrous and non-ferrous, excluding gold)	200	123	276	10.4
Large-scale gold production	111	66	156	5.78
Artisanal and small-scale gold production	351	225	475	18.2
Cement production	189	114	263	9.8
Chlor-alkali industry	46.8	29	64	2.43
Waste incineration (Europe and North America)	*35*			
Other	*26.1*			
Waste & other	*63.9*			
Waste incineration, waste and other	125	53	473	6.49
Dental amalgam (cremation)*	25.7	24	28	1.33
Total	1930			

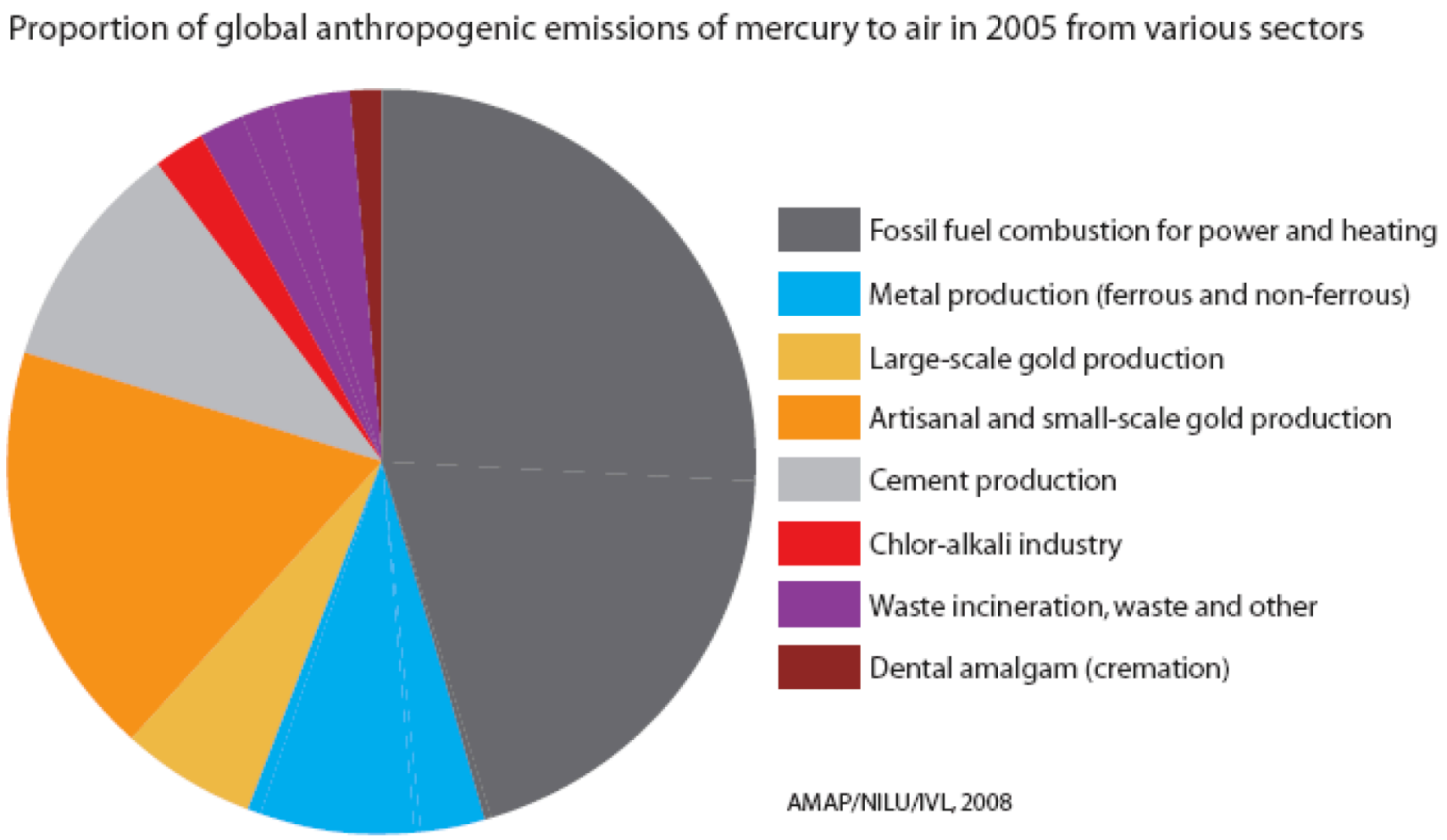


Figure 3.13. Proportion of global anthropogenic emissions of mercury to air in 2005 from various sectors.

Table 3.15 The largest mercury by-product emitting countries in 2005 (tonnes).

Rank	Country	Emissions in 2005	% of global total	Category			
				Stationary combustion	Industrial production	Artisanal gold	Other sources
1	China	825.2	42.85	387.4	243.2	156.0	38.6
2	India	171.9	8.93	139.7	21.6	0.5	10.1
3	USA	118.4	6.15	62.8	31.7	0.5	23.4
4	Russia	73.9	3.84	46.0	18.9	3.9	5.1
5	Indonesia	68.0	3.53	3.3	10.2	50.9	3.6
6	South Africa	43.1	2.24	33.4	5.7	2.6	1.4
7	Brazil	34.8	1.81	4.8	11.4	15.8	2.8
8	Australia	33.9	1.76	17.7	15.2	0.4	0.6
9	Republic of Korea	32.2	1.67	18.1	12.9	0	1.2
10	Columbia	30.	1.56	0.8	2.3	26.3	0.6
	Total		74.33				

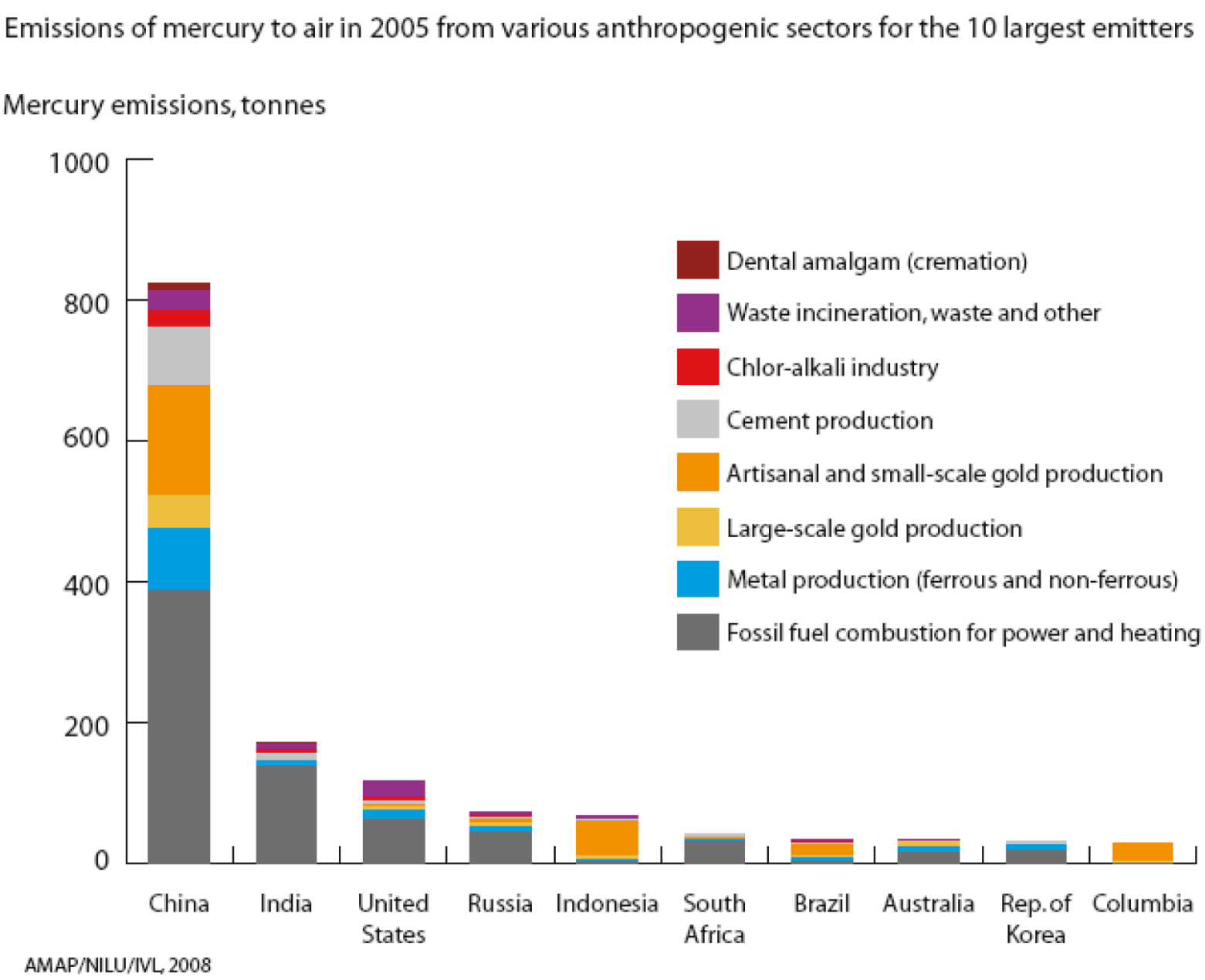


Figure 3.16. Emissions of mercury to air in 2005 from various anthropogenic sectors in the ten largest emittin countries.

