

# CHEMIE ŽIVOTNÍHO PROSTŘEDÍ IV

## Vybrané typy environmentálních polutantů

(01\_03)

Těžké kovy (HMs) – rtuť

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# Rtut' (Hg)

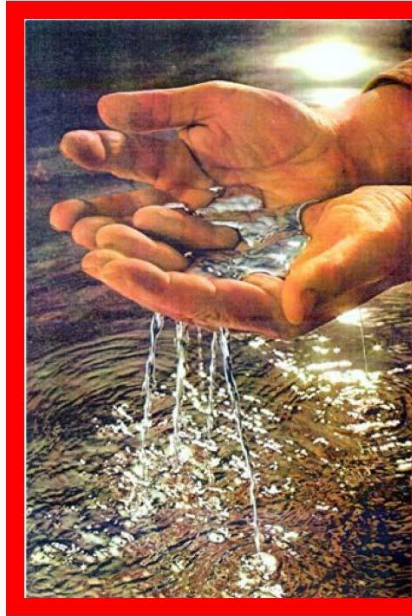
II.b podskupina periodické soustavy prvků, **bílostříbrný tekutý kov:**

- ↪ nejnižší bod tání a varu ze všech kovů (-38,87 °C; 358,53 °C)
- ↪ dobrá schopnost rozpouštět kovy a tvořit slitiny (amalgámy)
- ↪ vystupuje v oxidačním stupni II i I
- ↪ významnou skupinu tvoří organokovové sloučeniny, velmi toxická

# Rtut'



Heimaey, Iceland



Elemental Hg, hydrothermal spreading centre, New Zealand

# Rtut'

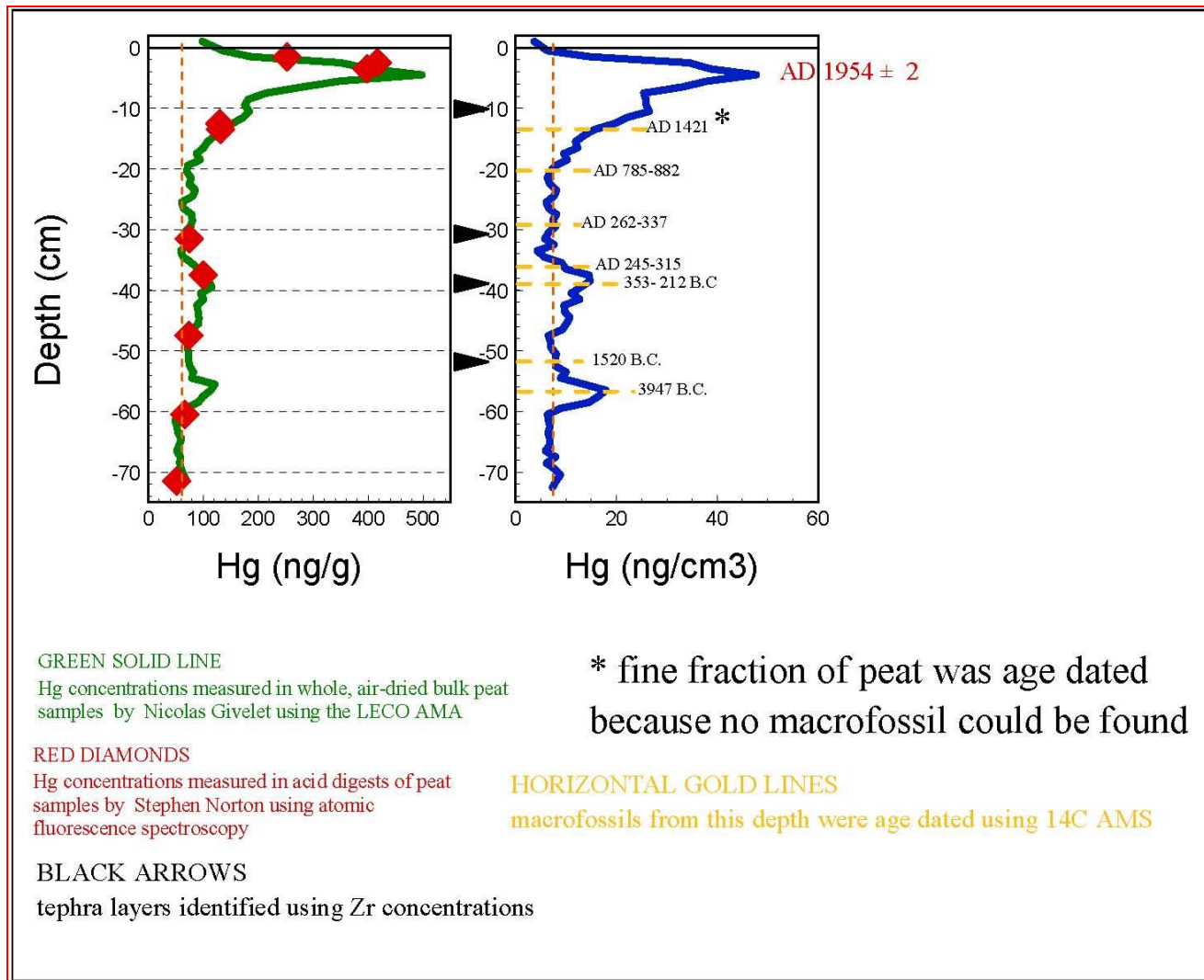


Myrarnar, Faroe Islands



Přírodní Hg ?  
Anthropogenní Hg ?

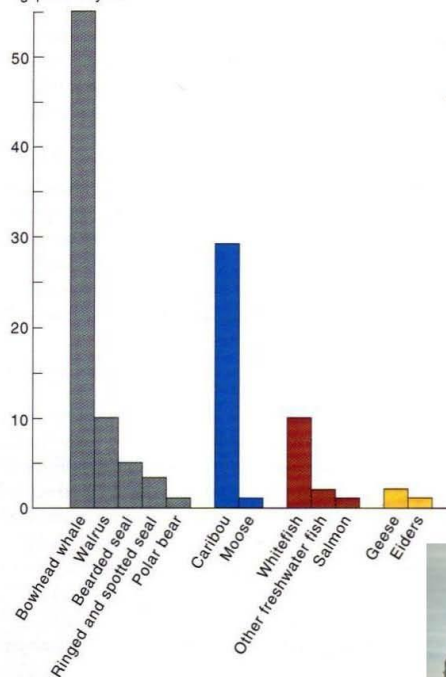
# Koncentrační profil Hg, Faroe Islands



# Rtut' v Arktice

“Up to half of Inuit women in the Canadian Arctic are consuming toxic pollutants at levels exceeding international safety limits. The fish, seals, and whales they eat are contaminated with pesticides, heavy metals, and PCBs from the developed world ”  
Arctic Monitoring and Assessment Program (AMAP)

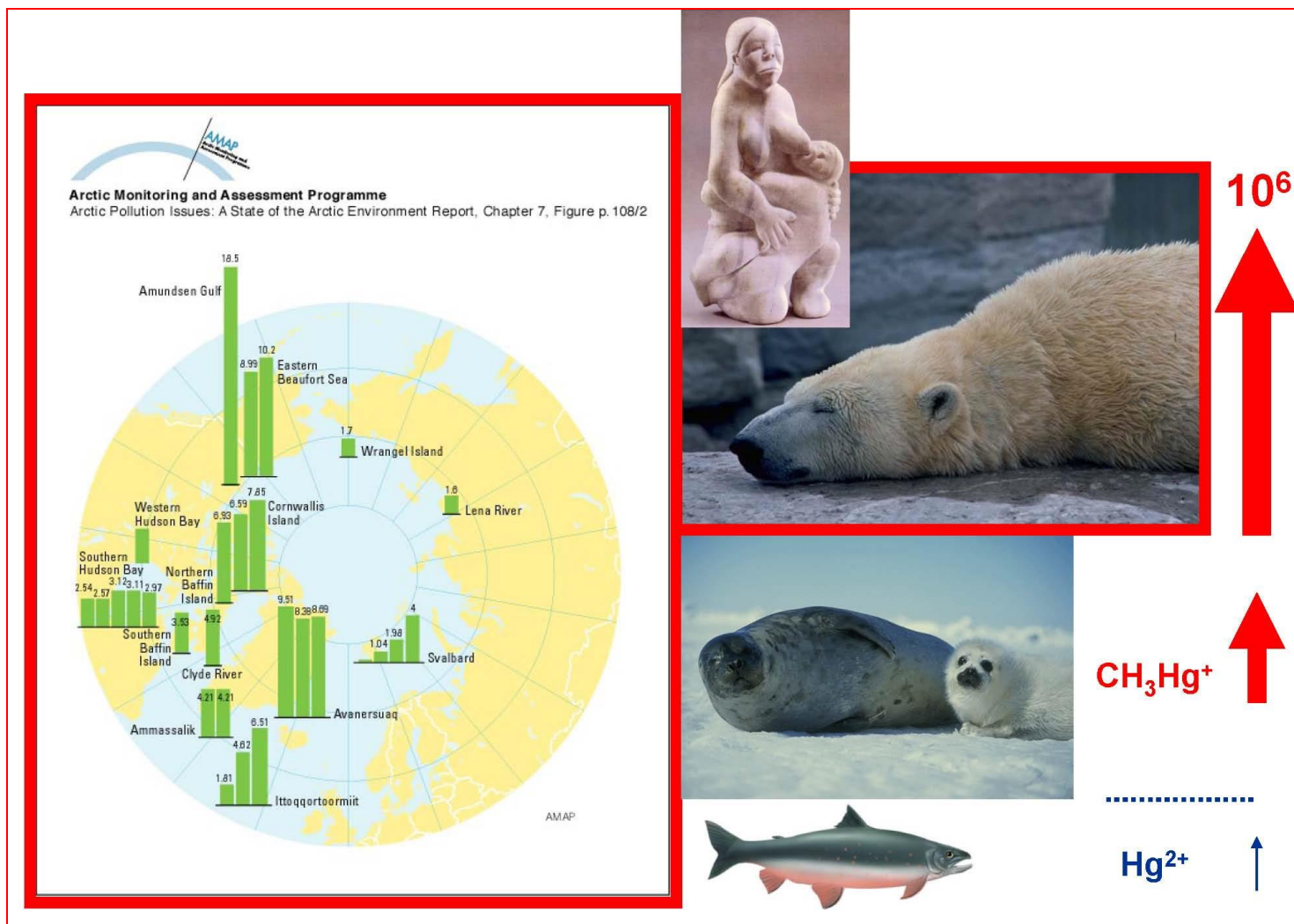
Composition of subsistence production, Inupiat households, Barrow, Alaska, kg/person/year



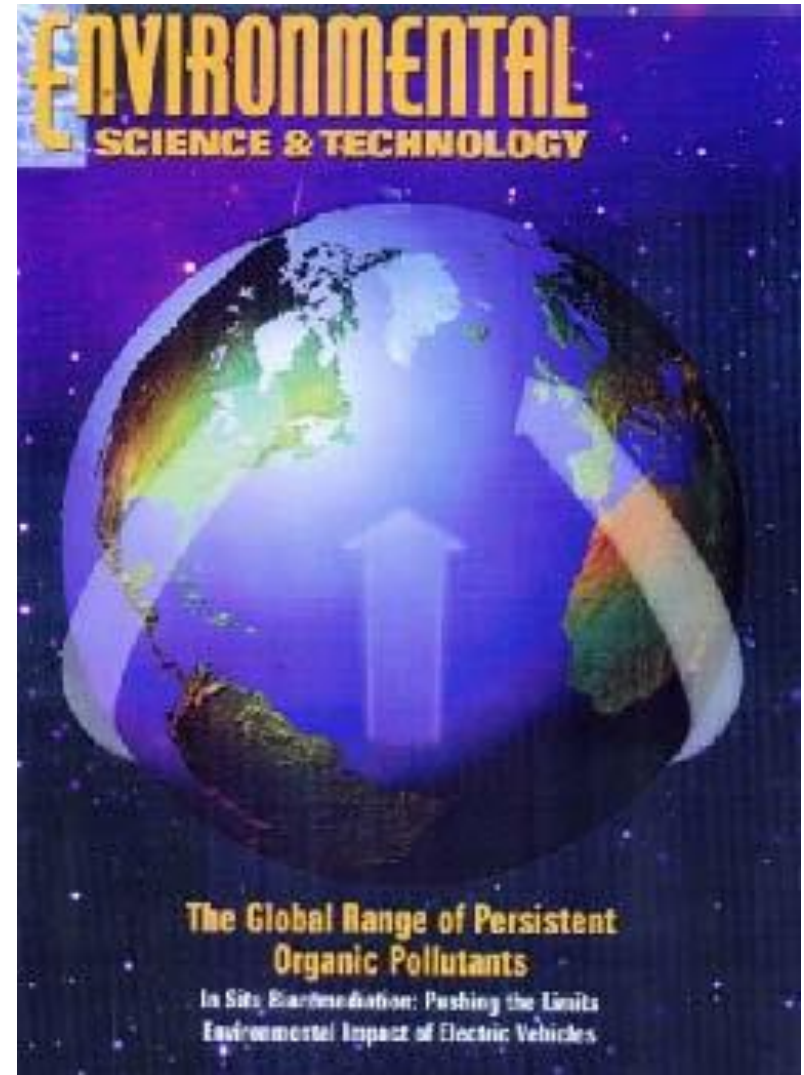
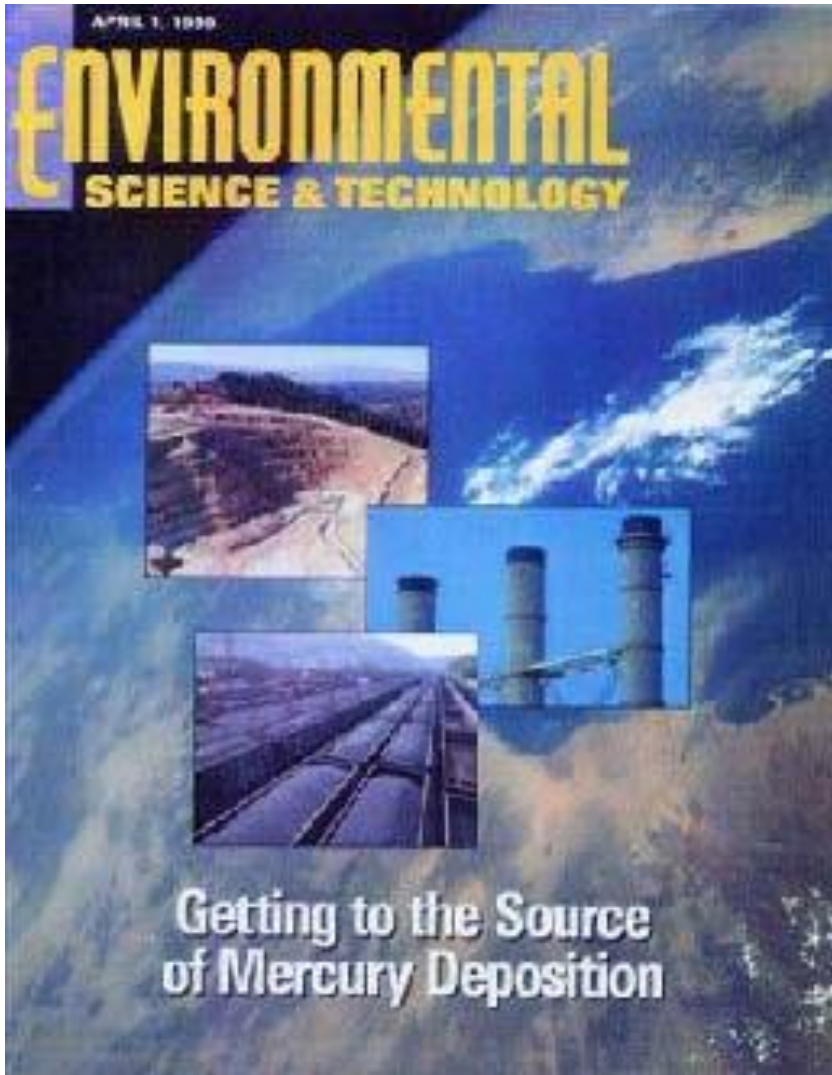
55  
Peoples of the North



# Rtut' v Arktice



# Globální výskyt Hg



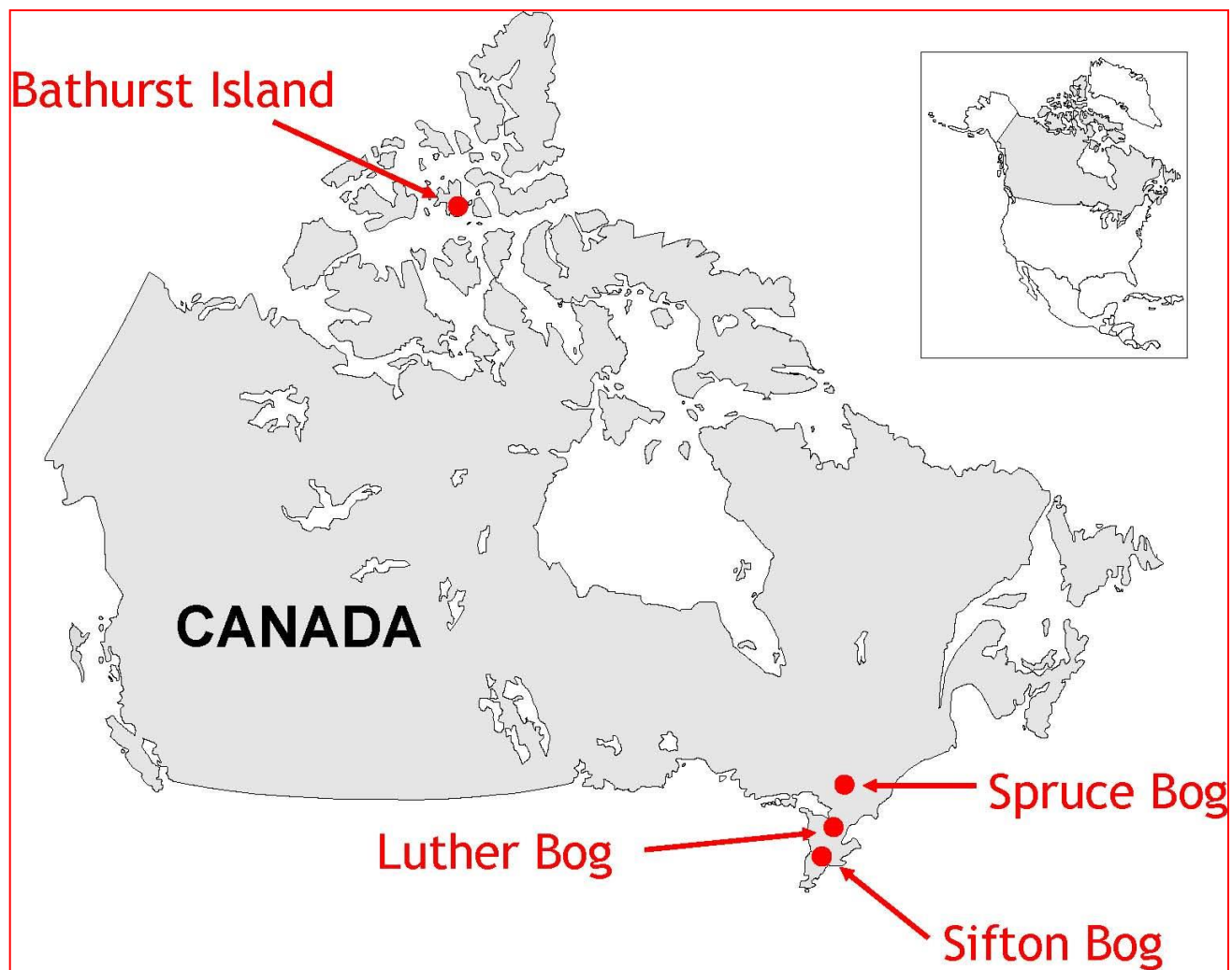


# Nedostatek časových trendů

“The most significant gap in our knowledge at the present time is the lack of temporal trend data for most contaminants”