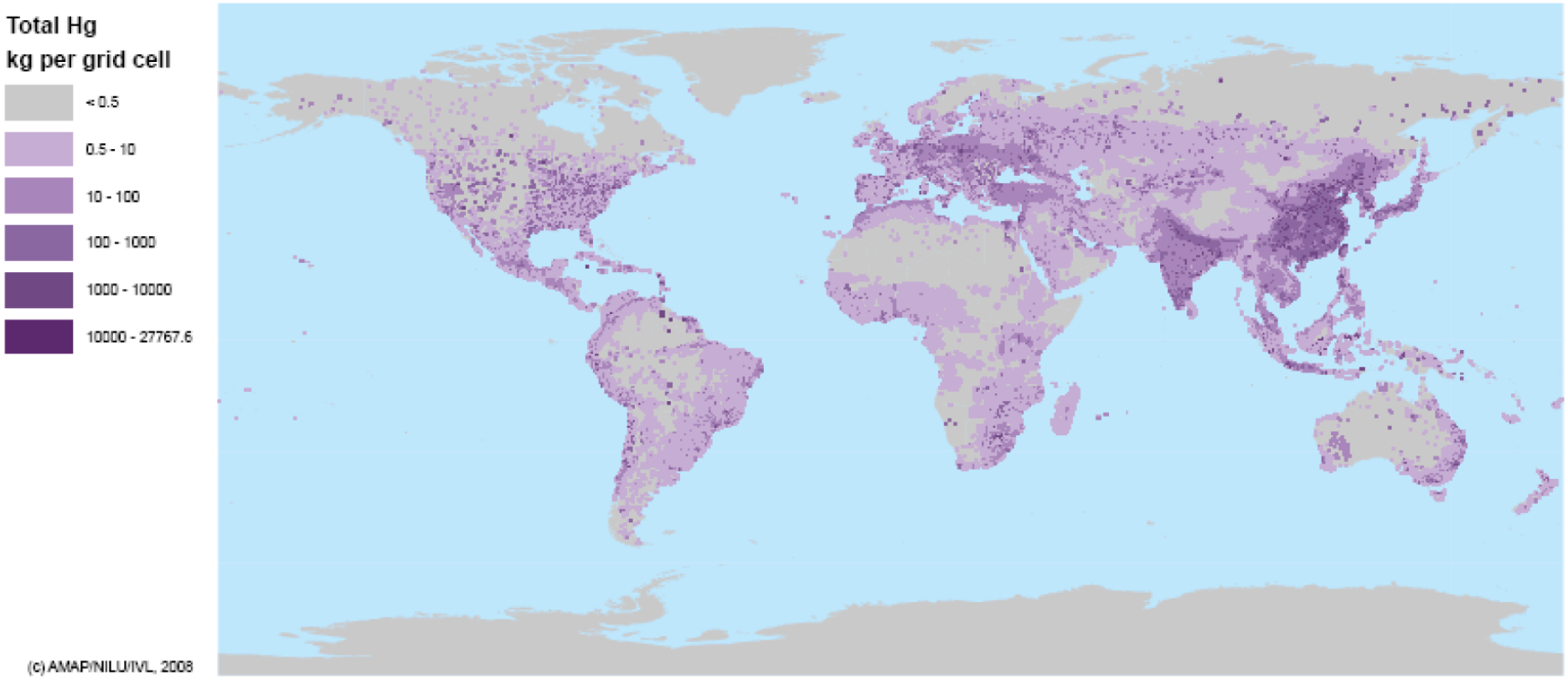
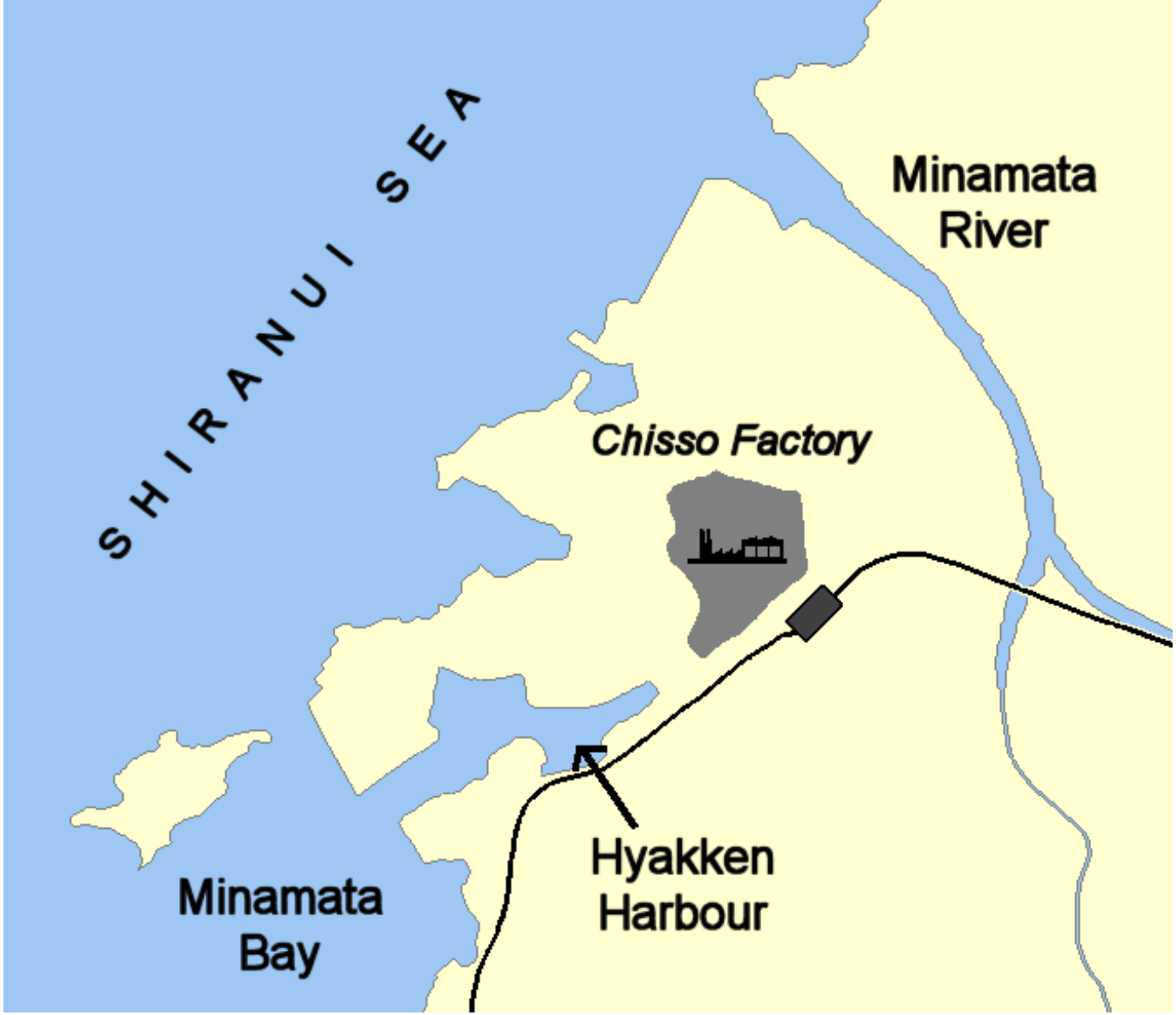


Figure 3.17. Global distribution of anthropogenic emissions of mercury in 2005.

Por quê é um problema?

http://www.japanfocus.org/data/553-2.jpg

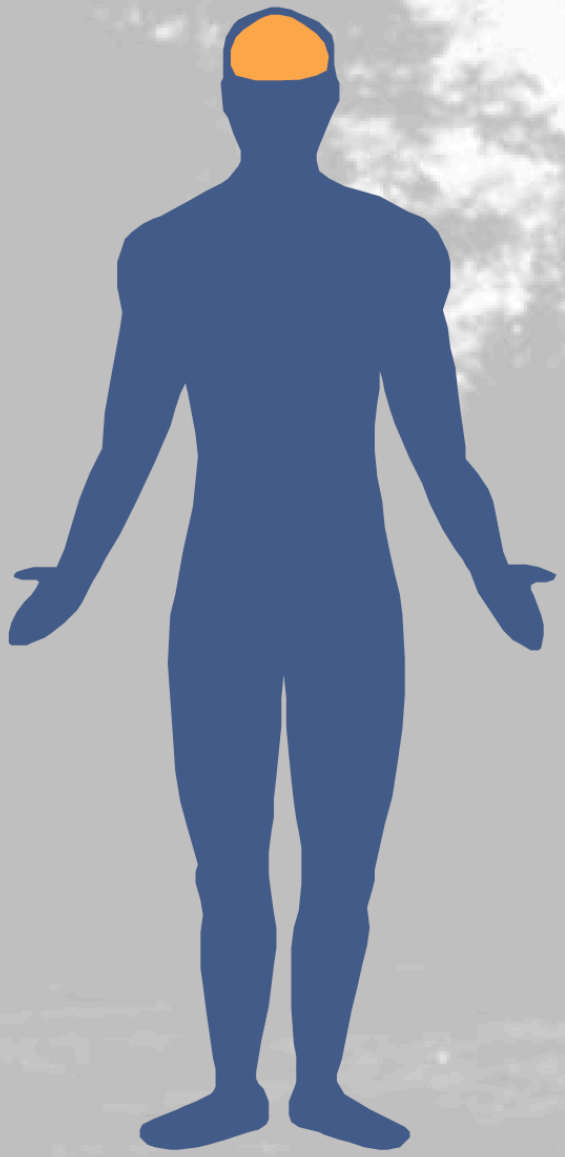


http://en.wikipedia.org/wiki/File:Minamata_map_illustrating_Chisso_factory_effluent_routes2.png

http://www.japanfocus.org/data/553-1.jpg

http://esromart.hubpages.com/hub/Tomoko-Uemura-in-Her-Bath-by-William-Eugene-Smith#slide5132520

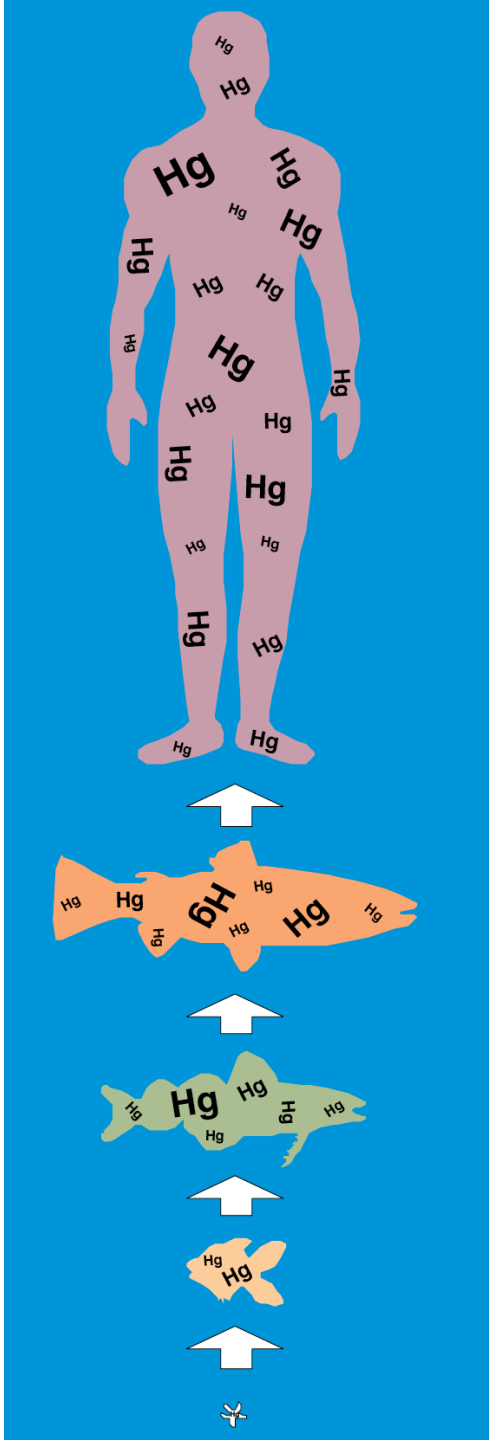
MERCURY
HEALTH EFFECTS



- Deteriorates nervous system
- Impairs hearing, speech, vision and gait
- Causes involuntary muscle movements
- Corrodes skin and mucous membranes
- Causes chewing and swallowing to become difficult

http://pubs.er.usgs.gov/publication/fs21695

Bioacumulação
e
Biomagnificação



http://pubs.er.usgs.gov/publication/fs21695

Mercúrio no meio ambiente

- A atmosfera é o caminho principal (6.000 ton/ano emitidas vs. 600 ton/ano transportadas por rios);
- Forma principal de emissão = GEM (gaseous elemental mercury = Hg^0);
- Pequenas quantidades de RGM (reactive gaseous mercury = mercúrio oxidado em compostos volatilizados);
- Pequenas quantidades de TPM (total particulate mercury = mercúrio oxidado associado a partículas)

Mercúrio no meio ambiente

- GEM = vida longa (0,5 a 1,5 anos) – poluente global;
- RGM e TPM = vida curta (horas a dias) – poluentes regionais.

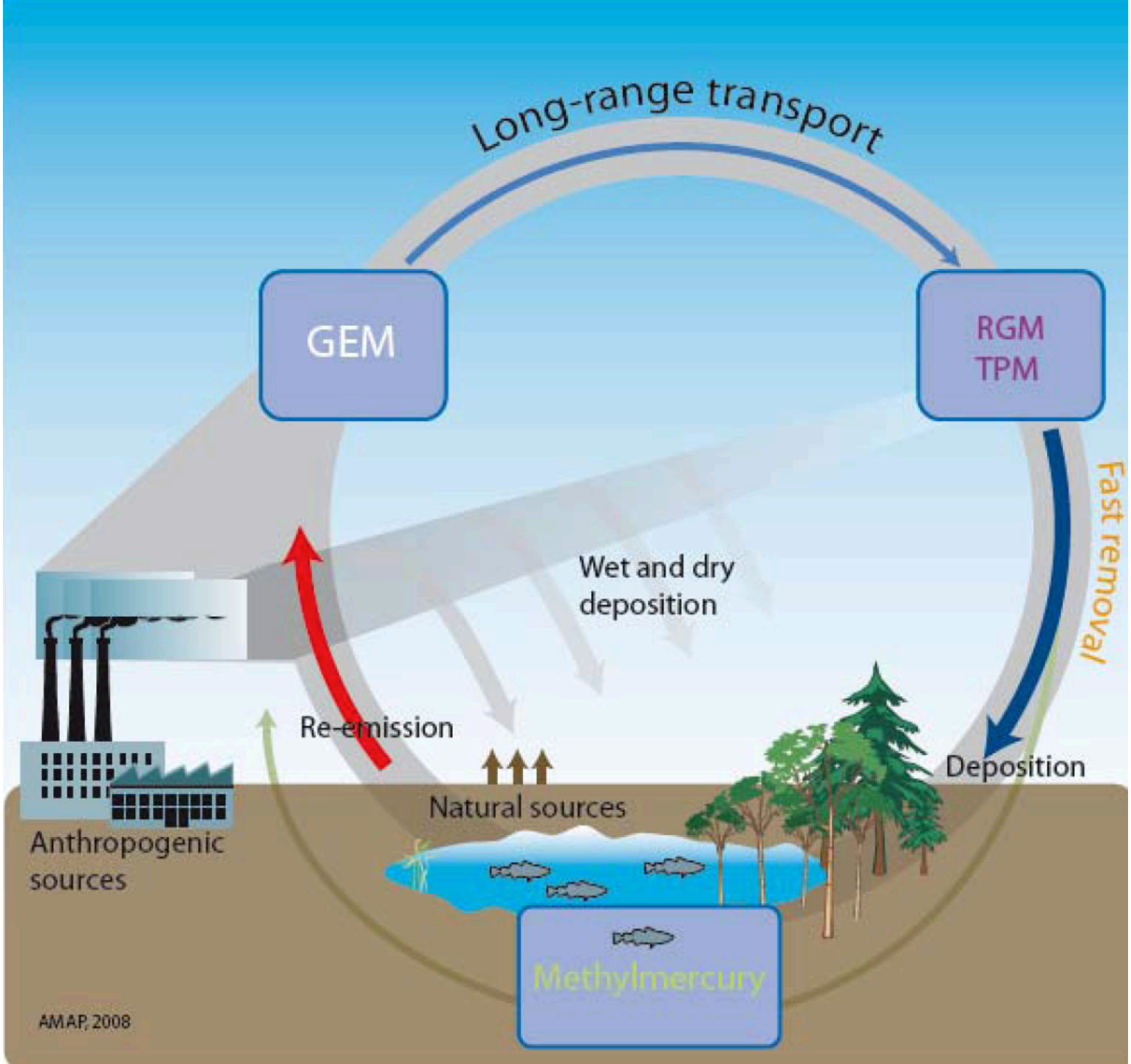
Mercúrio no meio ambiente

- GEM oxidado lentamente a RGM ou TPM;
- Oxidante = ozônio (leva a HgO_3);
- Oxidante = radical hidroxila (leva a HgOH – vida muito curta, menos importante);
- Oxidante = Bromo