# Nedostatek časových trendů



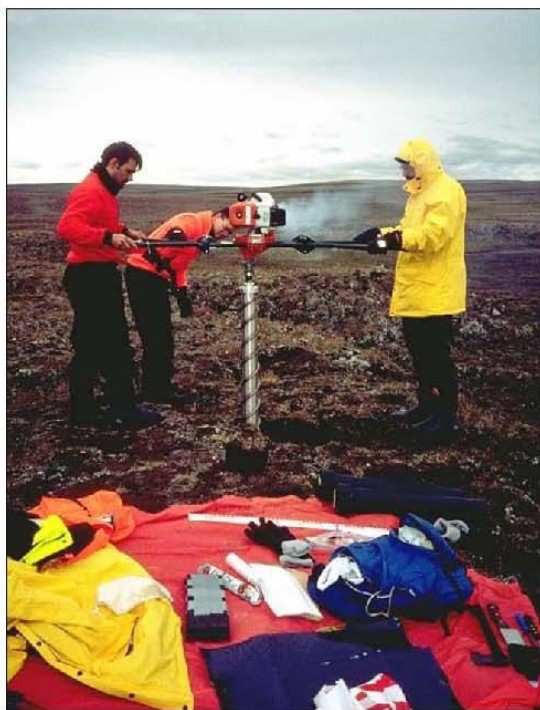
# Nedostatek časových trendů



*Bathurst Island, Nunavut (75 °N)*



Bracebridge Inlet Sampling site  
July 2000



# Nedostatek časových trendů



Bathurst Island,  
Nunavut,  
Canada,  
Summer 2000

Peat accumulation from  
4000 B.C. to 1000 A.D.

**Natural rates of atmospheric Hg  
accumulation**

**Arctic =**

**Switzerland =**

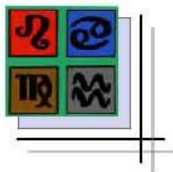
**Faroe Islands =**

**Southern Greenland =**

**southern Ontario = 1  $\mu\text{g}/\text{m}^2/\text{yr}$**



# Prostorové trendy

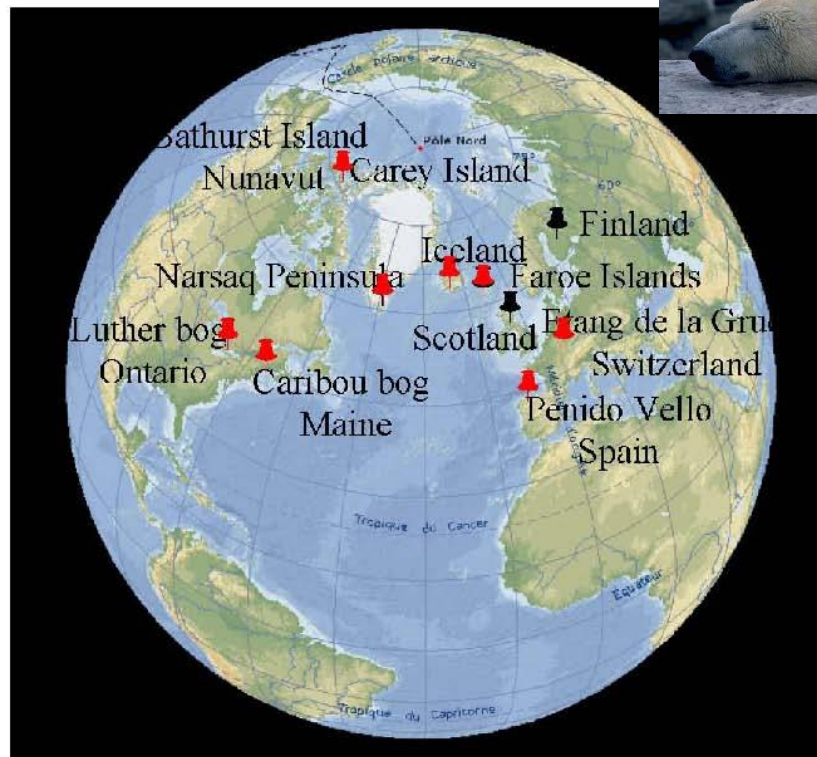


## Comparison with other locations



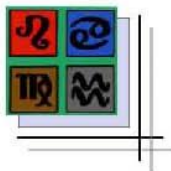
Natural background net  
deposition rate:

$0.5 - 1.5 \mu\text{g Hg m}^{-2} \text{ yr}^{-1}$



⇒ No evidence that the Arctic was an important natural sink for mercury in the global cycle

# Globální cyklus Hg



## *Implication for the global Hg cycle*

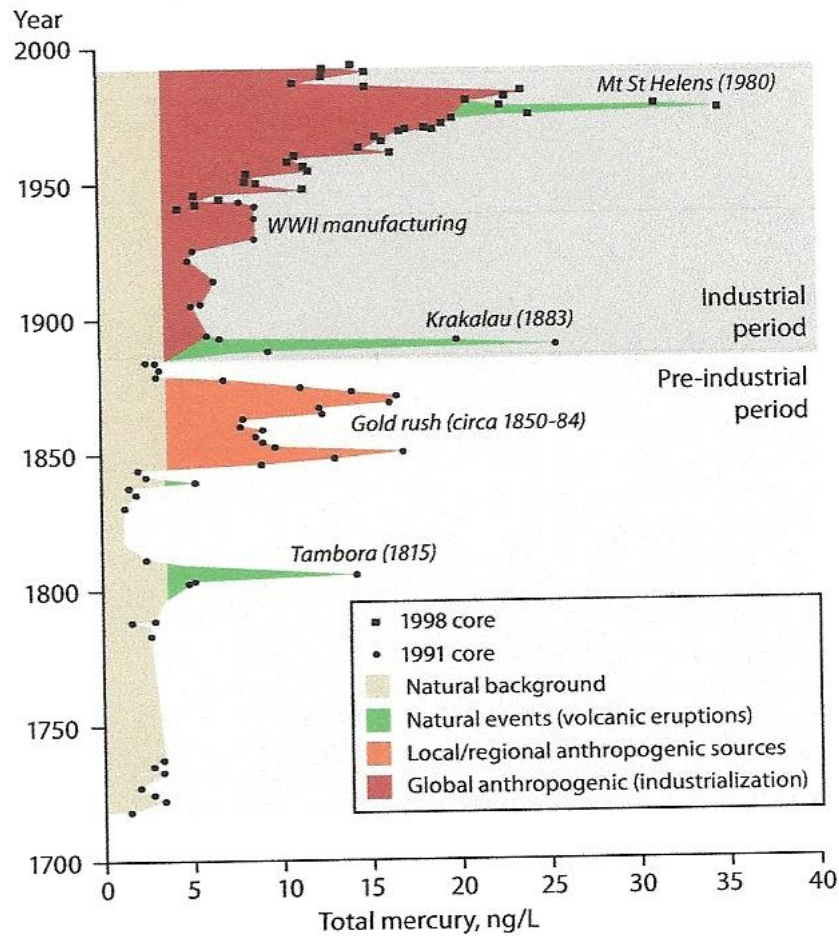
Estimated pre-anthropogenic global atmospheric mercury  
Flux: 450 t/yr (peat records)

Estimated pre-anthropogenic global atmospheric mercury  
Flux: 2500 t/yr (Nriagu, 1989)

Estimated global anthropogenic atmospheric mercury  
Flux: 1900 t/yr (Pacyna & Pacyna, 2002)

⇒ True impact of anthropogenic emissions of mercury  
to global atmosphere underestimated by a factor 5?

# Ice core Hg record, Wyoming, USA



*Ice core record of deposition from Wyoming, USA. The elevated levels associated with the 1850-84 US gold rush probably reflect local/regional sources rather than a global signature. Increasing environmental levels of mercury associated with industrialization, however, are found in environmental archives like this ice core around the globe.*

# Examples of CZ MoE development projects solving mercury and other heavy metal contamination

- ↪ **Mongolia:** Assessment of Environmental Risks of Mercury Pollution During the Mining of Gold Deposits in the Selenge River Basin
- ↪ GEOMIN Company; Implementation period: 2006-2008; Total budget: 9,820 mil.CZK (approx. 509 000 USD)





# Visible metallic mercury in alluvial sediments



**Mongolia: Technical and Technological Support for Ecological Burden Remediation  
Caused by Illegal Mining in Central Part of Mongolia, GEOMIN Company;**

# Zambia - Detail of the surface of the main tailings pond of chemical wastes at the Bwana Mkubwa Locality

Incrustations and efflorescence of toxic salts (light gray) originating through evaporation are wind blown over adjacent areas during the dry season.



# Hlavní sloučeniny Hg

Oxidační stav	Sloučenina	Zdroj
Hg (0)		Přírodní
Hg (I)	$\text{Hg}_2\text{Cl}_2$	Průmyslové
Hg (II)	$\text{Hg}(\text{OH})_2$ $\text{HgCl}_2$ , $\text{HgCl}^+$ , $\text{HgCl}_3^-$ , $\text{HgCl}_4^{2-}$ , $\text{HgOHCl}$ $\text{HgS}$	Přírodní/Průmyslové
$\text{R}_2 - \text{Hg}$ (II)	Chlorid monomethylrtuťnatý ( $\text{CH}_3\text{HgCl}$ ) Fenylmethylrtuť ( $\text{PhCH}_3\text{Hg}$ ) Dimethylrtuť ( $\text{CH}_3$ ) <sub>2</sub> Hg	Přírodní <i>Vznikající biomethylací působením mikroorganismů v půdách a sedimentech</i>

# Mercury and human health

## Mercury and human health

### GENERAL EXPOSURE



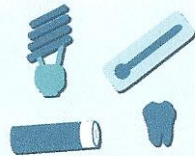
Large predatory fish



Vegetables from contaminated soils



Cosmetics, Soaps

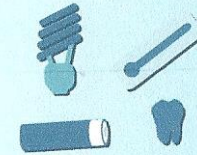


Use and damage of products containing mercury (e.g. compact fluorescent lamps, batteries, medical devices)



Waste

### OCCUPATIONAL EXPOSURE



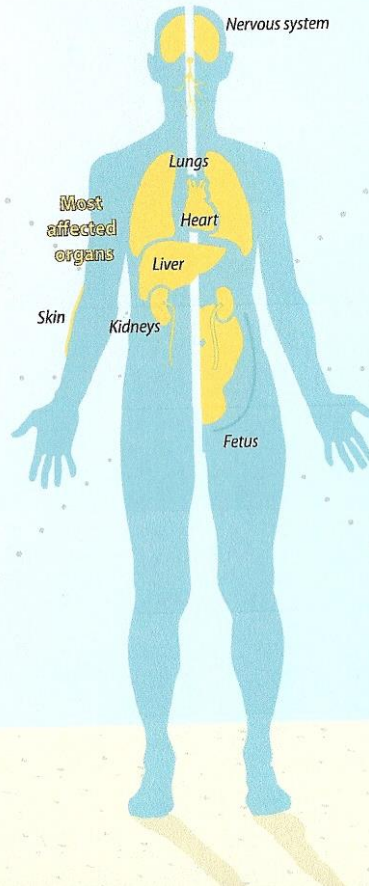
Manufacturing of products containing mercury (e.g. compact fluorescent lamps, batteries, medical devices)



Artisanal and small-scale gold mining



Industry  
(e.g. Chlor-alkali industry, cement production, metal production)



# Rtut' (Hg) – vlastnosti a toxické účinky

Do organismu vstupuje **dýchacím a zažívacím** traktem a přes kůži.

Elementární rtut' a anorganické sloučeniny se ve dvojmocné formě kumulují v ledvinách, v mozku se elementární rtut' hromadí 10-krát více než anorganická.

**Rtut' je schopna proniknout přes placentu** a zvyšovat expozici plodu - u chronických zátěží mateřského organismu plod vychytává rtut' prostupující placentou a akumuluje ji především v mozku a v červených krvinkách (ty dokáží akumulovat o 30% rtuti víc než erytrocyty matky).

# Rtut' (Hg) – vlastnosti a toxické účinky

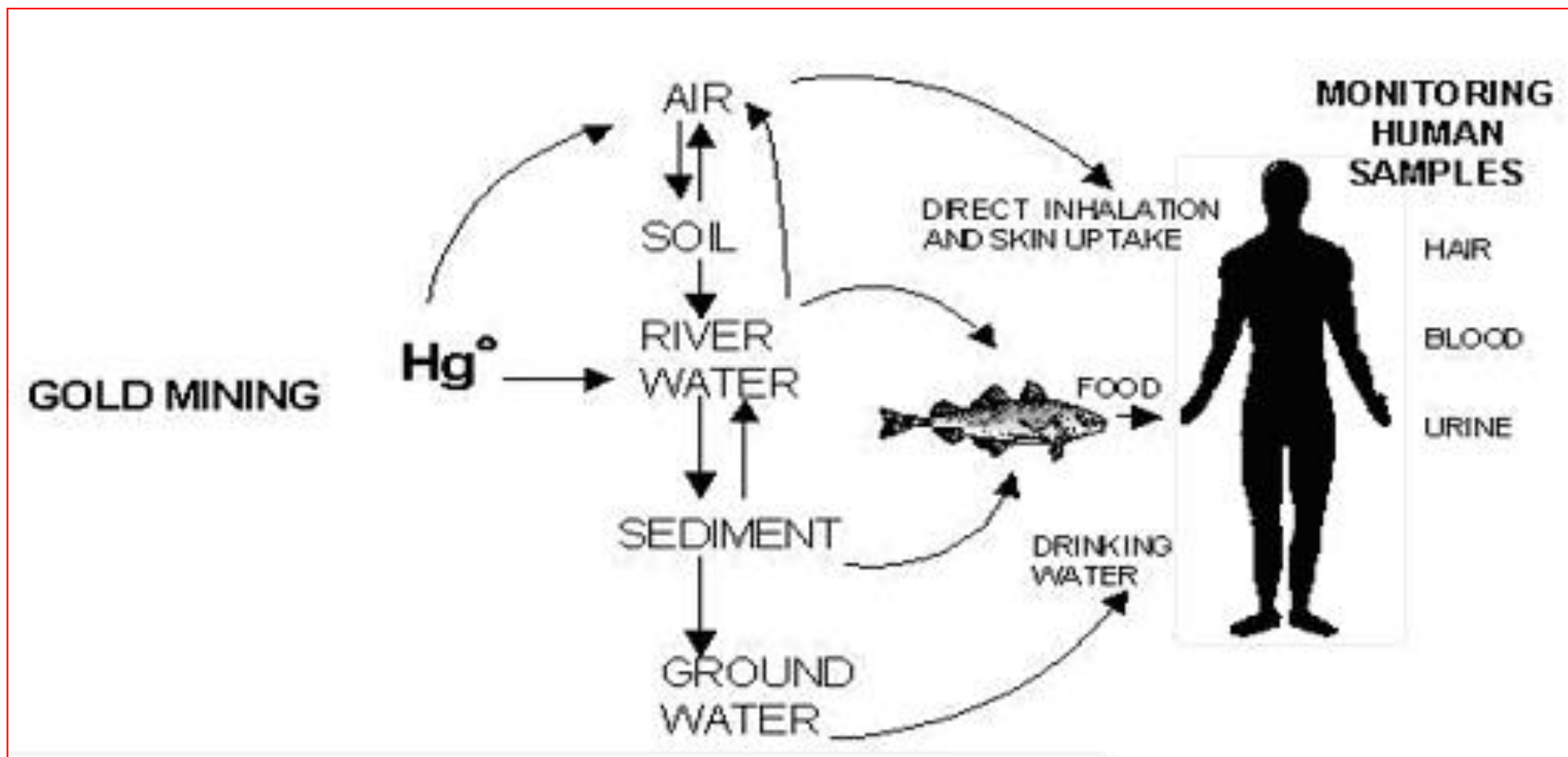
Z těla se vylučuje především močí a stolicí.

Játra rychle kumulují rtut' a vylučují ji žlučí do střev.

Jako dimethylrtut' je z 1/3 vyloučena z organismu a ze 2/3 vstřebána zpět do krve; v játrech se z dimethylrtuti částečně uvolňuje rtut', která je opět žlučí vylučována do střev a je vázána na bílkovinný nosič.

**Biologický poločas** u člověka je u elementární rtuti 58 dní, u anorganických sloučenin 30 - 60 dní a u dimethylrtuti 70 - 74 dní.