$Hg^0(g) \rightarrow Hg^0(aq)$
$Hg^0(aq) + O_3(aq) \rightarrow Hg(II)(aq)$
$Hg(II)(aq) + soot/possible\ evaporation \rightarrow Hg(II)(p)$
$Hg(II)(aq) + SO_3^{-2}(aq) \rightarrow Hg^0(aq)$
(g) = gas phase molecule
(aq) = aqueous phase molecule
(p) = particulate phase molecule

Mercúrio no meio ambiente

- Redução fotolítica com HO_2 mantém [GEM]


Long-range transport
GEM
RGM
TPM
Fast removal
Wet and dry
deposition
Re-emission
Deposition
Natural sources
Anthropogenic
sources
Methylmercury
AMAP, 2008

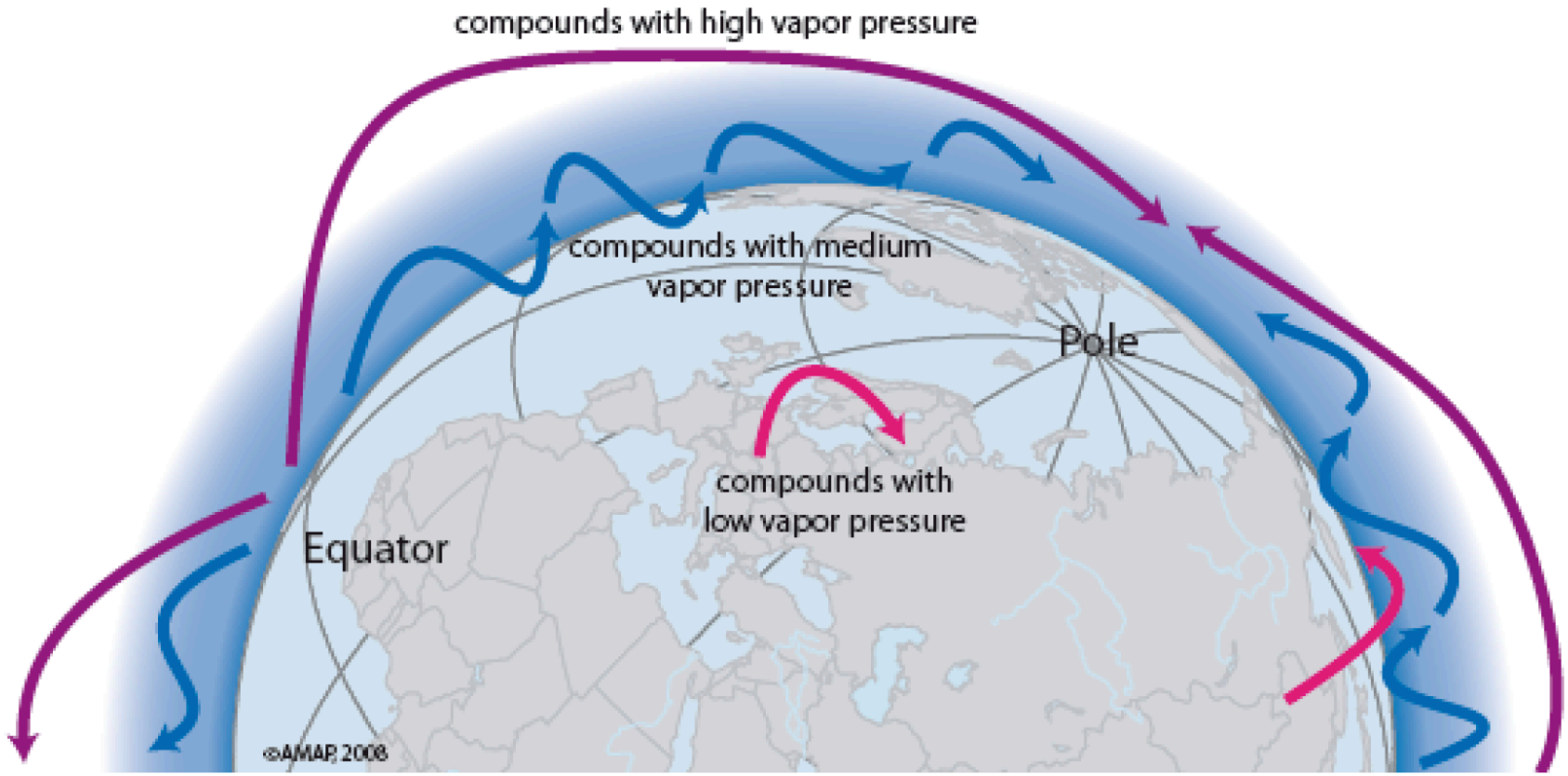
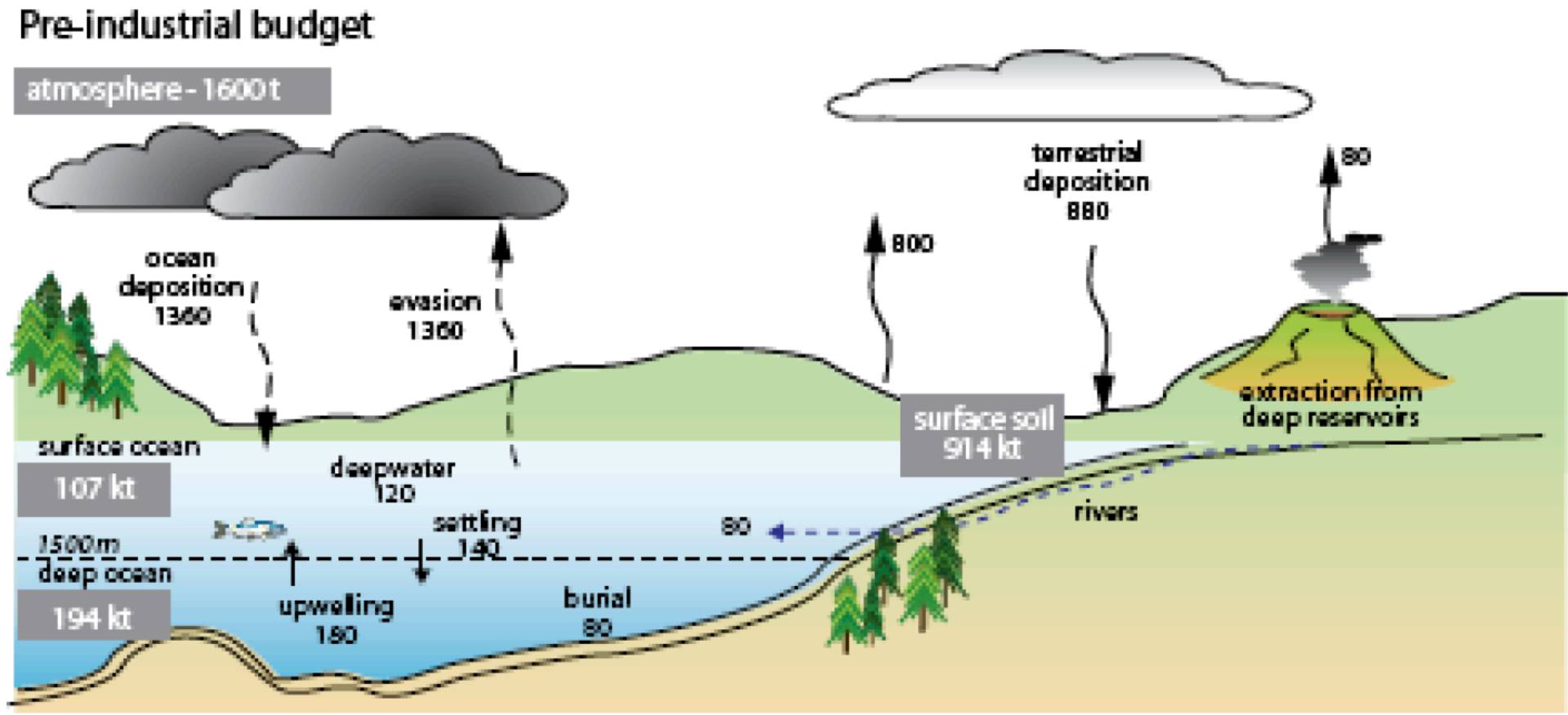
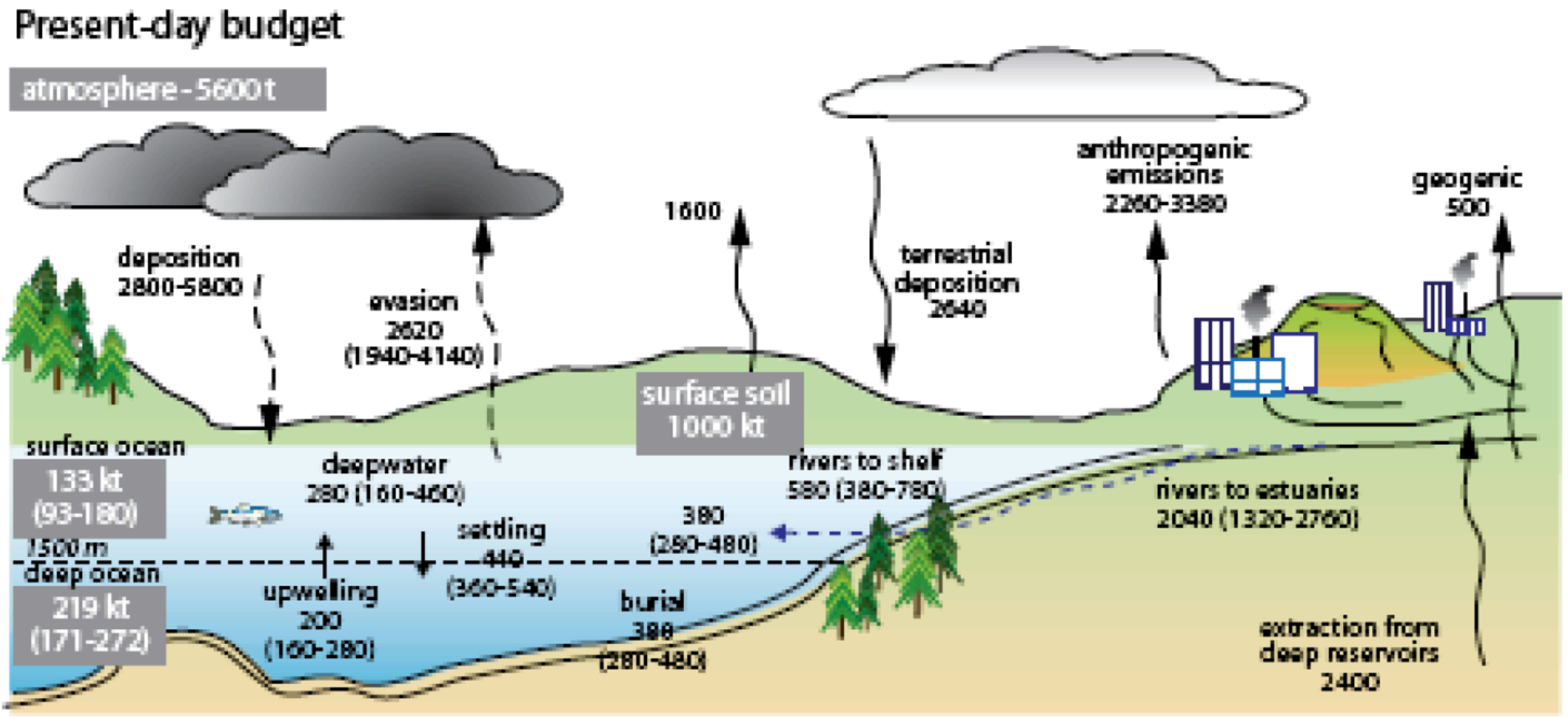
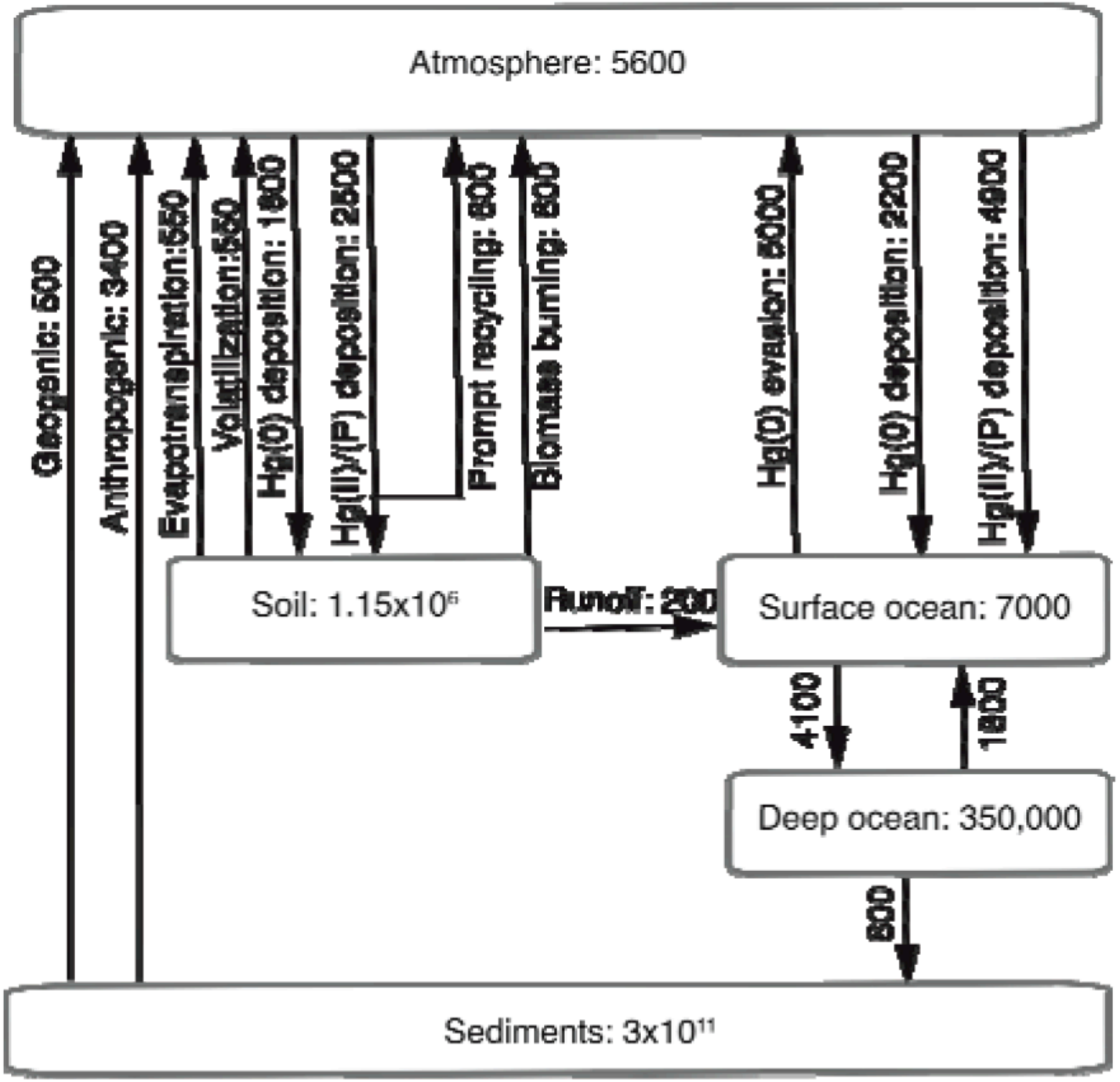


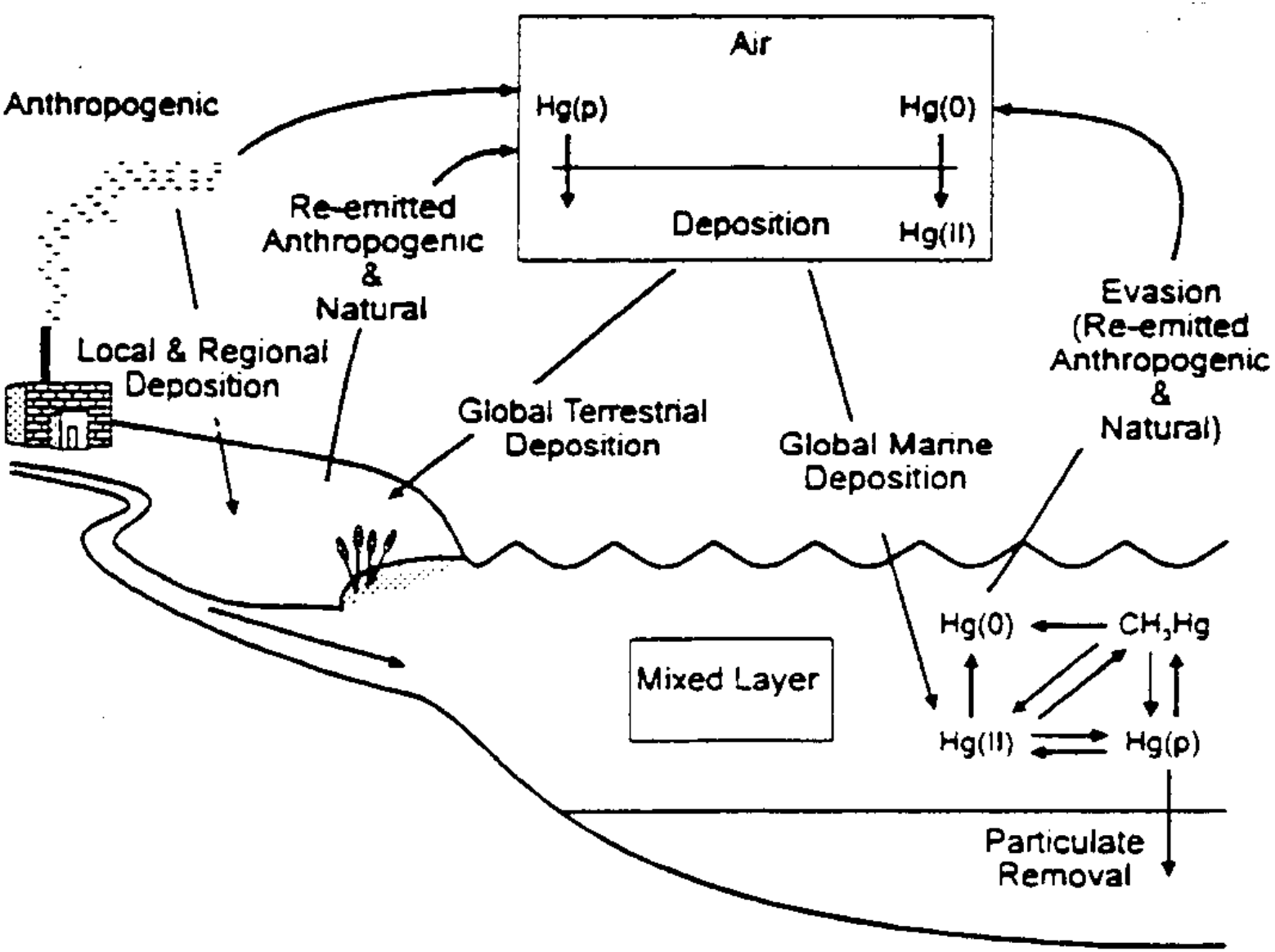
Figure 5.2. Schematic picture of long-range transport of persistent compounds directly or by the 'grasshopper' effect.