# Vstupy Hg do lidského organismu



# Toxikologické vlastnosti Hg

<b>Akutní účinky na lidské zdraví</b>	Inhalace elementární Hg: bezprostřední poškození sliznice úst; stomatitis; zvracení; dyspnea, anemia; smrt.
<b>Chronické účinky na lidské zdraví</b>	Degenerativní změny nervového systému, ovlivnění chování, retardace vývoje, reprodukční účinky, fertilita
<b>Hodnocení karcinogenních účinků (EPA)</b>	Hg <sup>0</sup> není klasifikován jako karcinogen pro člověka Hg <sup>2+</sup> možný karcinogen pro člověka R- Hg možný karcinogen pro člověka
<b>Expoziční cesty</b>	Inhalace par Hg  Požití vody a potravy kontaminované anorganickou/organickou Hg
<b>MCL (voda)</b>	2 ppb (EPA)
<b>TLV (vzduch)</b>	0.05 mg/m <sup>3</sup>



# Toxikologické vlastnosti Hg

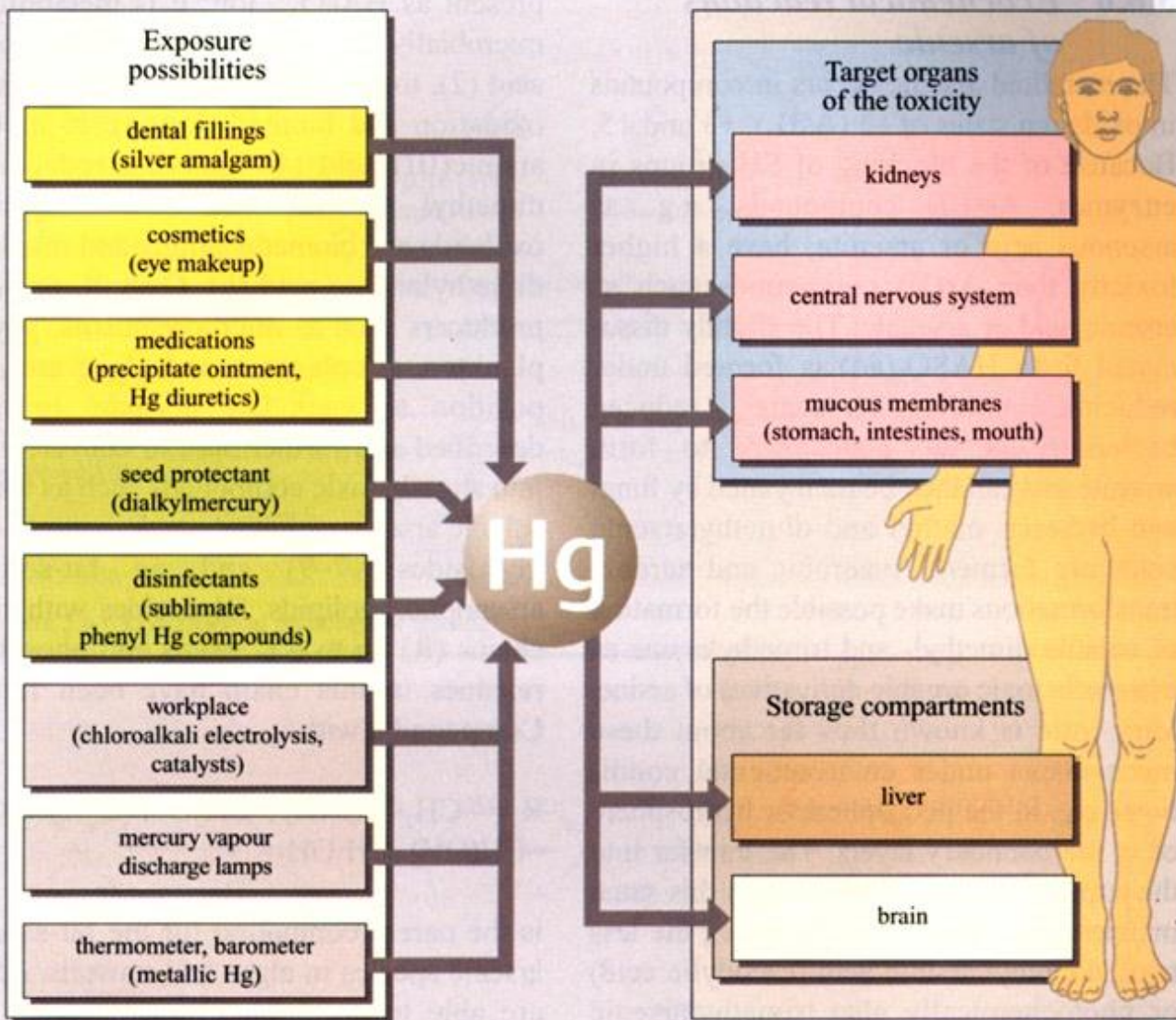
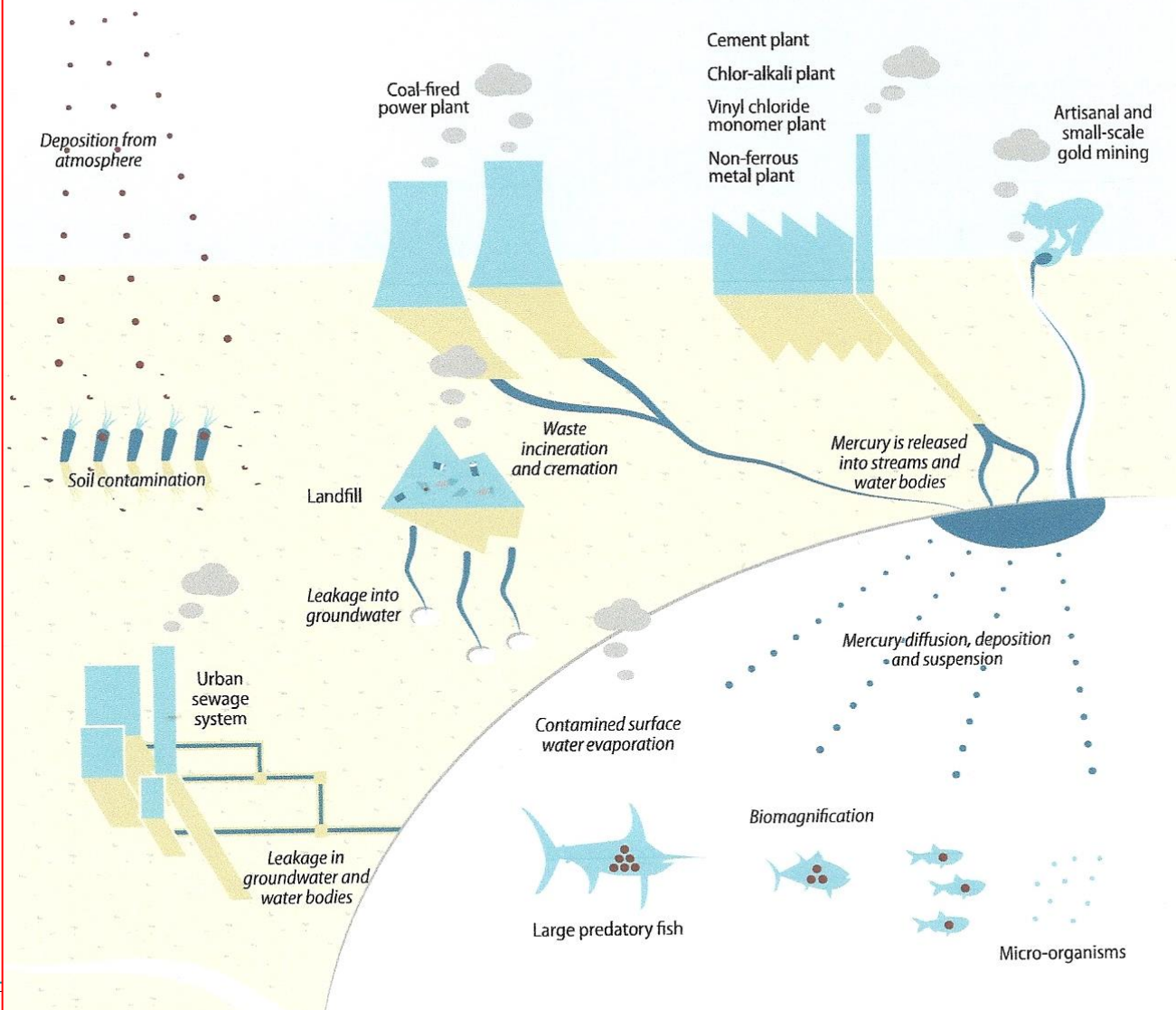


Figure 5.6.4 Mercury 'spider': applications and activity

# Mercury environmental enters

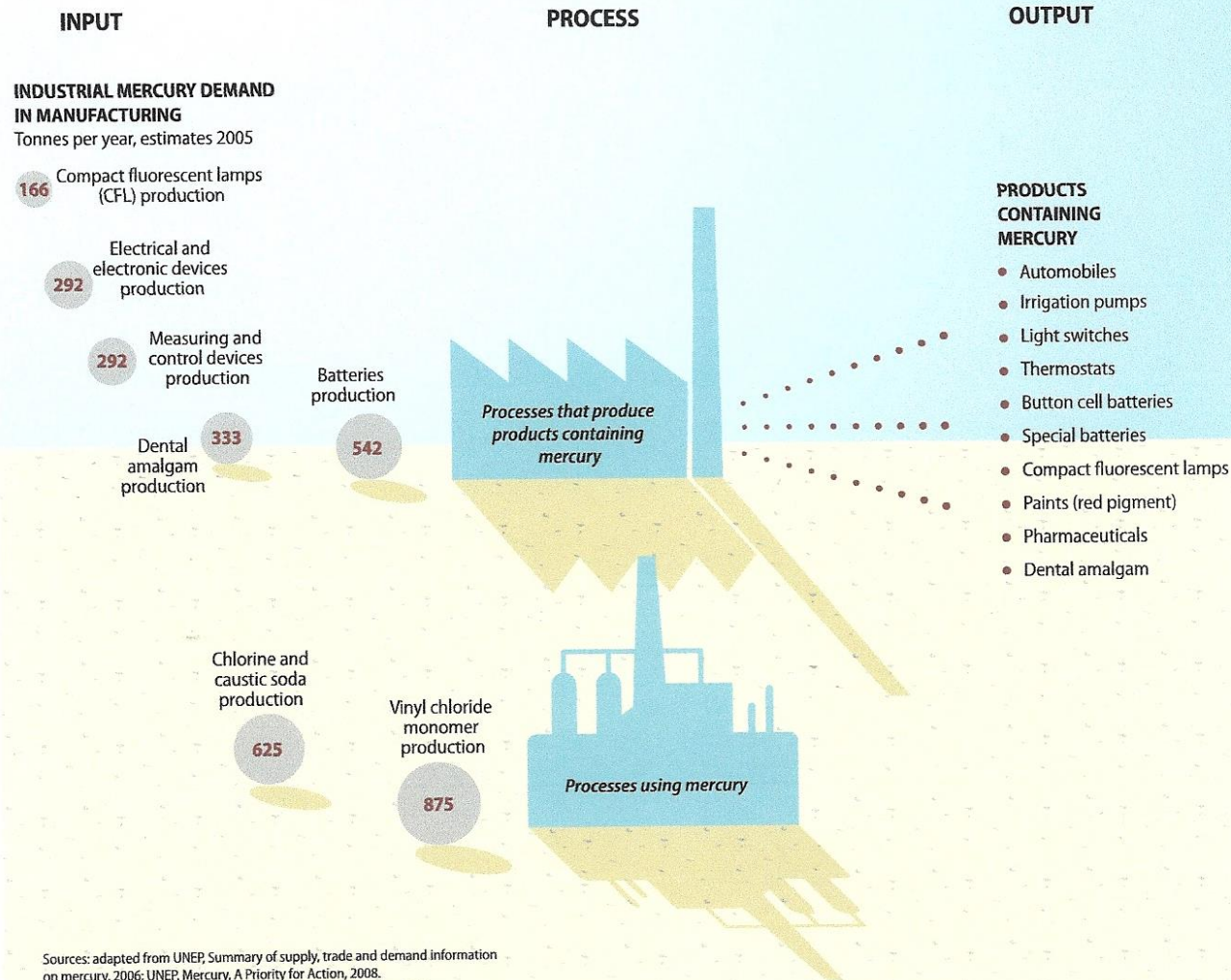
## How mercury can enter our environment



Sources: adapted from UNEP, Mercury Awareness Raising Package, accessed on line in September 2012 (<http://www.unep.org/hazardoussubstances/>); Institute for Agriculture and Trade Policy, High fructose corn syrup's not-so-sweet surprise: mercury, 2009. Designed by Zoi Environment Network / GRID-Arendal, December 2012.

# Industrial processes – input and output of Hg

## Industrial processes: input and output of mercury



Sources: adapted from UNEP, Summary of supply, trade and demand information on mercury, 2006; UNEP, Mercury, A Priority for Action, 2008.  
Designed by Zof Environment Network / GRID-Arendal, December 2012

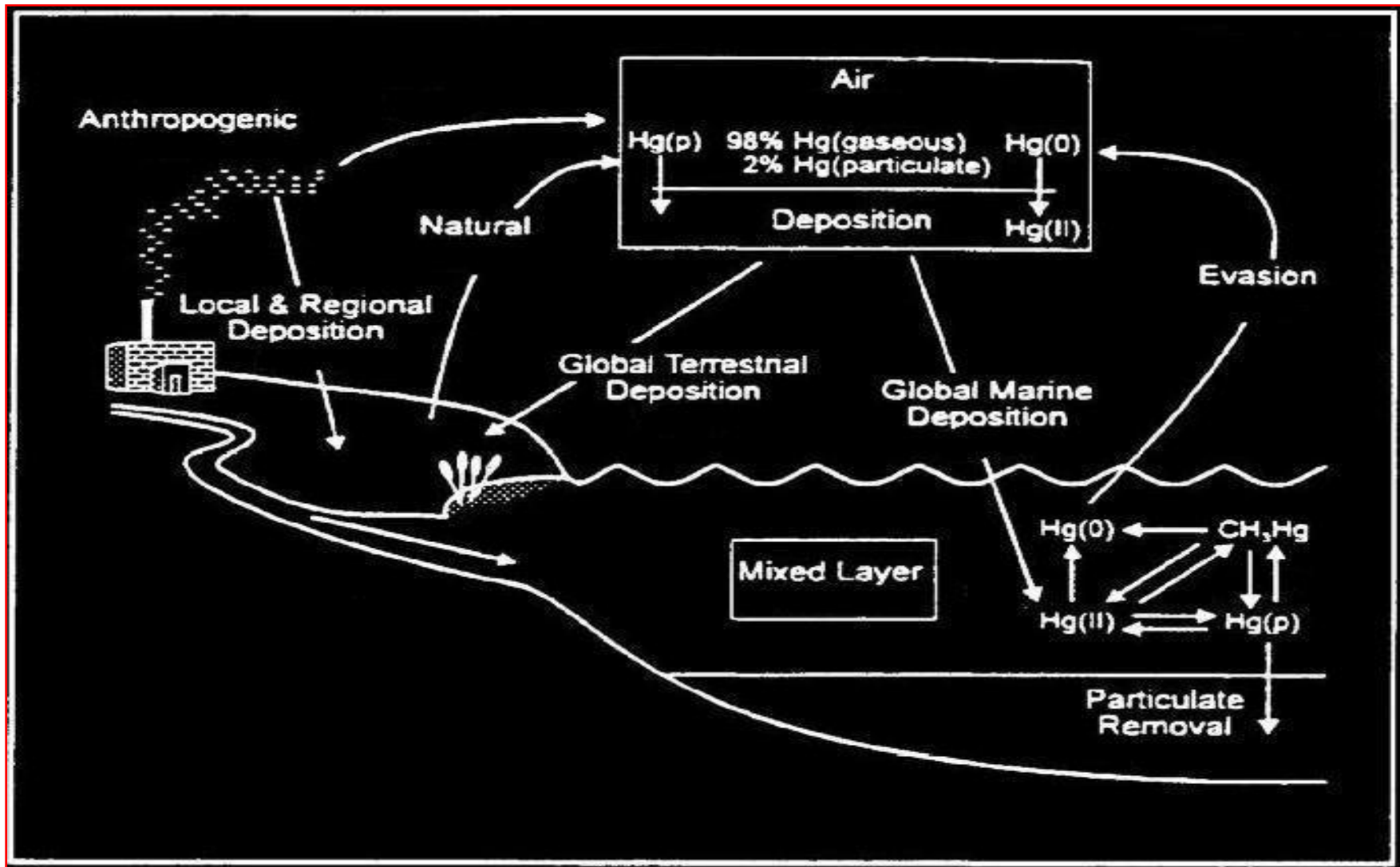
# Rtut' (Hg) – zdroje a využití

**Přírodní zdroje:** ve formě sloučenin - vyvřelé horniny, sedimentované sulfidové minerály, v elementární formě vzácně.

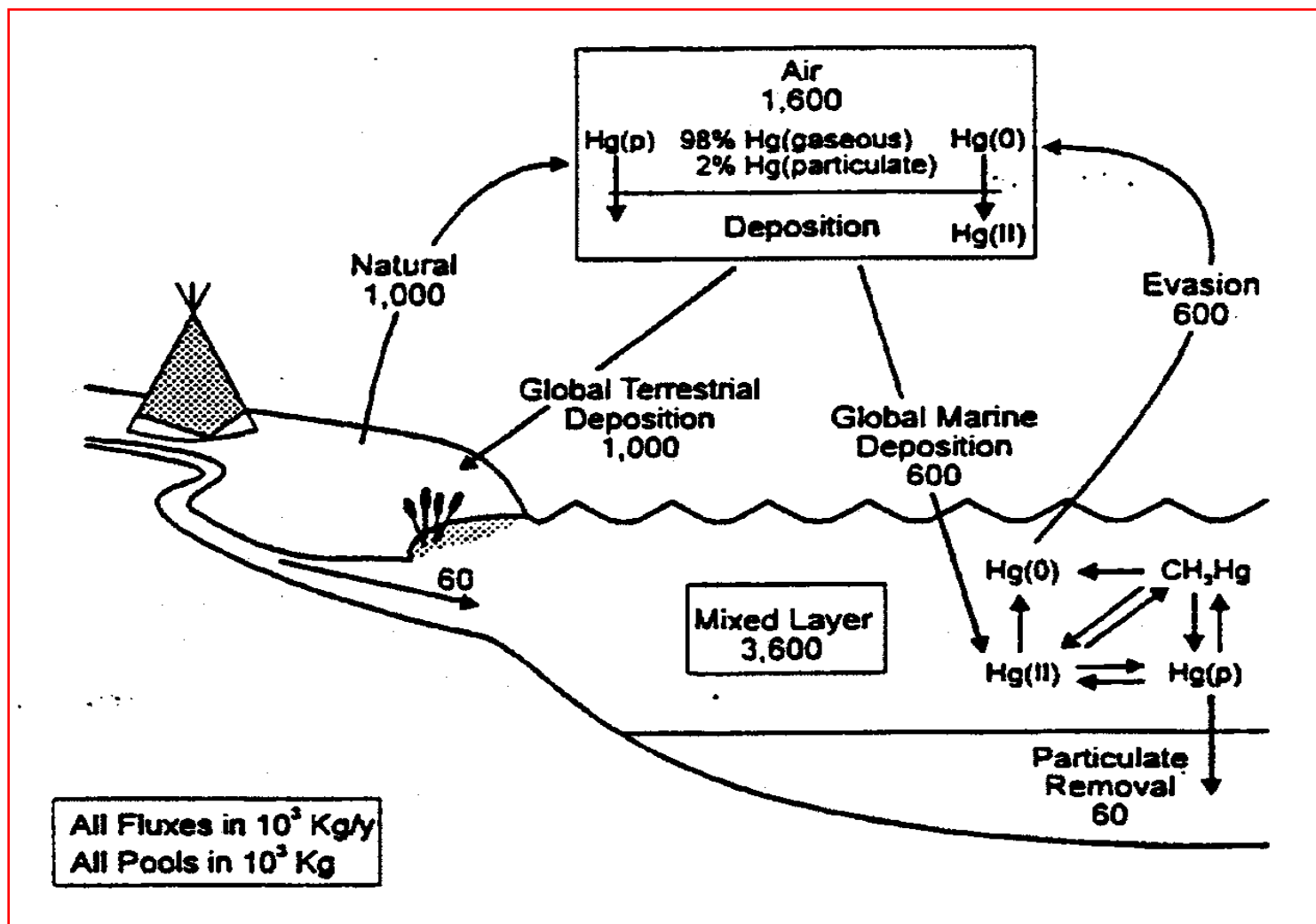
## Antropogenní zdroje:

- ↙ některé fungicidy používané při výrobě celulózy a papíru
- ↙ zpracování chlorovaných uhlovodíků
- ↙ destilace olejů a uhlí
- ↙ výroba elektrických kontaktů
- ↙ zemědělská mořidla
- ↙ zpracování rud
- ↙ amalgamace
- ↙ elektrochemická výroba
- ↙ regulační technika
- ↙ lékařství - aktivní složka různých diuretik, antiseptik, kožních léčiv, zubních amalgámů
- ↙ laboratorní barviva

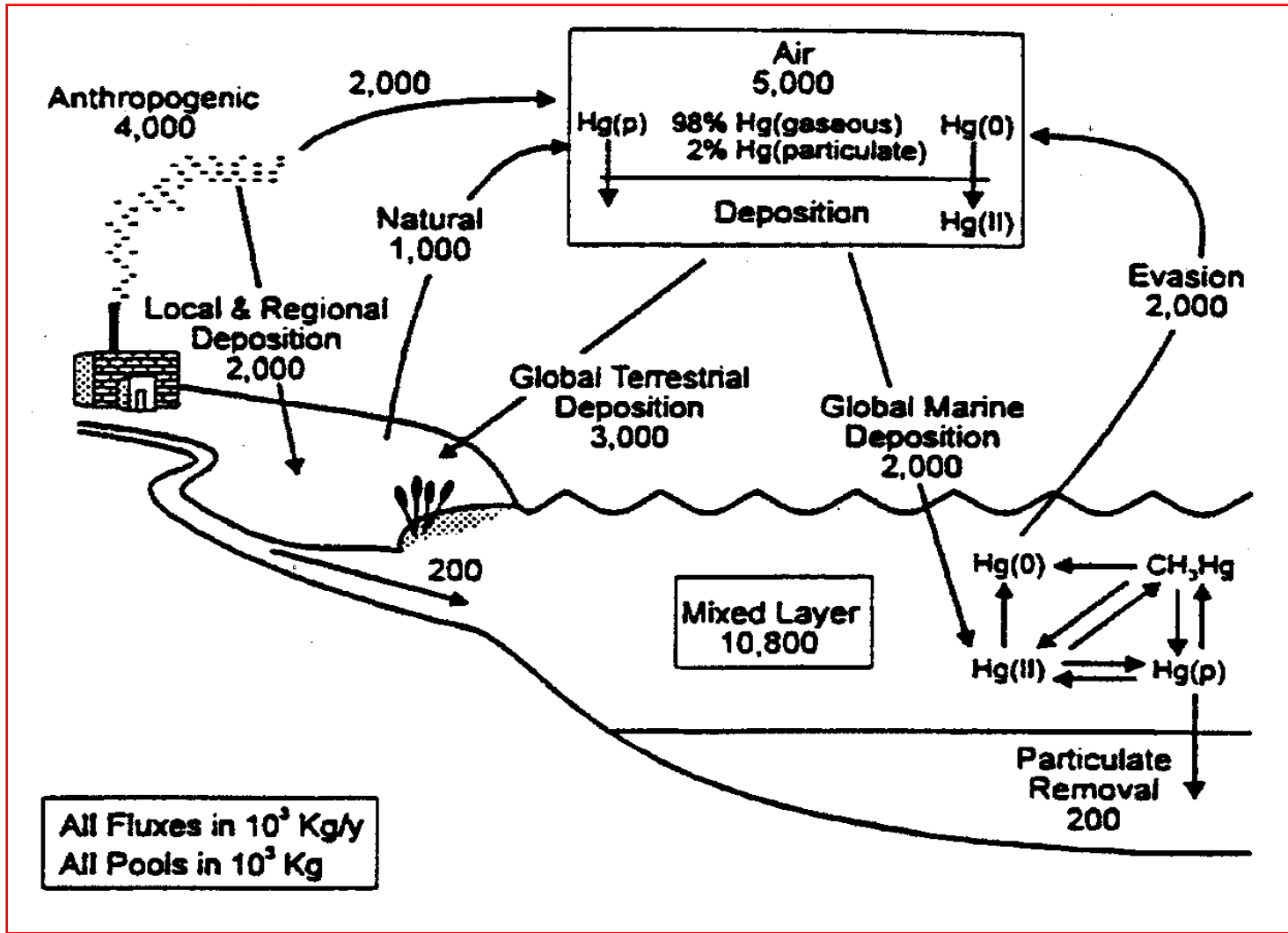
# Cyklus rtuti



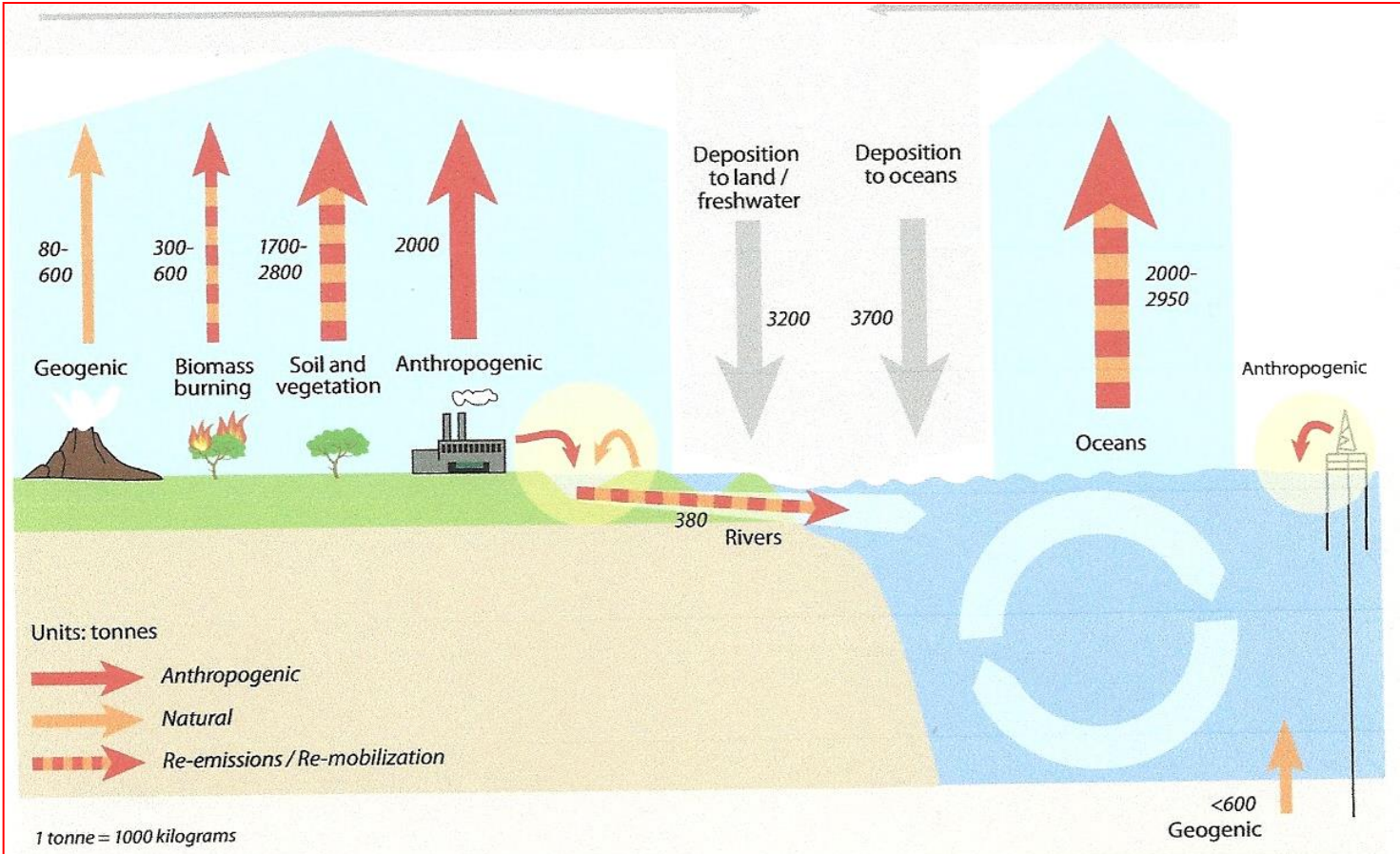
# Pre-industriální zásoby a toky Hg



# Současné zásoby a toky Hg



# Estimation of the the global Hg cycle



Global mercury budgets, based on models, illustrate the main environmental compartments and pathways that are of importance in the global mercury cycle, and the ways in which natural and anthropogenic releases to air land and water move between these compartments. Emissions to air arise from natural sources and anthropogenic sources, as well as re-emissions of mercury previously deposited from air onto soils, surface waters, and vegetation.



# Pozad'ové koncentrace Hg v různých složkách prostředí

Složka	Koncentrace [ppb]
Vzduch	0.002
Řeky a podzemní vody	0.05
Mořská voda	0.1
Dešťová voda	0.15
Surový kal	2.0
Povrchové horniny	50
Půdy a sedimenty	50
Uhlí	200
Ryby	100
Člověk	100

# Typy antropogenních emisních zdrojů Hg

<b>Spalování</b>	Fosilní paliva (uhlí, ropa, plyn) a dřevo
	Odpady (komunální, nemocniční, nebezpečné)
	Odpadní kaly
	Krematoria
<b>Vysokoteplotní procesy</b>	Tavení
	Výroba koksu
	Výroba litiny
	Výroba cementu a vápna
<b>Výrobní procesy</b>	Výroba chloru amalgámovým způsobem
	Zpracování kovů
	Chemické a výrobní procesy (Hg sloučeniny, barvy, baterie, teploměry, výchozí látky a katalyzátory pro různé chemické výroby)

# Typy antropogenních emisních zdrojů Hg

<b>Těžba zlata</b>	
<b>Další zdroje</b>	<b>Fluorescenční lampy</b>
	<b>Skládky nebezpečných a komunálních odpadů</b>
	<b>Skládky hlušiny</b>
	<b>Narušení povrchu</b>

# Distribuce ročních vstupů Hg významných pro různé spalovací a výrobní procesy

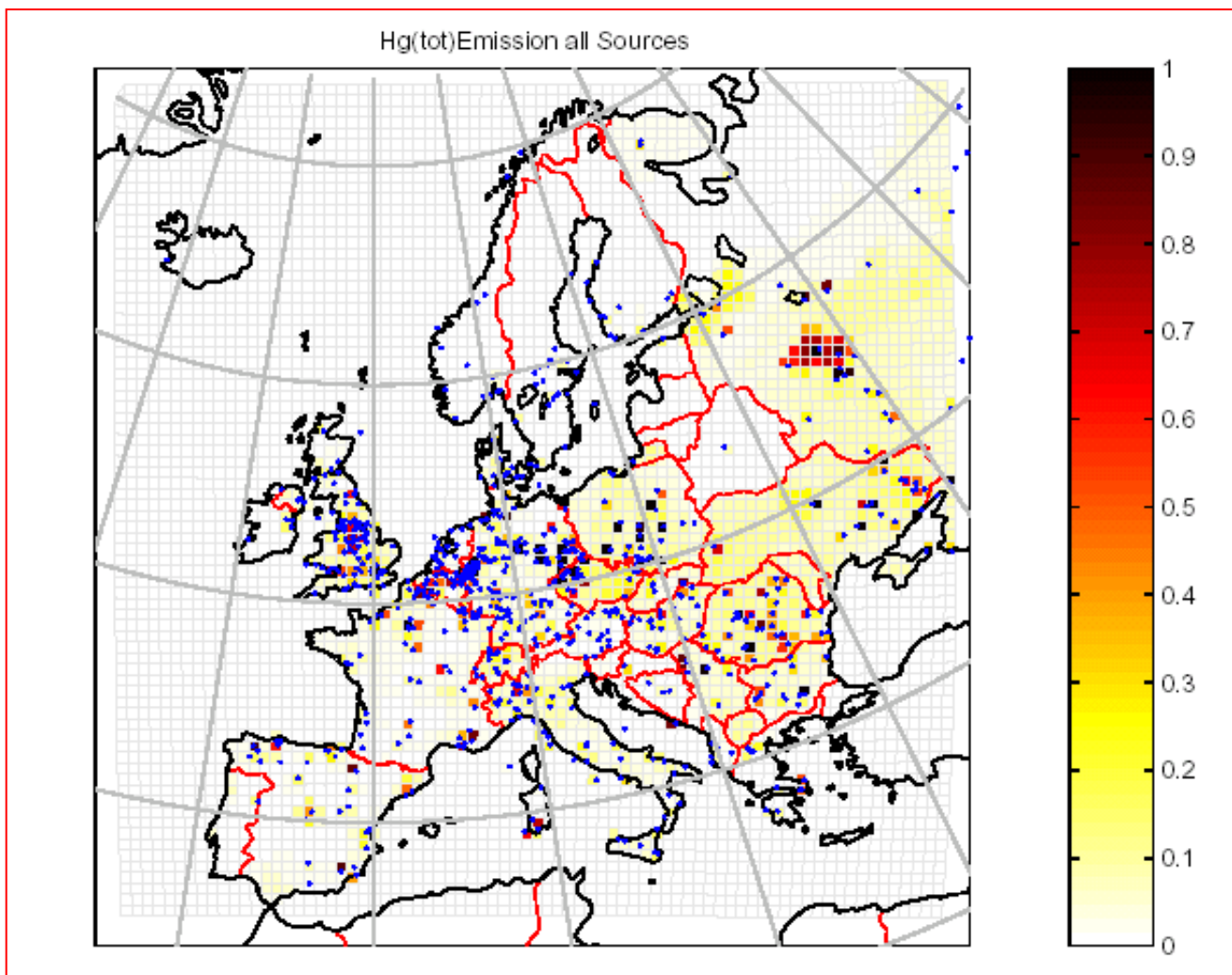
Zdroj	Distribuce [%]
Spalovací zdroje – celkem	80.95
Elektrická zařízení	
<i>Spalující ropu nebo plyn</i>	0.12
<i>Splalující uhlí</i>	33.19
Spalovny	
<i>Spalování komunálních odpadů</i>	19.03
<i>Spalování nemocničních odpadů</i>	10.29
<i>Domácí/průmyslové vytopy</i>	18.27
Výroba chloru amalgámovým způsobem	4.17
Primární výroba olova	0.05
Primární výroba mědi	0.03
Další spalovací zdroje	6.98
Další zdroje	7.80

# Zdroje znečištění prostředí Hg v Evropě



<b>Průmyslové procesy</b>	Bývalá NDR, Slovensko, Česko, Belgie, Holandsko
<b>Spalování</b>	Rusko Země NIS, Bývalá Jugoslavie Polsko Rumunsko
<b>Průmyslové procesy a spalování</b>	Bulharsko Francie Italie Portugalsko Španělsko UK

**Celkové Hg emise v t/rok/buňku síť (Suma všech bodových a regionálních zdrojů. Každá buňka pokrývá přibližně 56x56 km<sup>2</sup>. Bodové zdroje jsou vyznačeny modrými body)**