Pre-industrial budget
atmosphere - 1600 t
ocean deposition 1360
evasion 1360
800
terrestrial deposition 880
80
surface soil 914 kt
extraction from deep reservoirs
surface ocean
107 kt
deepwater 120
settling 140
80
rivers
1500m
deep ocean
194 kt
upwelling 180
burial 80


Present-day budget
atmosphere - 5600 t
deposition
2800-5800
evasion
2620
(1940-4140)
1600
terrestrial
deposition
2640
anthropogenic
emissions
2260-3380
geogenic
500
surface soil
1000 kt
surface ocean
133 kt
(93-180)
1500 m
deep ocean
219 kt
(171-272)
deepwater
280 (160-460)
settling
440
(360-540)
upwelling
200
(160-280)
burial
380
(280-480)
380
(280-480)
rivers to shelf
580 (380-780)
rivers to estuaries
2040 (1320-2760)
extraction from
deep reservoirs
2400

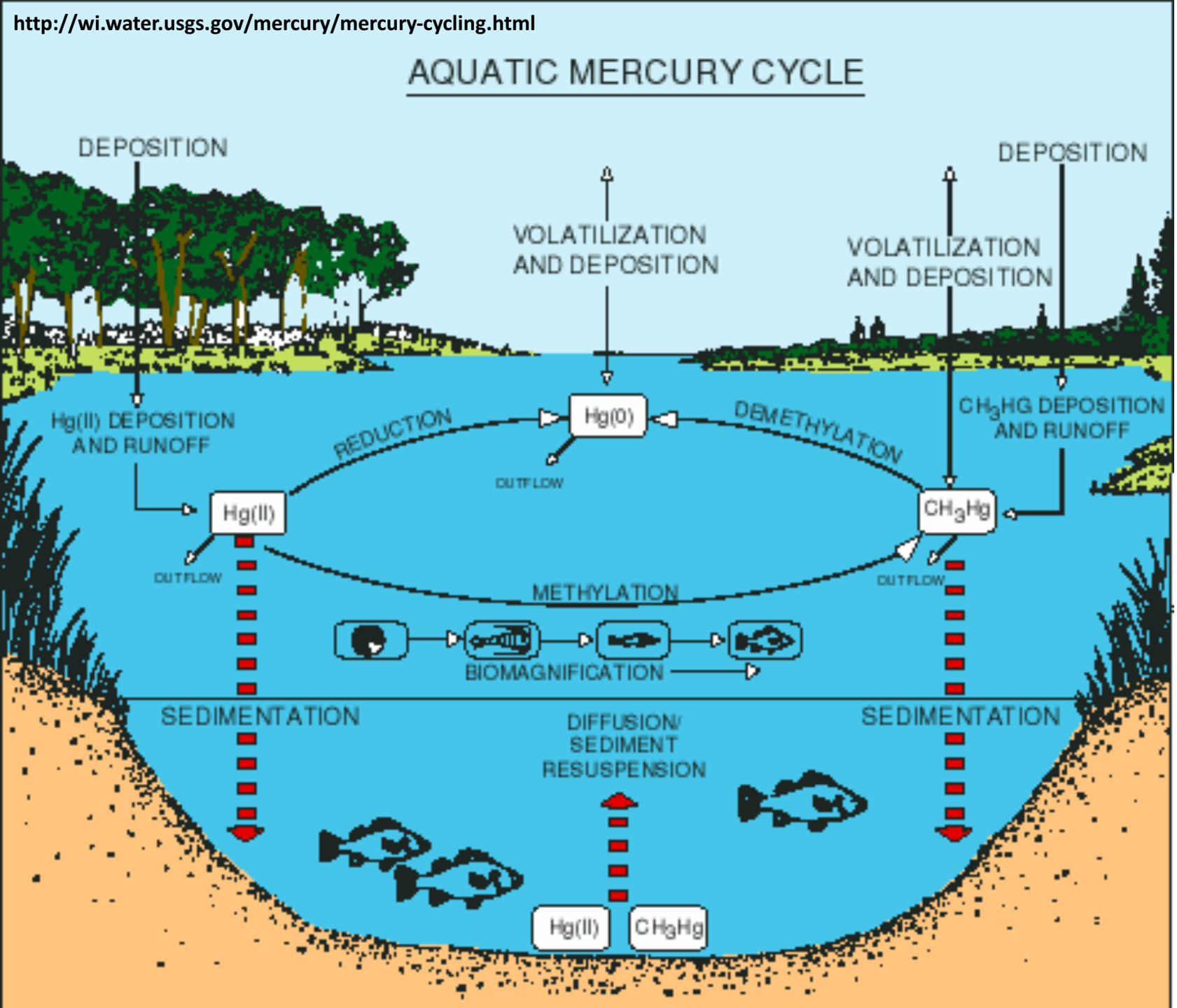

Atmosphere: 5600
Geogenic: 500
Anthropogenic: 3400
Evapotranspiration:550
Volatilization:550
Hg(0) deposition: 1600
Hg(II)/(P) deposition: 2500
Prompt recycling: 600
Biomass burning: 600
Hg(0) evasion: 5000
Hg(0) deposition: 2200
Hg(II)/(P) deposition: 4900
Soil: 1.15x10^6
Runoff: 200
Surface ocean: 7000
4100
1800
Deep ocean: 350,000
800
Sediments: 3x10^11