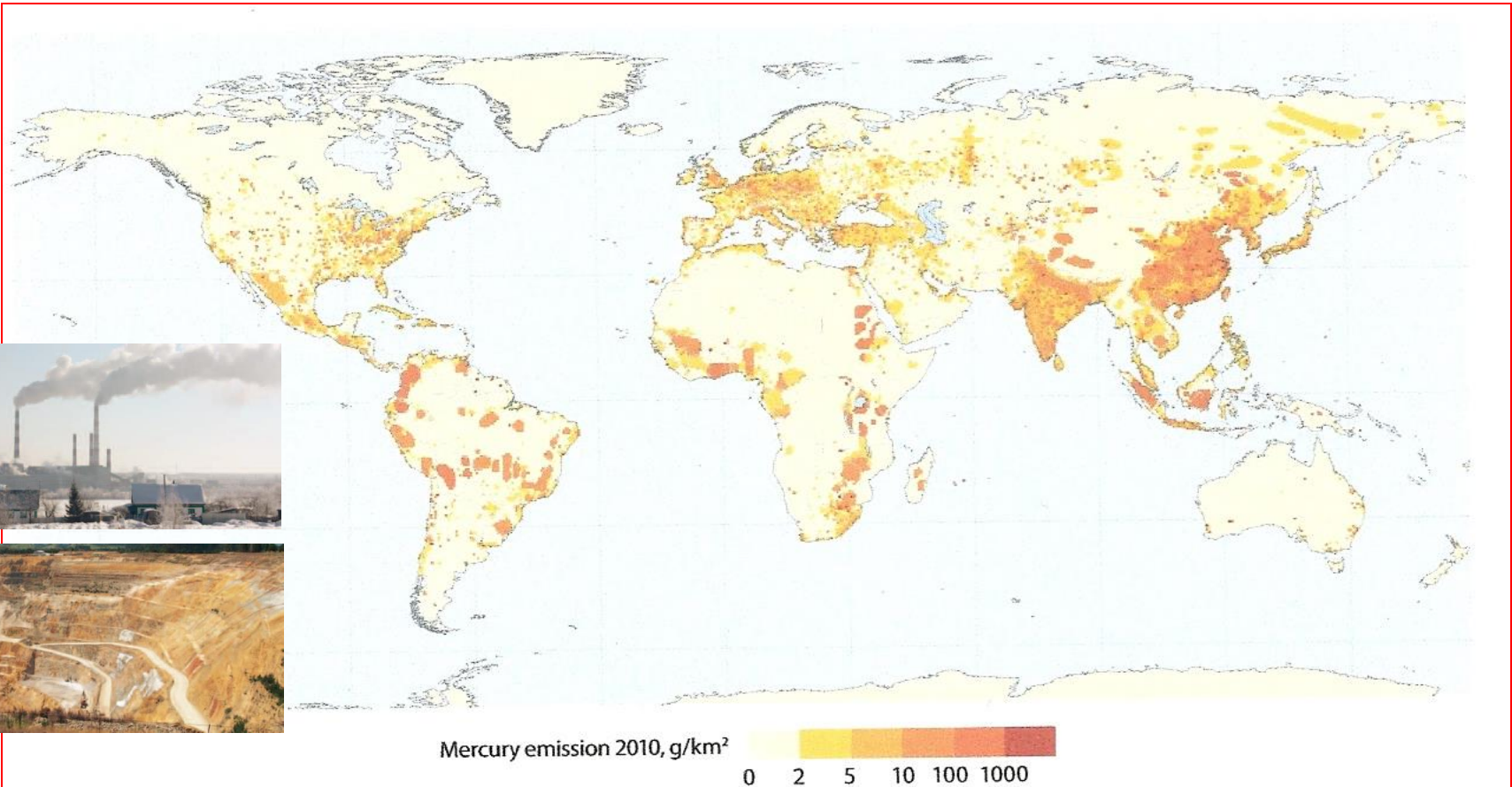


# Globální emise celkové Hg z hlavních antropogenních zdrojů v roce 1995 [t]

Kontinent	Stationární spalování	Výroba neželezných kovů	Výroba litiny a oceli	Výroba cementu	Likvidace odpadu	Celkově
Evropa	185.5	15.4	10.2	26.2	12.4	249.7
Afrika	197.0	7.9	0.5	5.2		210.6
Asie	860.4	87.4	12.1	81.8	32.6	1 074.3
Severní Amerika	104.8	25.1	4.6	12.9	66.1	213.5
Jižní Amerika	26.9	25.4	1.4	5.5		59.2
Australie & Oceanie	99.9	4.4	0.3	0.8	0.1	105.5
<b>Celkem</b>	<b>1 474.5</b>	<b>165.6</b>	<b>29.1</b>	<b>132.4</b>	<b>111.2</b>	<b>1 912.8<sup>1</sup></b>

<sup>1</sup> In addition, emission of about 514 tonnes of Hg was estimated for chlor-alkali plants, gold production, and the use of Hg for various purposes (primary battery production, production of measuring and control instruments, production of electrical lighting, wiring devices, and electrical switches) in 1995.

# Global distribution of anthropogenic Hg emissions - 2010

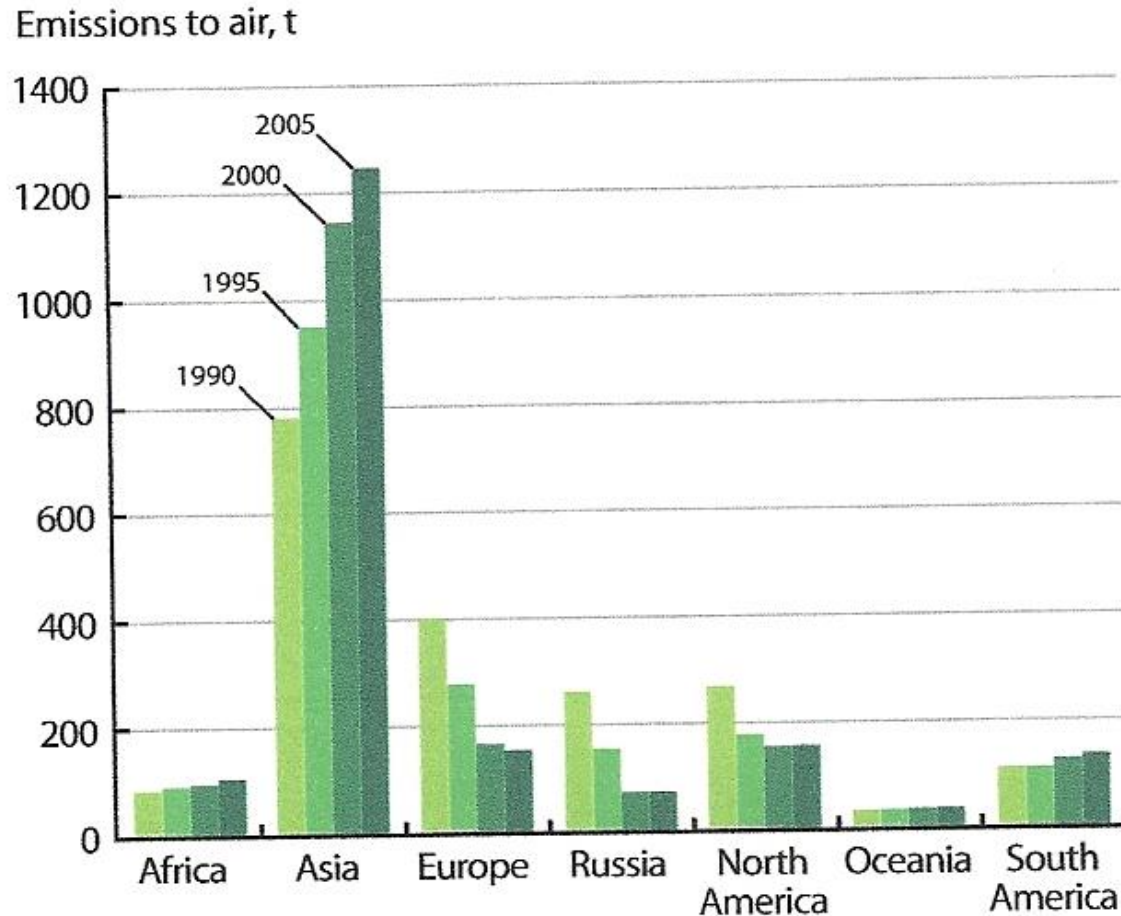


*Global distribution of anthropogenic mercury emissions to air in 2010.*



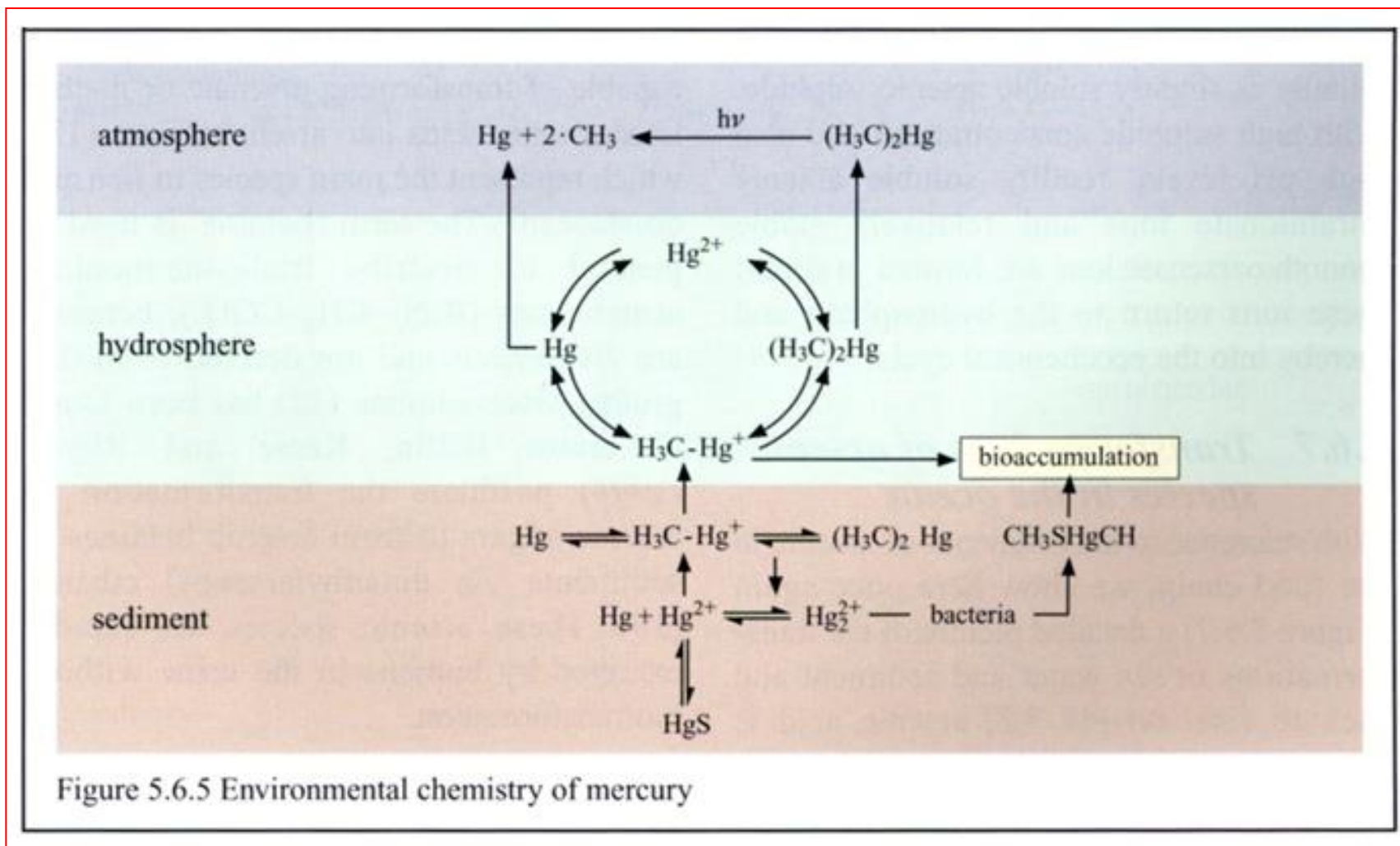


# Estimation of annual anthropogenic Hg emissions

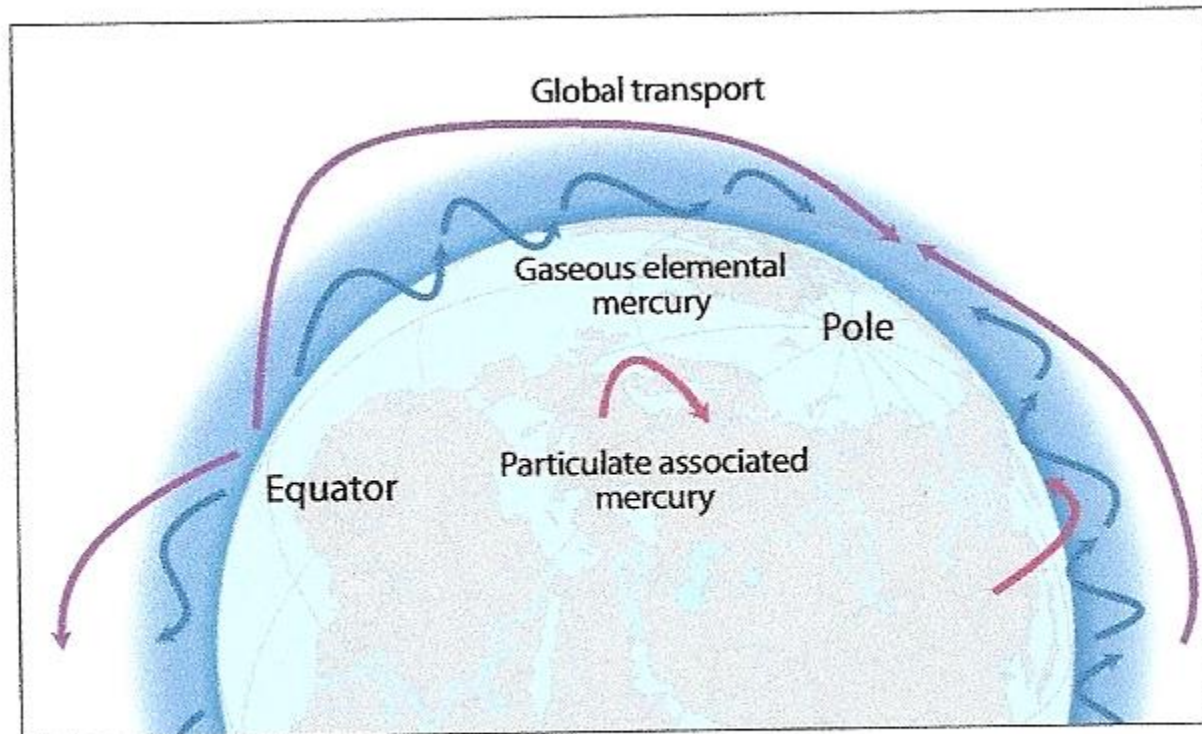


*Estimates of annual anthropogenic mercury emissions from different continents/regions, 1990-2005.*

# Environmentální chemie Hg

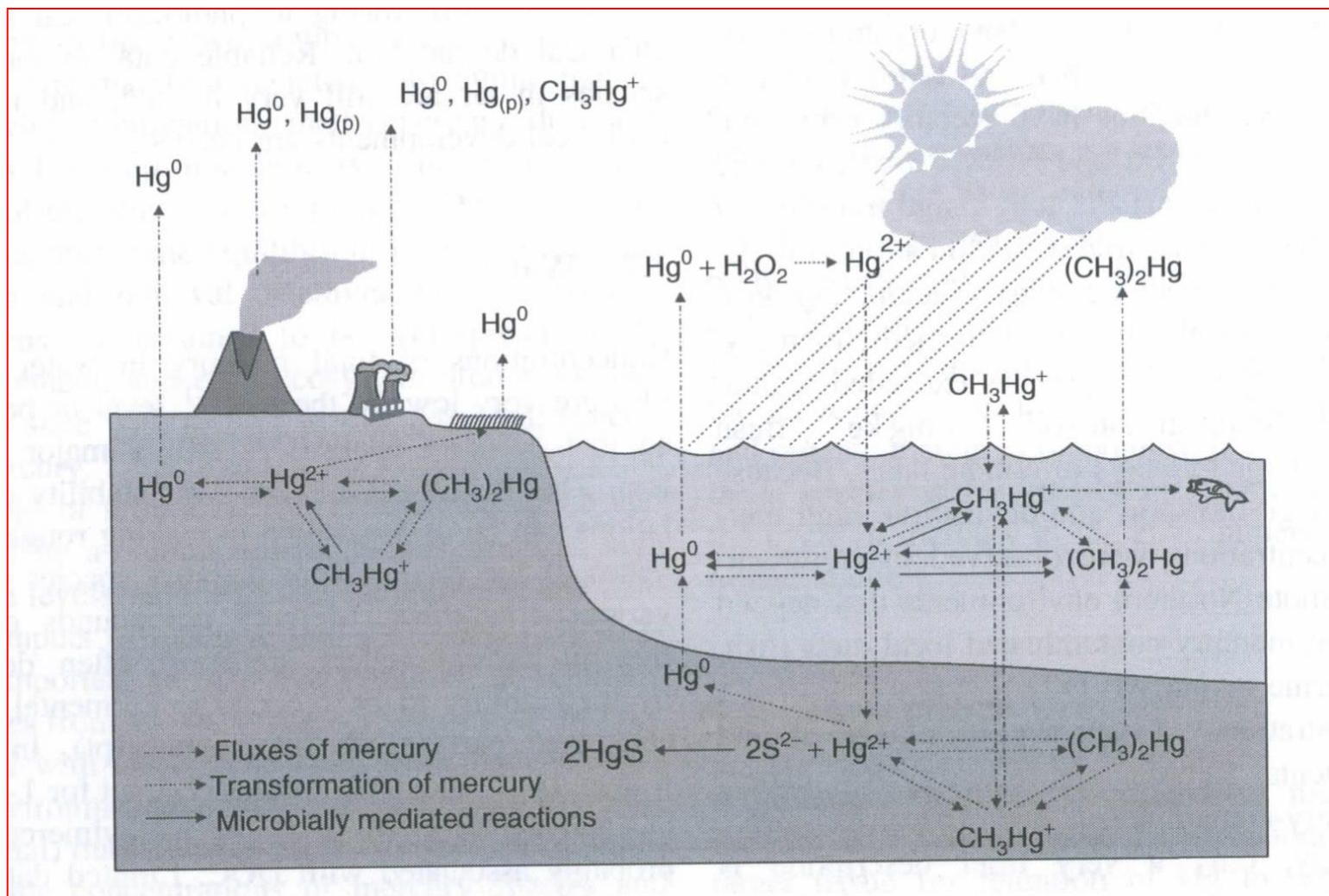


# Globální osud Hg

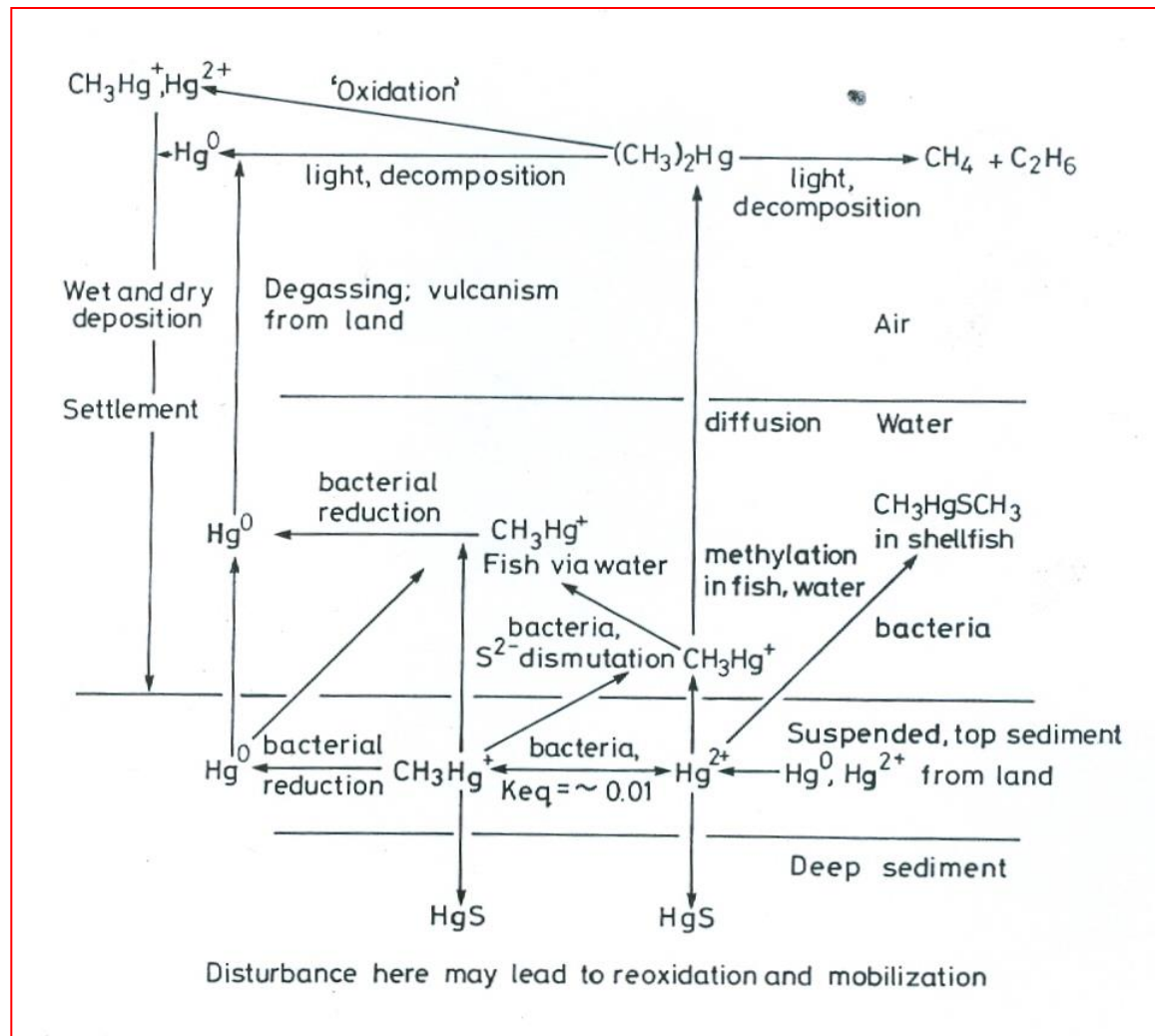


*Gaseous elemental mercury can be transported globally.  
Mercury emitted in particulate form tends to deposit closer to sources.*

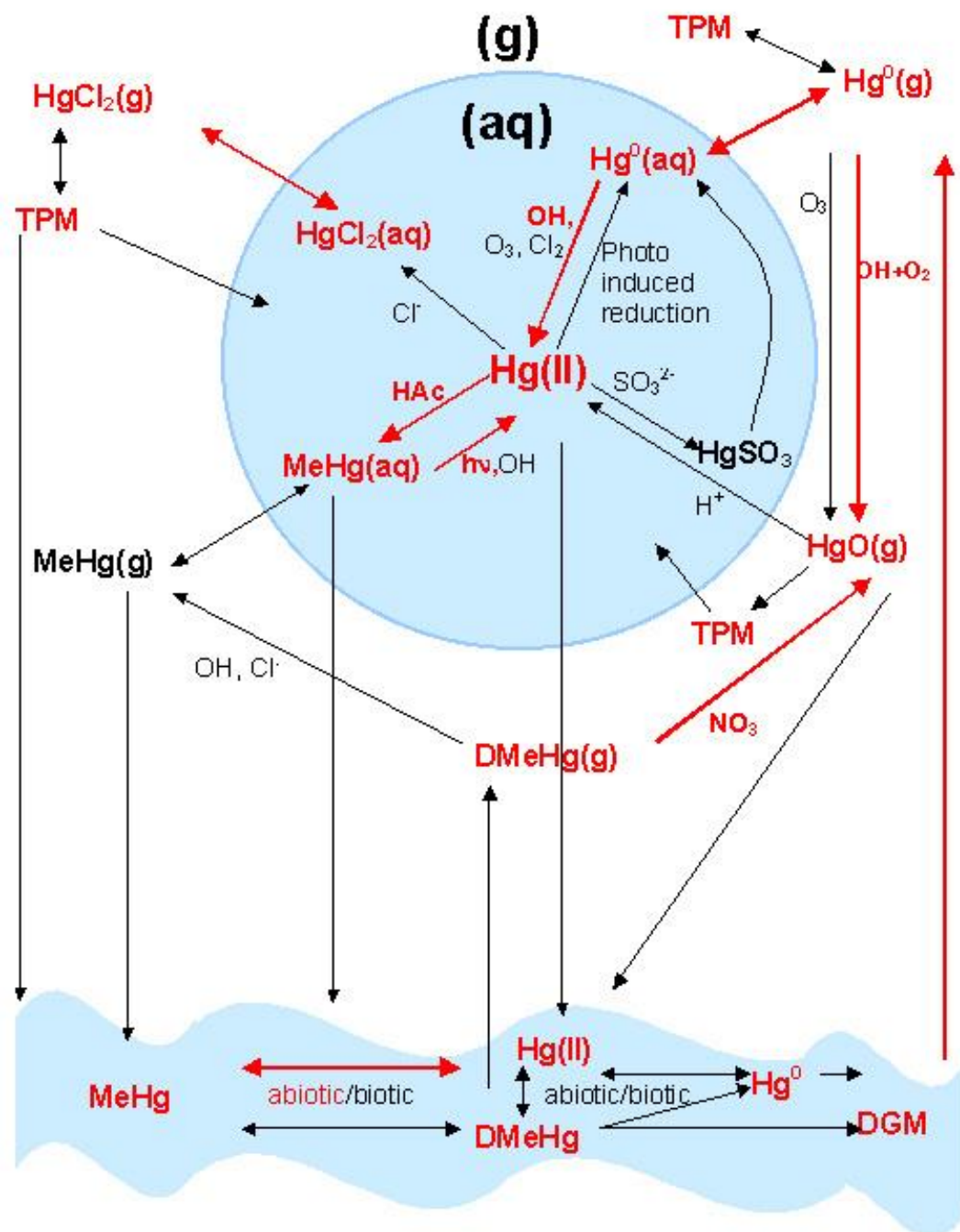
# Cyklus Hg v prostředí



# Environmentální osud Hg



# Atmosférický cyklus Hg



# Souhrn chemických transformačních procesů Hg

Reaction	Results
1) $\text{Hg}^0 + \text{OH} \rightarrow \text{HgOH}$ (g)	Rate constant $k = (8.7 \pm 2.8) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
2) $\text{Hg}^0 + \text{OH} \rightarrow \text{HgOH}$ (aq)	Rate constant $k = (2.4 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
3) $\text{HgCl}_2 + \text{e}^- \rightarrow \text{HgCl} + \text{Cl}^-$ (aq)	Reduction potential $E^0 = -0.47 \text{ V}$
4a) $\text{HgCl}_2 + \text{O}_2^{\cdot-} \rightarrow \text{HgCl} + \text{O}_2 + \text{Cl}^-$ (aq) 4b) $\text{HgCl}_2 + \text{O}_2^{\cdot-} \leftrightarrow \text{HgCl} + \text{O}_2 + \text{Cl}^-$ (aq)	Rate constant $k = 6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ Equilibrium constant $K = 5.7 \times 10^{-6}$
5) $[\text{Hg}(\text{C}_2\text{O}_4)_n]^{(2-2n)+} + \text{h}\nu \rightarrow \text{Hg}^0 + 2\text{CO}_2 + (n-1)\text{C}_2\text{O}_4^{2-}$ (aq)	Identification of $\text{Hg}^0$ as a reaction product at $\lambda > 290 \text{ nm}$
6) $(\text{CH}_3)_2\text{Hg} + \text{NO}_3^{\cdot-} \rightarrow \text{HgO} + \text{NO}_2$ (g)	Identification of $\text{HgO}$ as the main product
7) $\text{CH}_3\text{HgX} + \text{h}\nu \rightarrow \text{CH}_3 + \text{HgX}^{\cdot}$ (aq)	$\tau \sim 230 \text{ h}$ , at $60^\circ\text{N}$ during summer season. Identification of the final product $\text{Hg(II)}$ as a consequence of the reaction between intermediate $\text{HgX}^{\cdot}$ and molecular oxygen
8) $\text{CH}_3\text{HgX} + \text{OH} \rightarrow \text{CH}_3 + \text{HgX}^{\cdot}$ (aq)	Identification of the final product $\text{Hg(II)}$ as a consequence of the reaction between intermediate $\text{HgX}^{\cdot}$ and molecular oxygen
9) $[\text{Hg}(\text{CH}_3\text{COO})_n] \rightarrow \text{CH}_3\text{Hg}^+ + \text{CO}_2 + (n-1)[\text{Hg}(\text{CH}_3\text{COO})_n]^-$ (aq)	Rate constant $k = (9.0 \pm 0.9) \times 10^{-7} \text{ s}^{-1}$ at pH 3.6-3.7
10) $\text{Hg}(\text{Cl})_2(\text{aq}) \leftrightarrow \text{Hg}(\text{Cl})_2(\text{g})$	Henry's law constant $\sim 5 \times 10^{-7} \text{ atm M}^{-1}$

# Atmospheric forms of Hg

Mercury in the atmosphere is in **three primary forms**.

**Gaseous elemental mercury** is the most common in anthropogenic and natural emissions to the atmosphere.

**Gaseous oxidized mercury and mercury bound to particulates** are less common.

**The transport and deposition** of atmospheric mercury depend greatly on whether the mercury is elemental or oxidized.

**Elemental mercury** stays in the atmosphere long enough for it to be transported around the world, whereas oxidized and particulate mercury are more readily captured in existing pollution control systems or deposited relatively rapidly after their formation.

As a result, most mercury in the air is in the gaseous elemental phase.

Relatively little elemental mercury is deposited directly, but instead must first **be oxidized**.



# Atmospheric forms of Hg

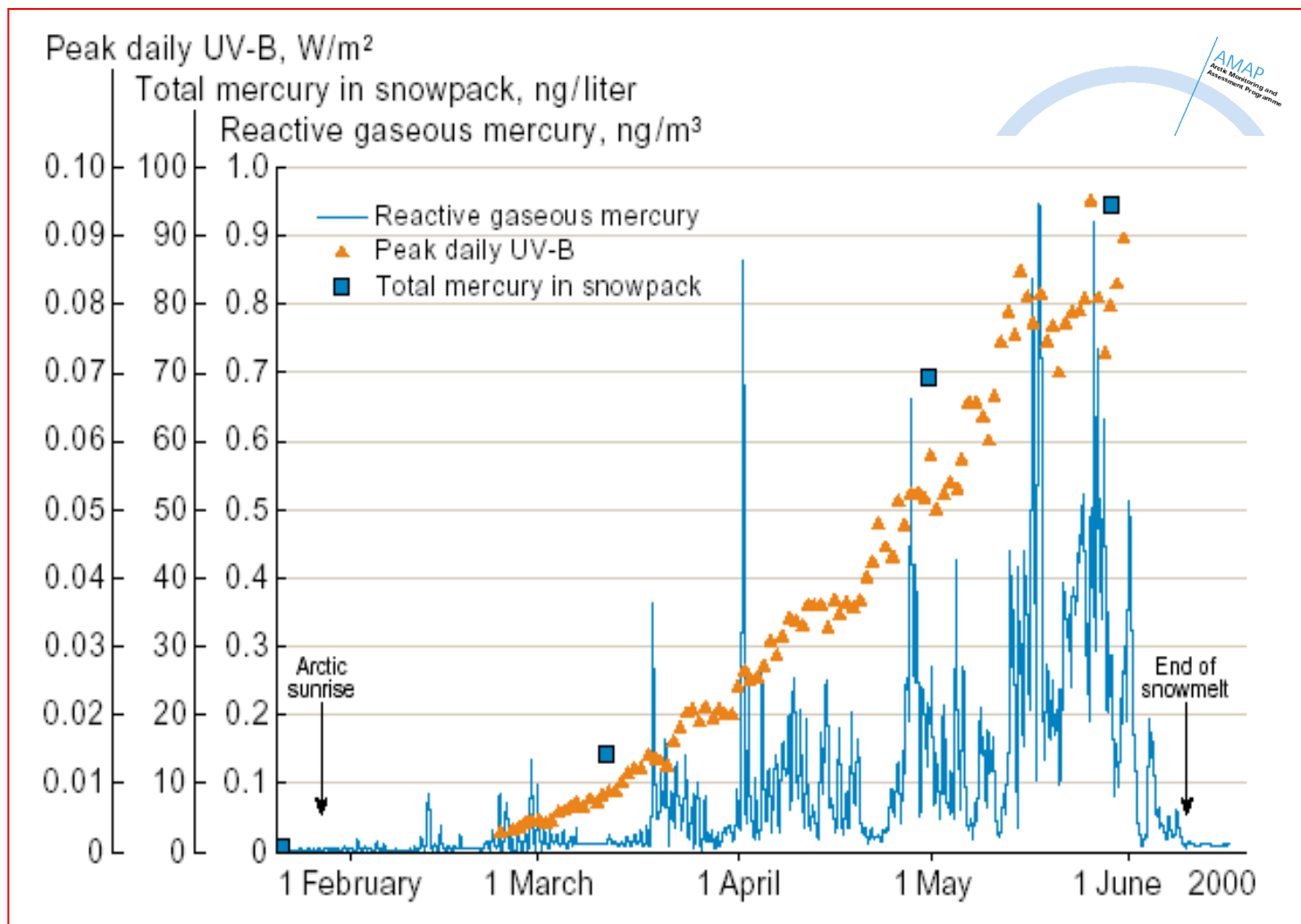
Although **gaseous oxidized mercury** is very important in mercury cycling between air and other environmental compartments, the process of oxidation in the air is poorly understood, with reactions and resulting compounds yet to be verified in observations.

**When mercury moves from air to water and land, it is generally in an oxidized gaseous or particulate form,** whereas when it is re-emitted to air it has been converted back to gaseous elemental mercury.

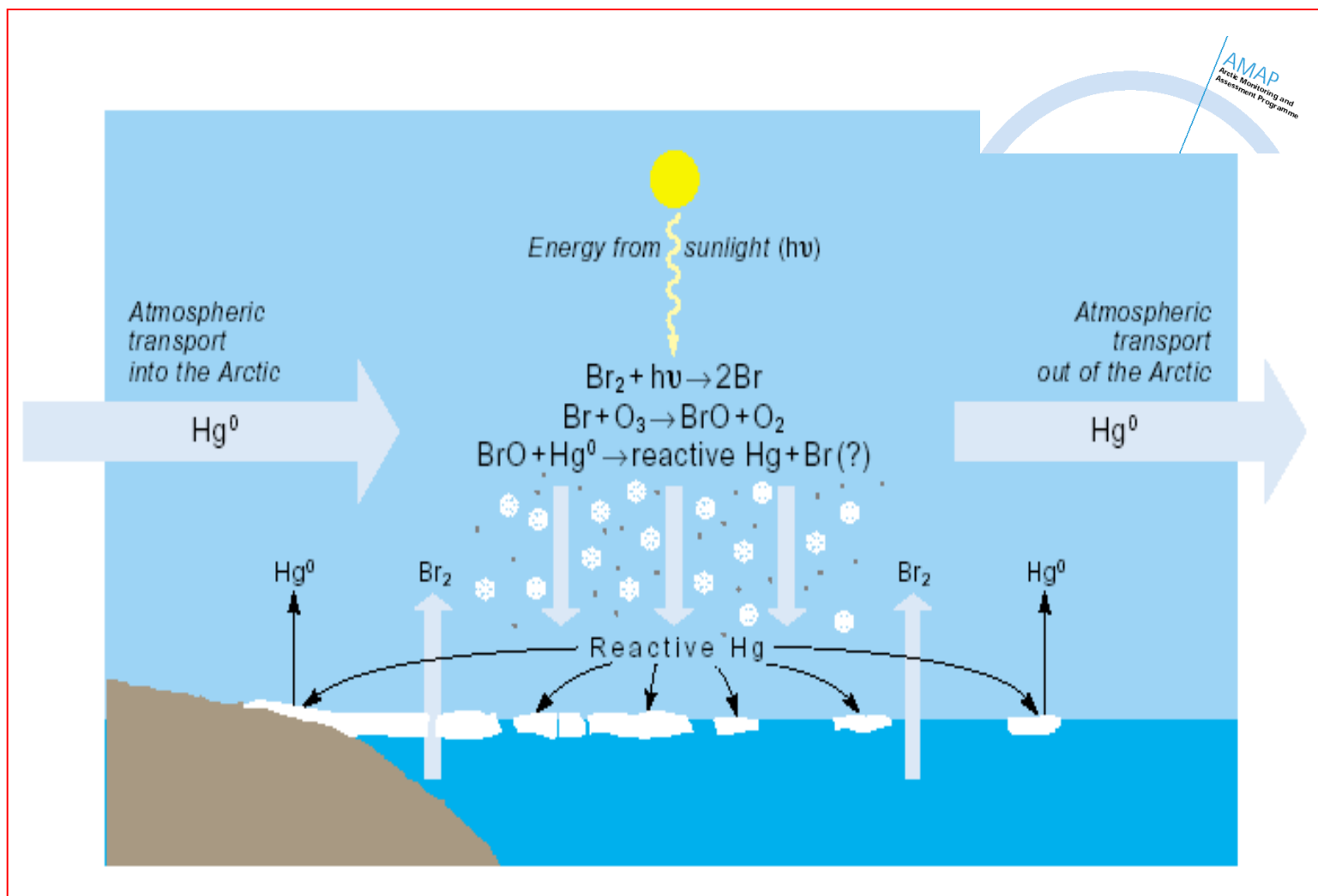
Sunlight appears to play a **large role in both oxidation and reduction of mercury,** but temperature and biological interactions are also likely to be involved to some degree. Here, too, much uncertainty remains.