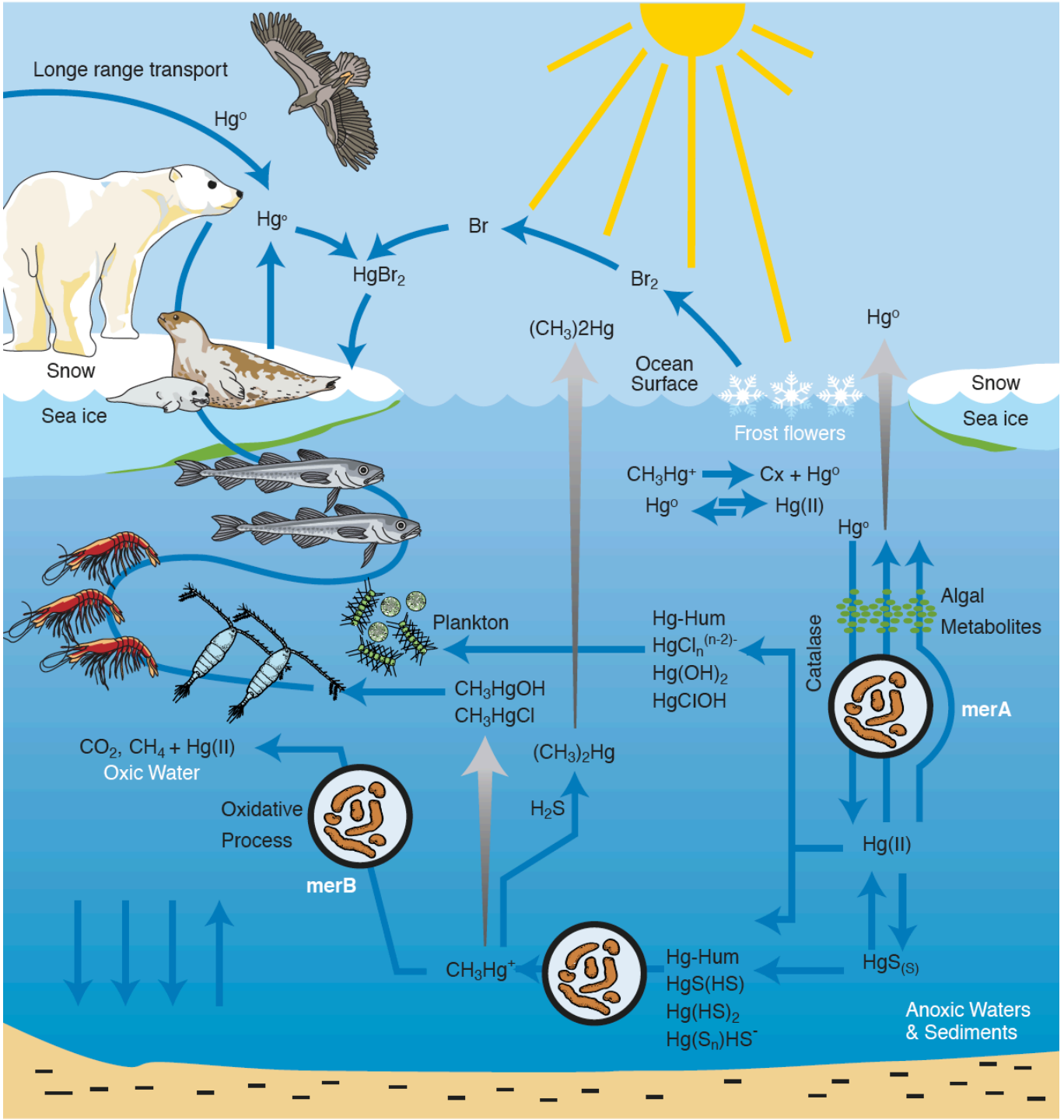
Ciclo do Mercúrio

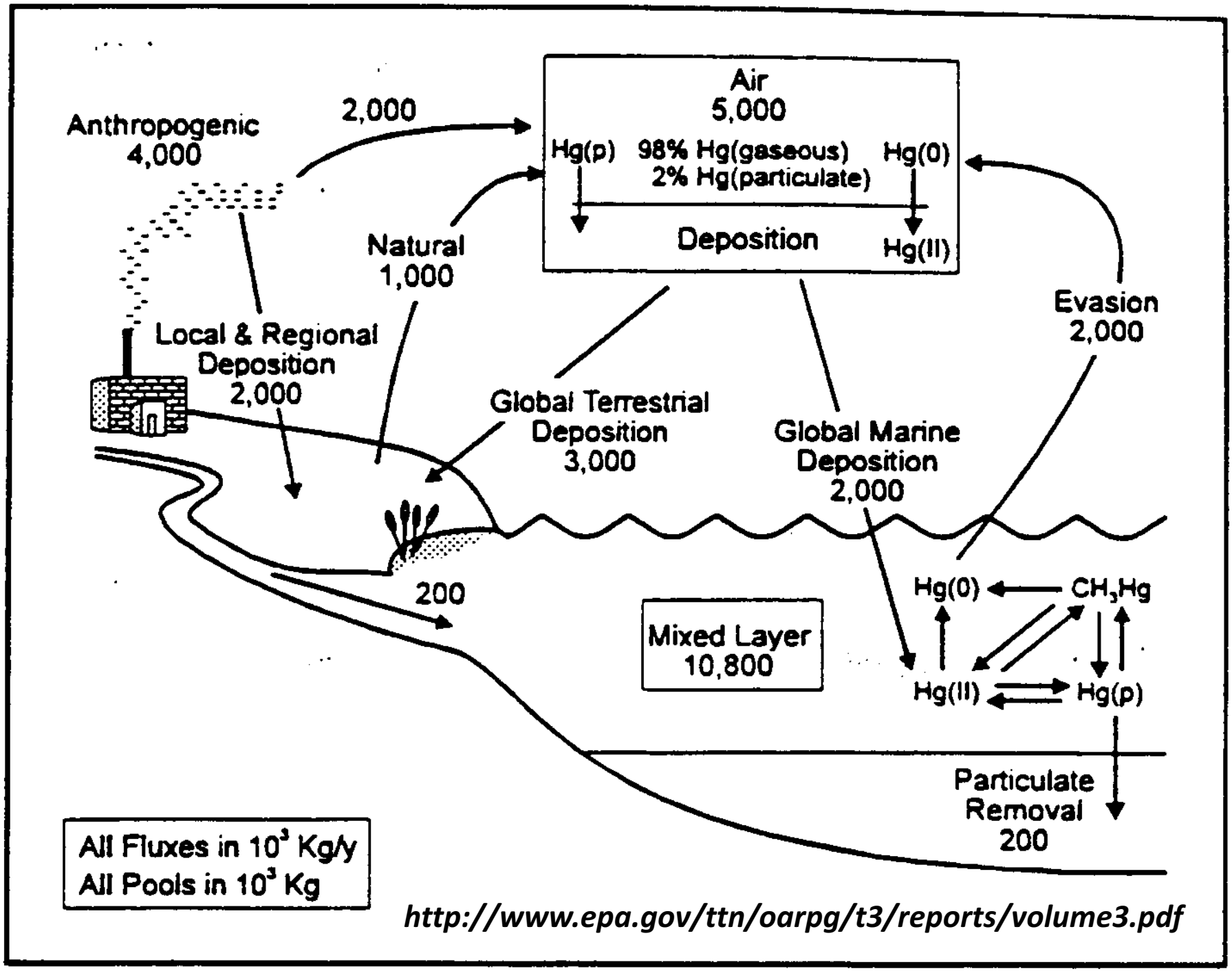


U.S. EPA: **Mercury Study Report to Congress - Volume III: Fate and Transport of Mercury in the Environment**
http://www.epa.gov/ttn/oarpg/t3/reports/volume3.pdf

http://wi.water.usgs.gov/mercury/mercury-cycling.html




Longe range transport
Hg°
Hg°
HgBr2
Br
Br2
(CH3)2Hg
Hg°
Ocean Surface
Snow
Sea ice
Frost flowers
Snow
Sea ice
CH3Hg+ → Cx + Hg°
Hg° ⇄ Hg(II)
Hg°
Algal Metabolites
Catalase
merA
Plankton
Hg-Hum
HgCln(n-2)-
Hg(OH)2
HgClOH
CH3HgOH
CH3HgCl
CO2, CH4 + Hg(II)
Oxic Water
(CH3)2Hg
H2S
Oxidative Process
merB
Hg(II)
CH3Hg+
Hg-Hum
HgS(HS)
Hg(HS)2
Hg(Sn)HS-
HgS(S)
Anoxic Waters & Sediments