Nonetheless, the reactions are important in determining net **deposition and fate of mercury.**

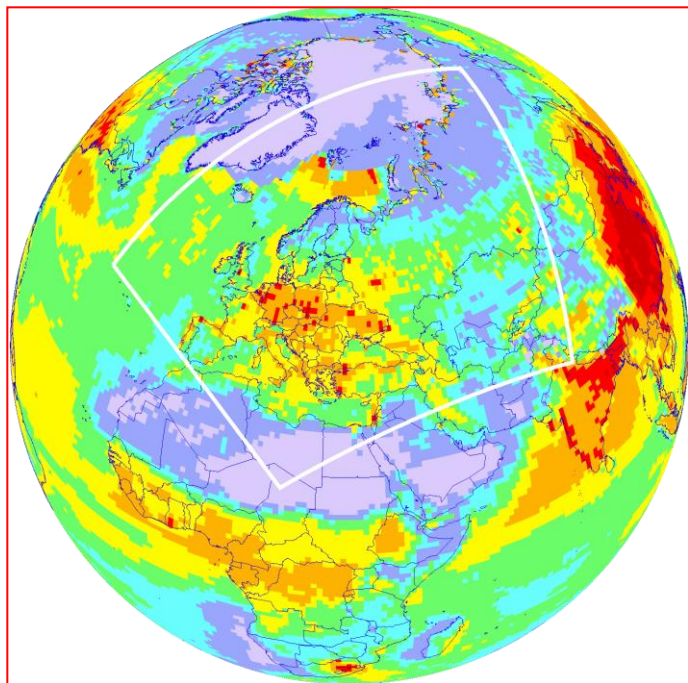
# Vztah mezi UV zářením a Hg



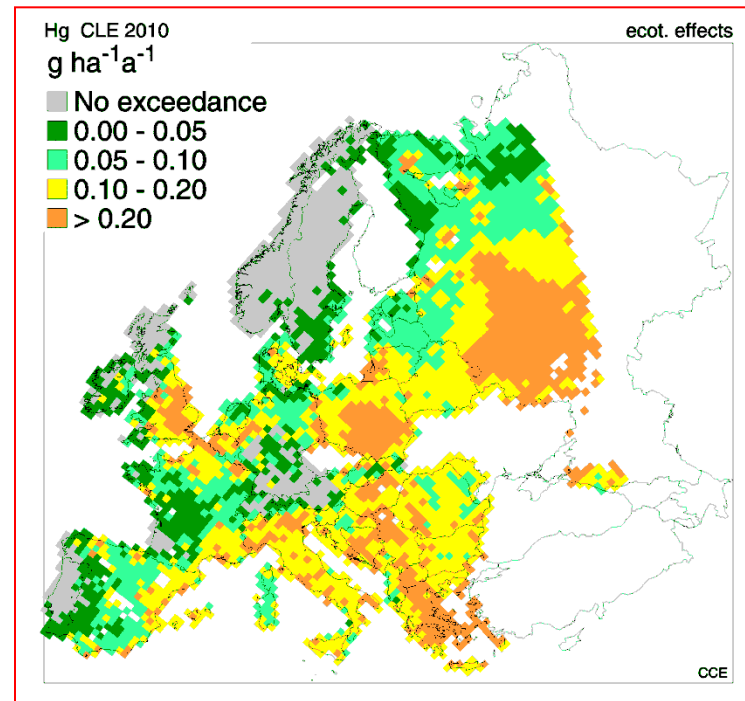
# Polární východ slunce a vynášení Hg



# Rtut' – globální polutant



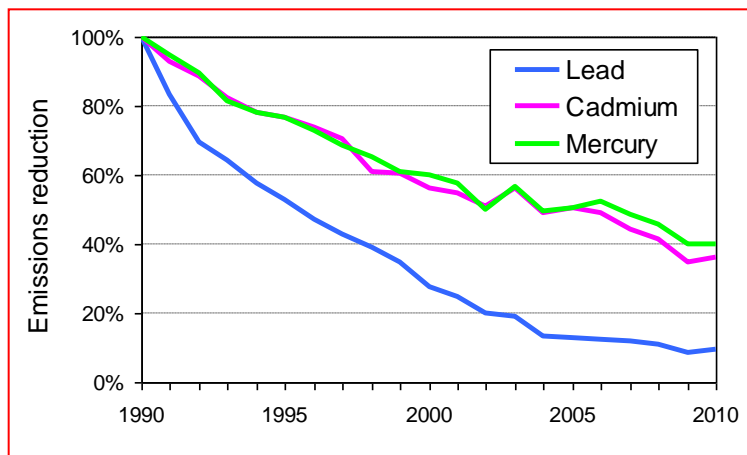
0 2.5 5 7 10 15 25 50 g/km<sup>2</sup>/y



„kritické zátěže“

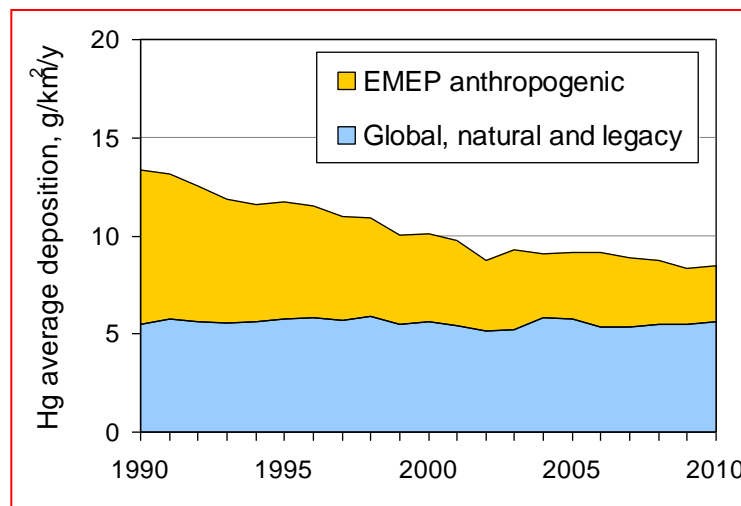
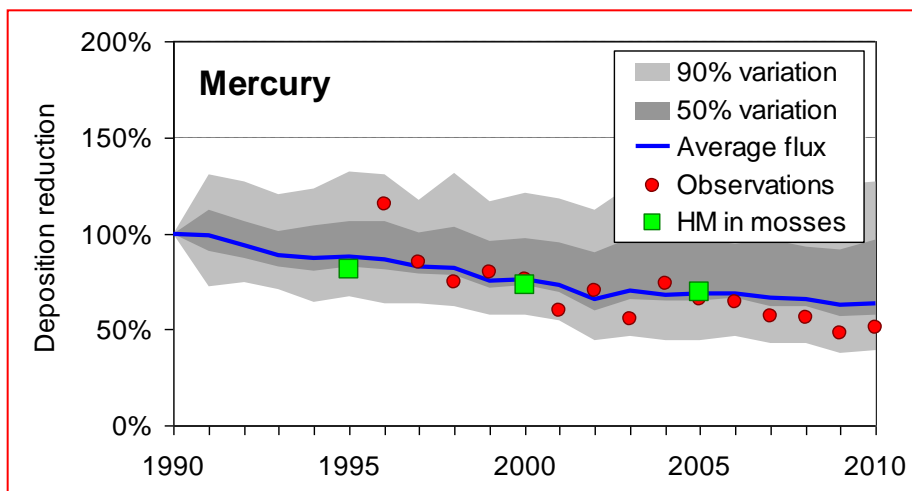
Celosvětová depozice a  
situace v Evropě

# Emise a depozice



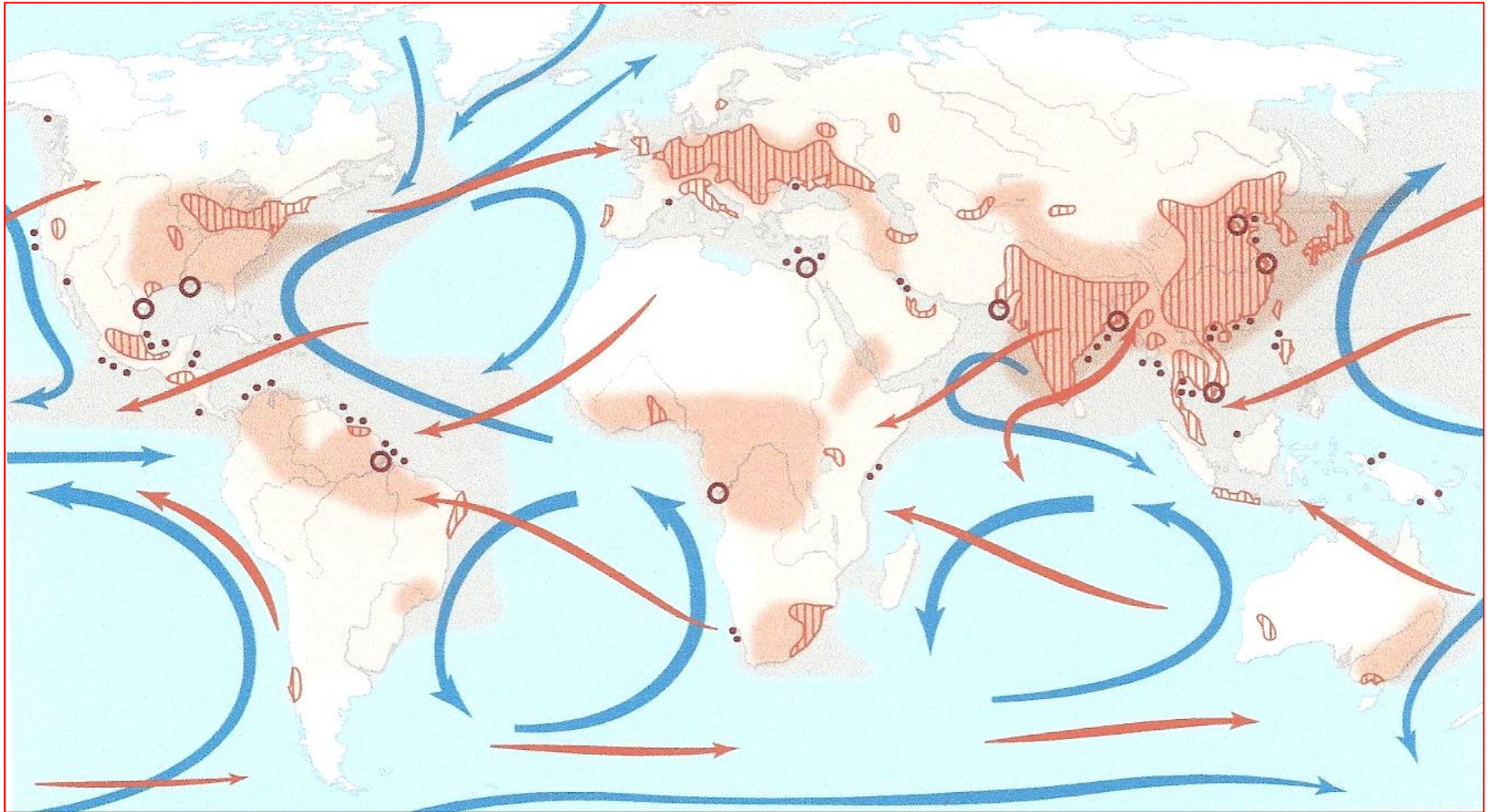
Snížení emisí v členských zemích  
EMEP – okolo 60%