http://www.epa.gov/ttn/oarpg/t3/reports/volume3.pdf

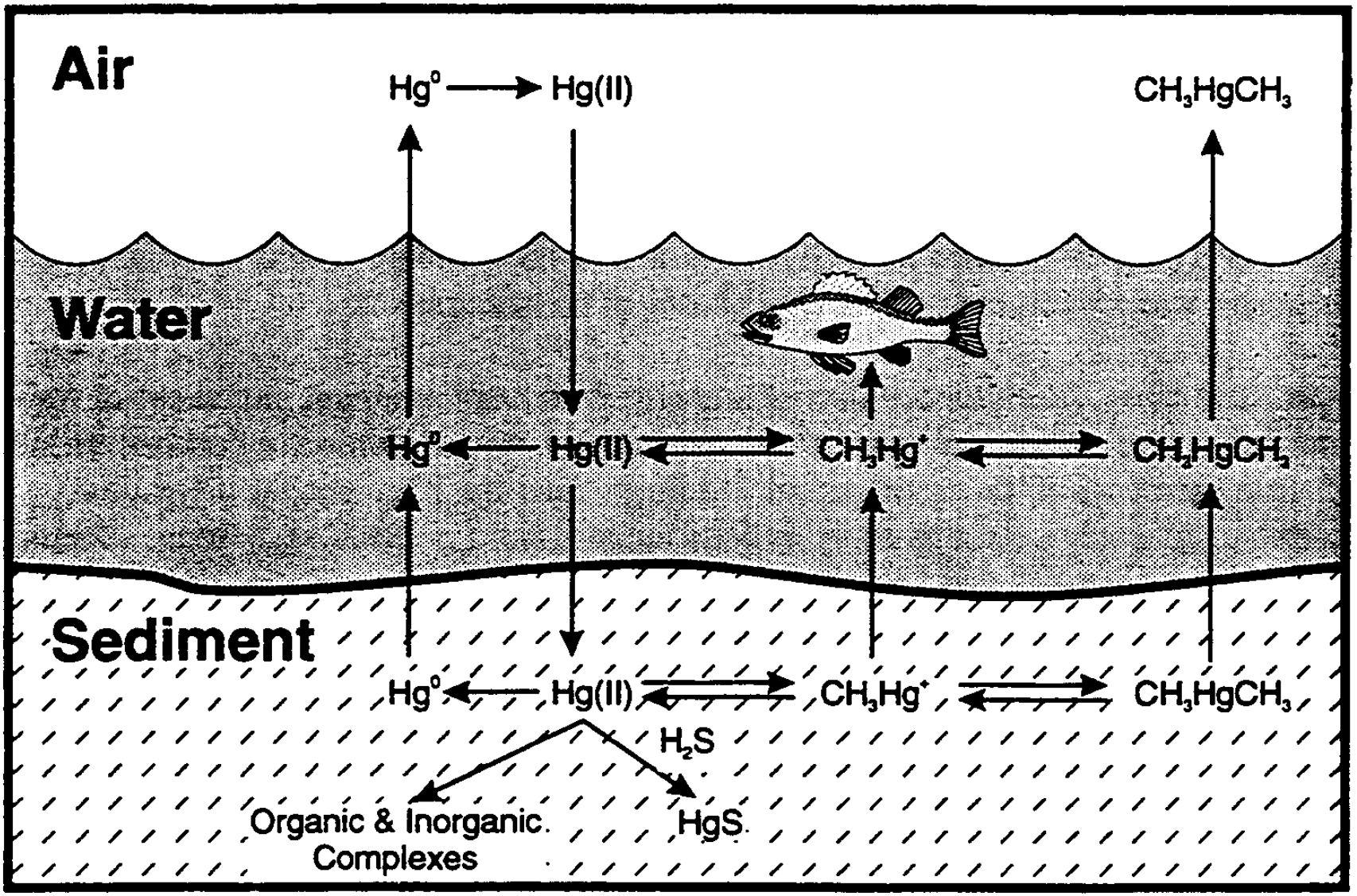
Química do Mercúrio

- 3 estados de oxidação: Hg^{0}, Hg_{2}^{+2}, Hg^{+2};
- Inorgânico ($HgCl_2$, $Hg(OH)_2$, HgS);
- Orgânico (metilmercúrio, cloreto de metilmercúrio, hidróxido de metilmercúrio)

Metilmercúrio

- Todas formas de mercúrio podem ser convertidas nele;
- Bioacumula e biomagnifica em cadeias alimentares aquáticas;
- Forma mais tóxica do mercúrio.

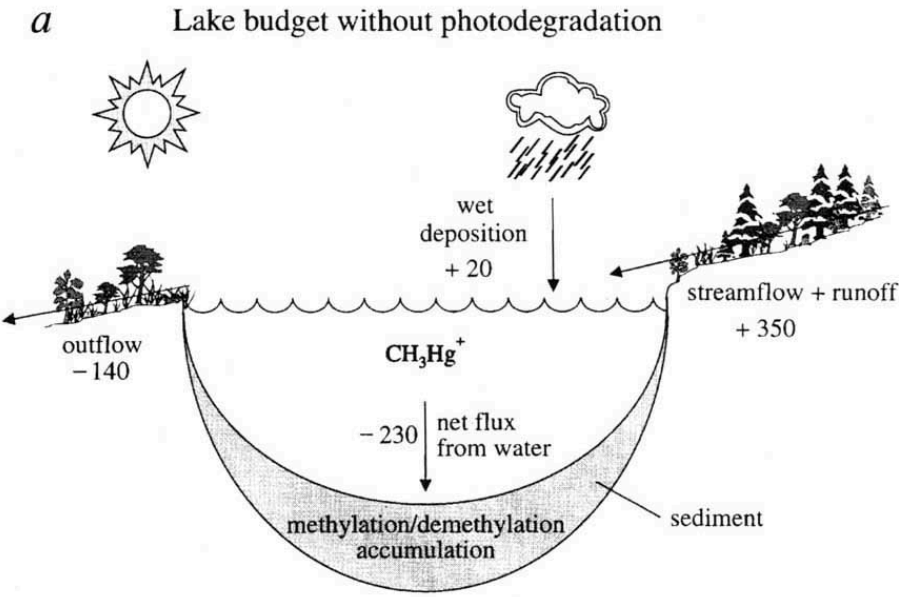
Figure 2-1
Cycling of Mercury in Freshwater Lakes (adapted from Winfrey and Rudd, 1990)

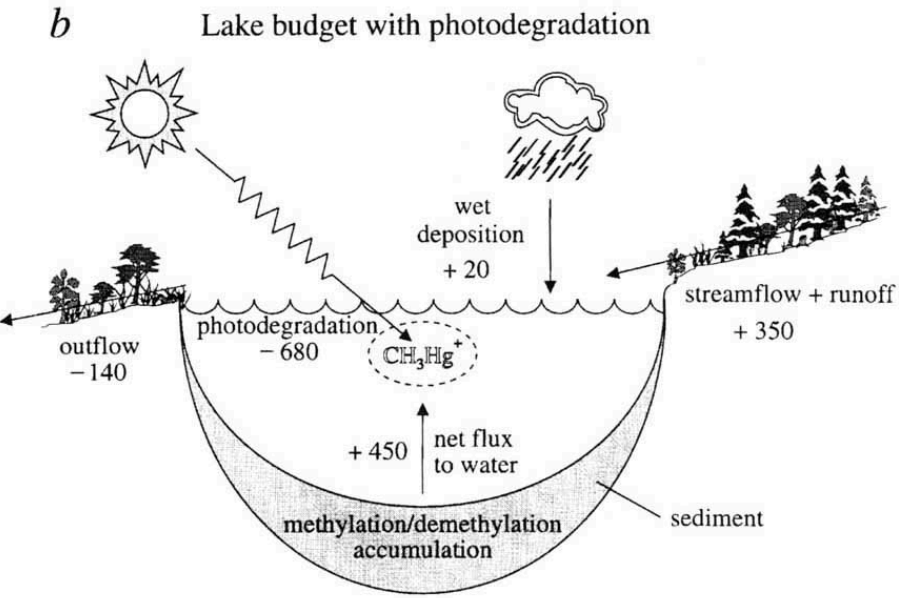


http://www.epa.gov/ttn/oarpg/t3/reports/volume6.pdf

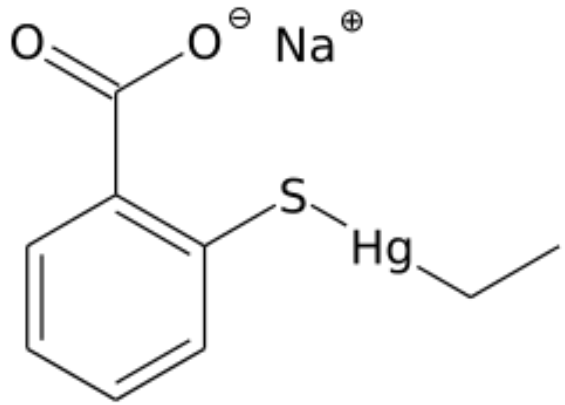
Mercúrio em águas superficiais

- Hg^{0} na superfície pode ser oxidado a Hg^{+2} ou volatilizado;
- Hg^{+2} pode ser metilado nos sedimentos ou na coluna de água formando metilmercúrio (via bactérias);
- Metilmercúrio pode ser alquilado a dimetilmercúrio;
- $Hg^{+}2$ e metilmercúrio podem formar complexos orgânicos ou inorgânicos (sedimento e material particulado).





http://www.nature.com/nature/journal/v380/n6576/pdf/380694a0.pdf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Convenção de Minamata

- Banimento de novas minas de mercúrio
- Abandono das atuais (15 anos);
- Medidas de controle de emissões gasosas;
- Regulação internacional de mineração artesanal de ouro;
- Banimento de fabricação e uso de produtos contendo mercúrio (2020) – lâmpadas, cosméticos, baterias, termômetros;
- Cloro-álcali (até 2025);
- Acetaldeído (até 2018);
- Uso restrito em produção de cloreto de vinila.