Snížení depozice Hg  
v UNECE-zemích - okolo 30%



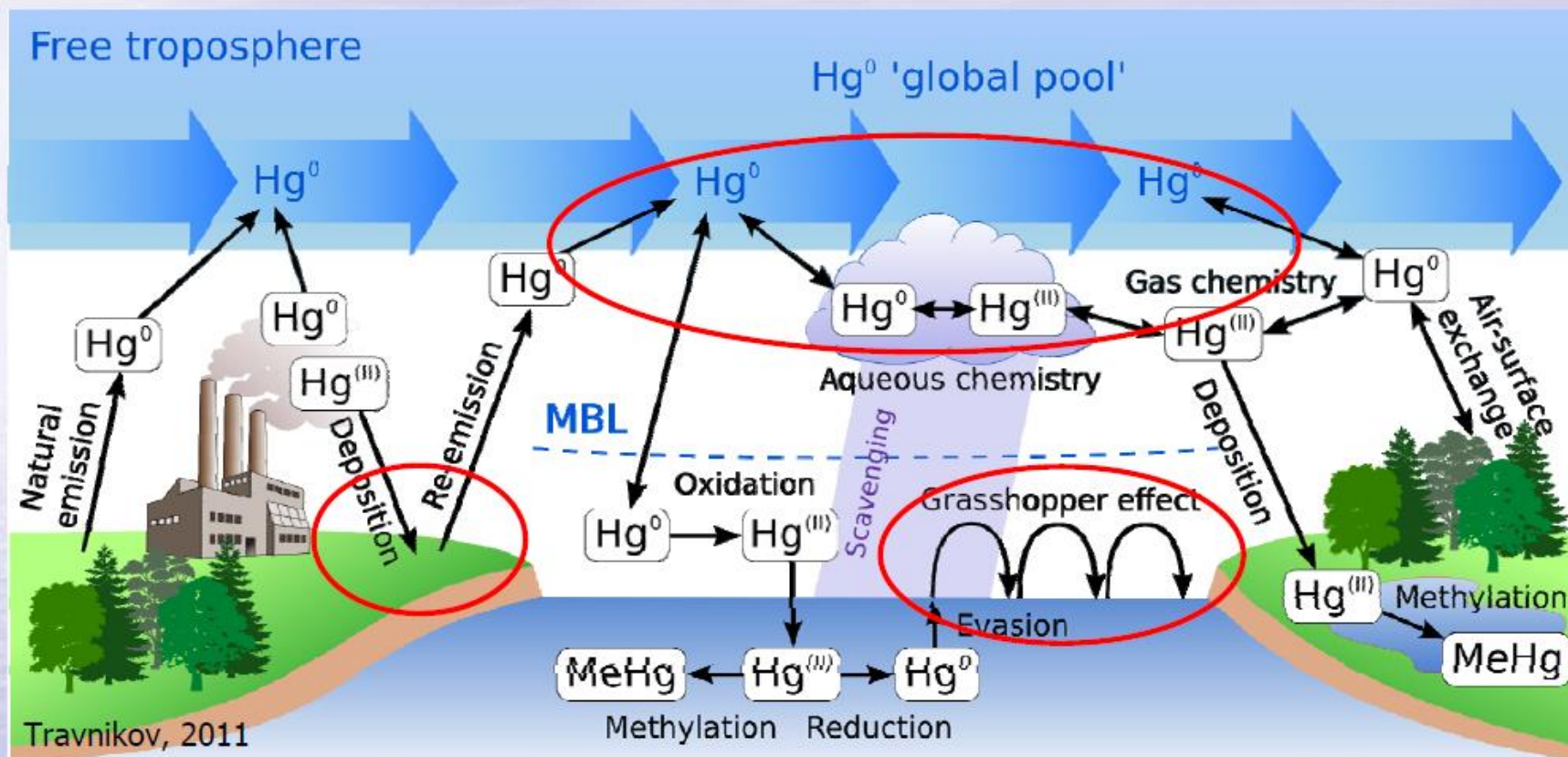
Quelle: EMEP 2012

# Long-range mercury transport

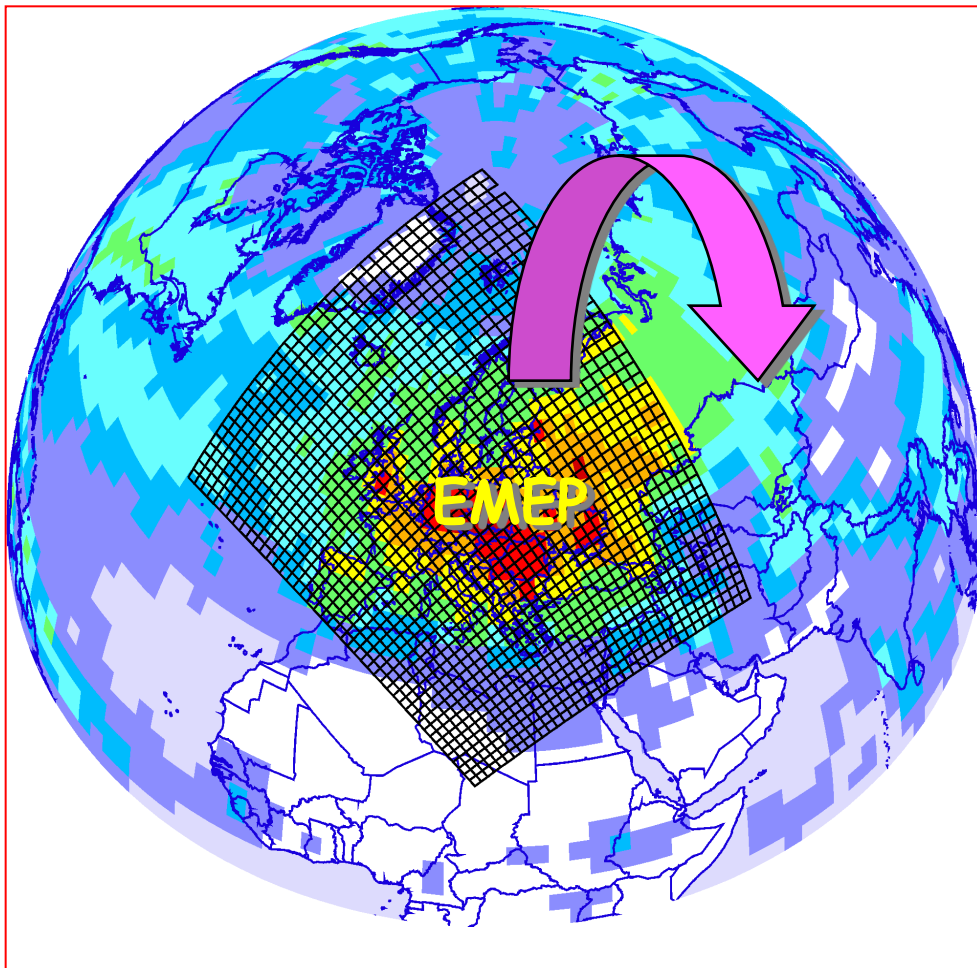


# Hg - interkontinentální transport

## Hg intercontinental transport



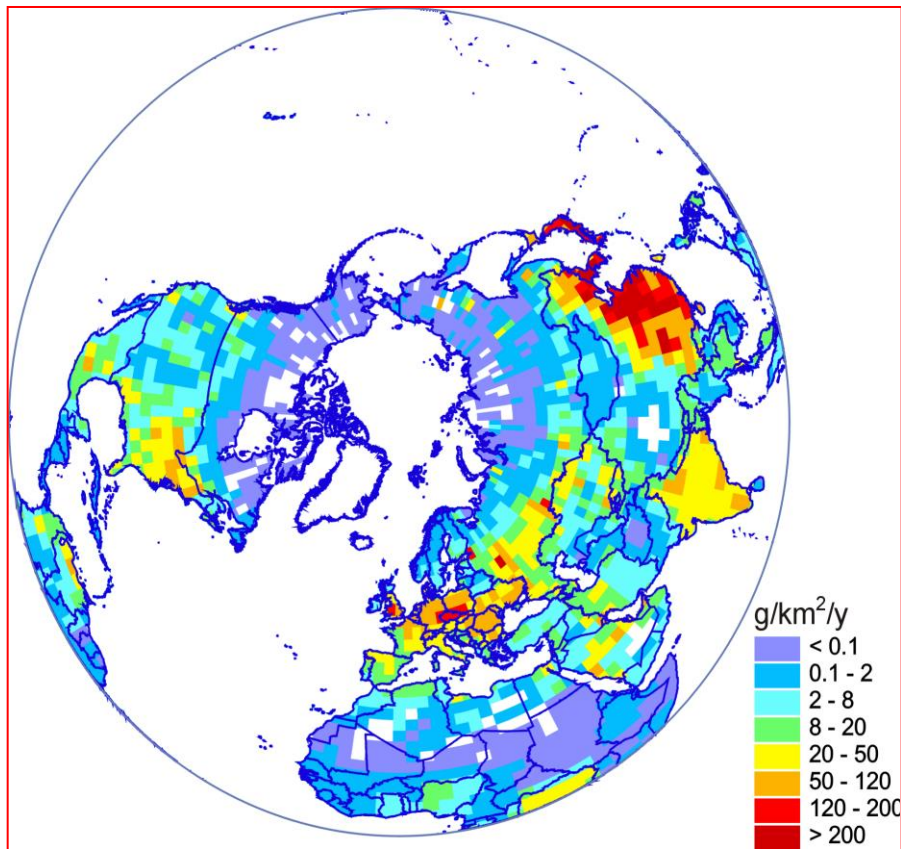
# Transport Hg mimo region EMEP



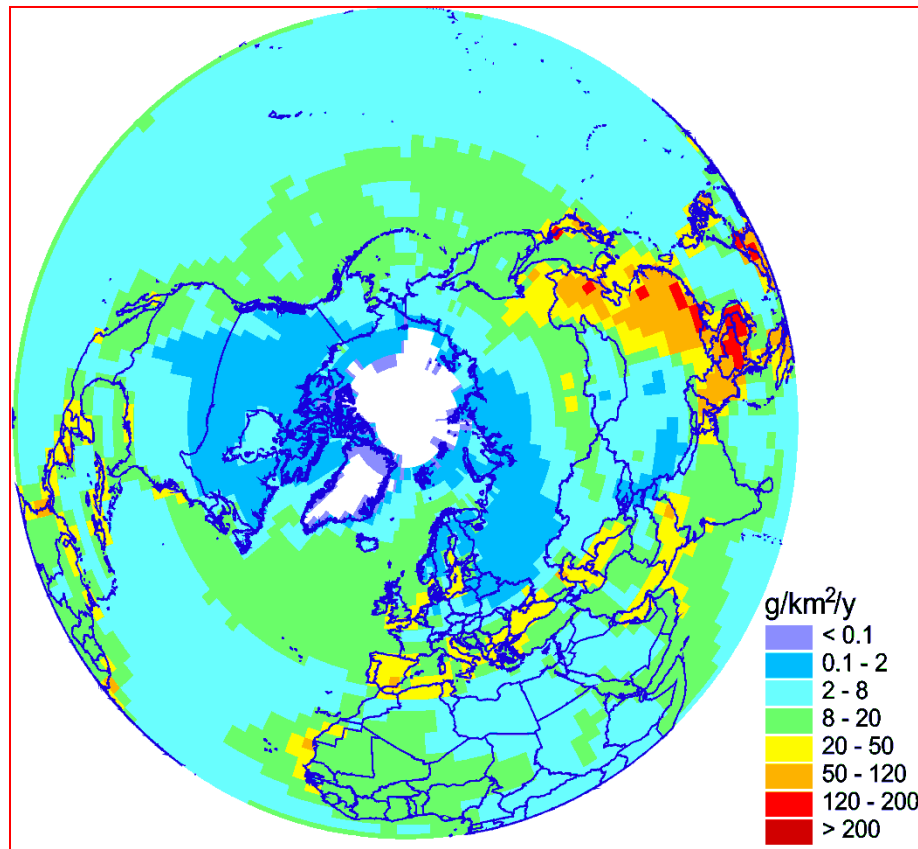
~ 60% antropogenních  
emisí Hg



# Emise Hg na severní polokouly

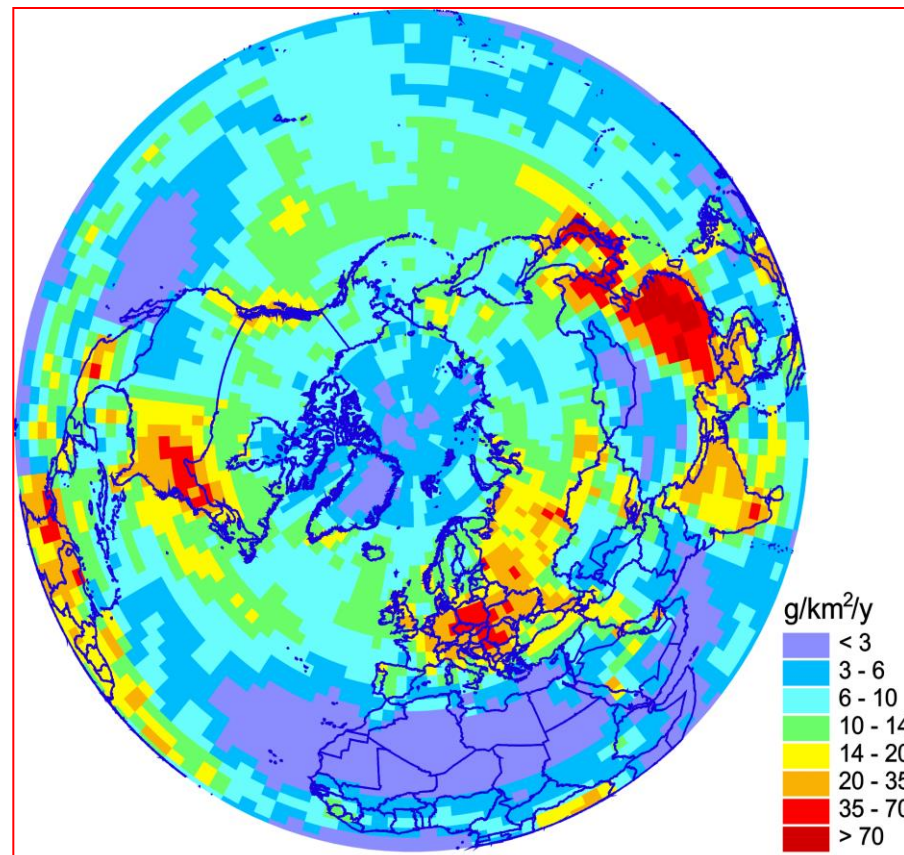
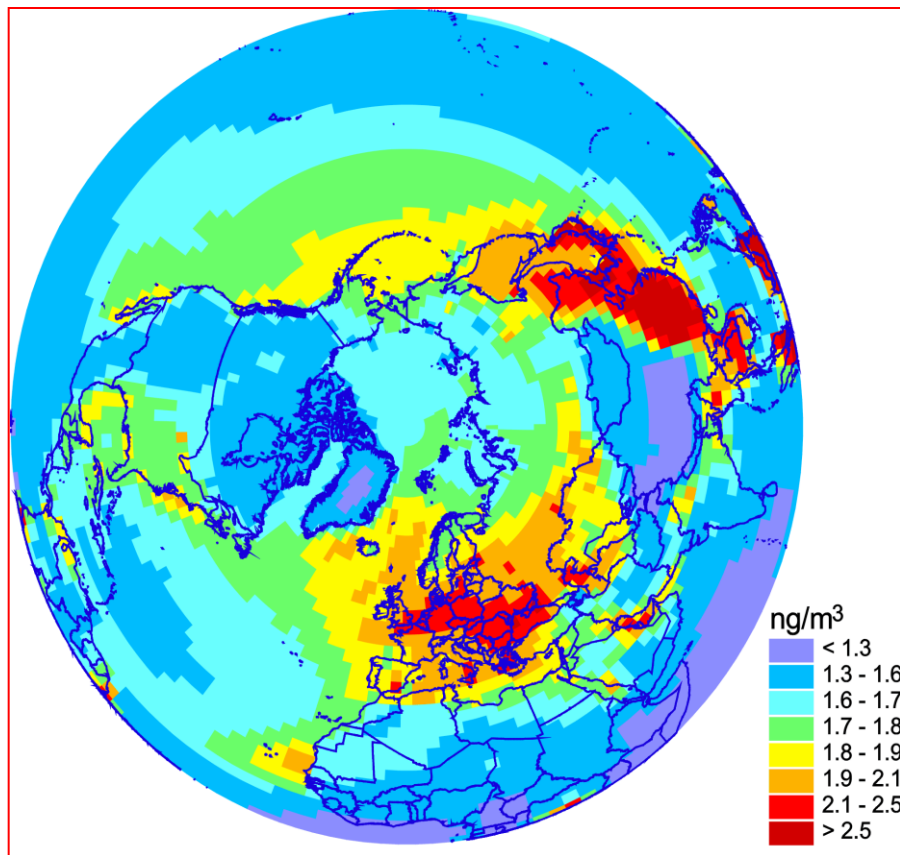


**Hg antropogenní emise**  
(dle AMAP)



**Hg přírodní emise**  
(odhad MSC-E)

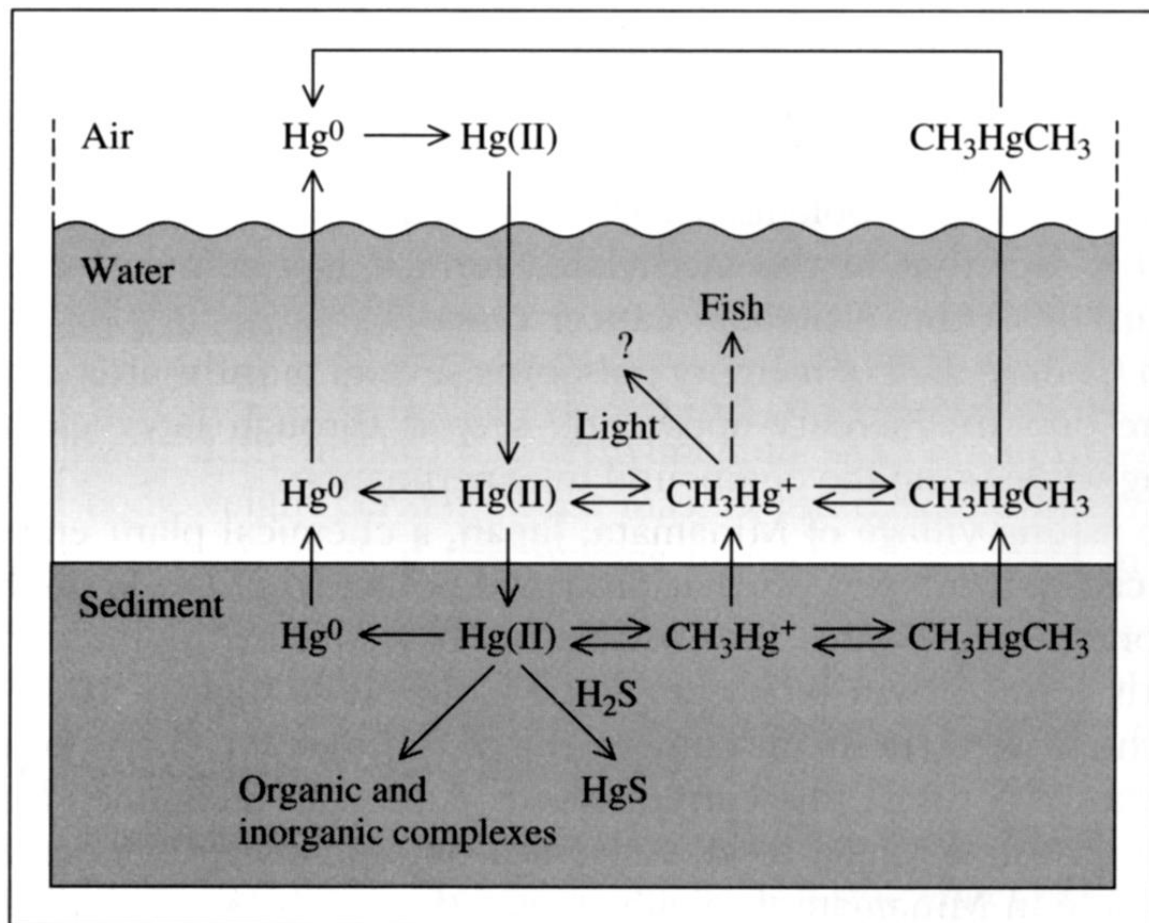
# Transport Hg - severní polokoule



Roční průměrná koncentrace  
celkové plynné Hg

Celková hustota roční  
depozice Hg

# Cyklus Hg v jezerech



**Figure 7-3**

The cycling of mercury in freshwater lakes. (Source: Adapted from M. R. Winfrey and J. W. M. Rudd. 1990. Environmental factors affecting the formation of methylmercury in low pH lakes. *Environmental Toxicology and Chemistry* 9: 853–869. Copyright 1990. Reprinted with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1AB, England.)

# Residua Hg v játrech švédských ptáků

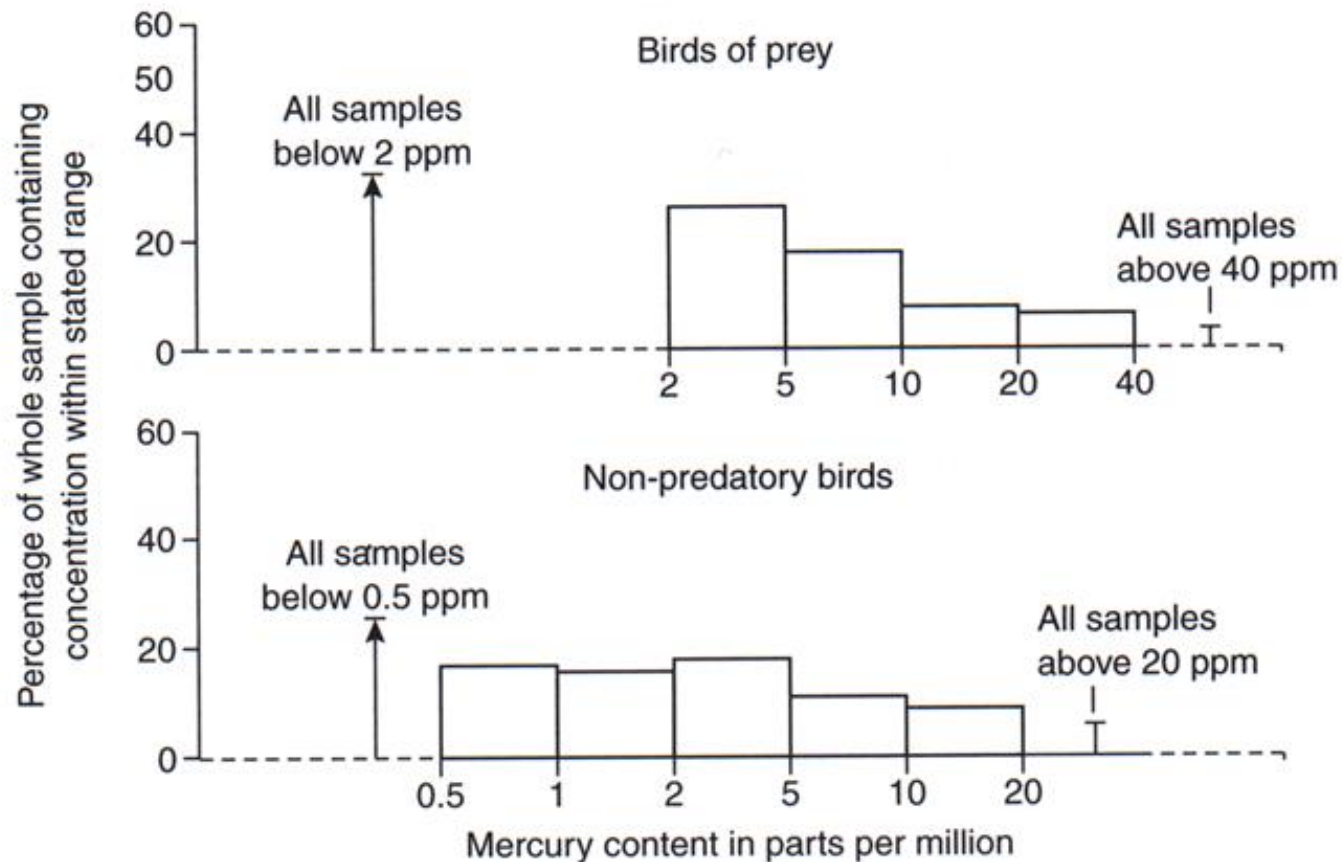
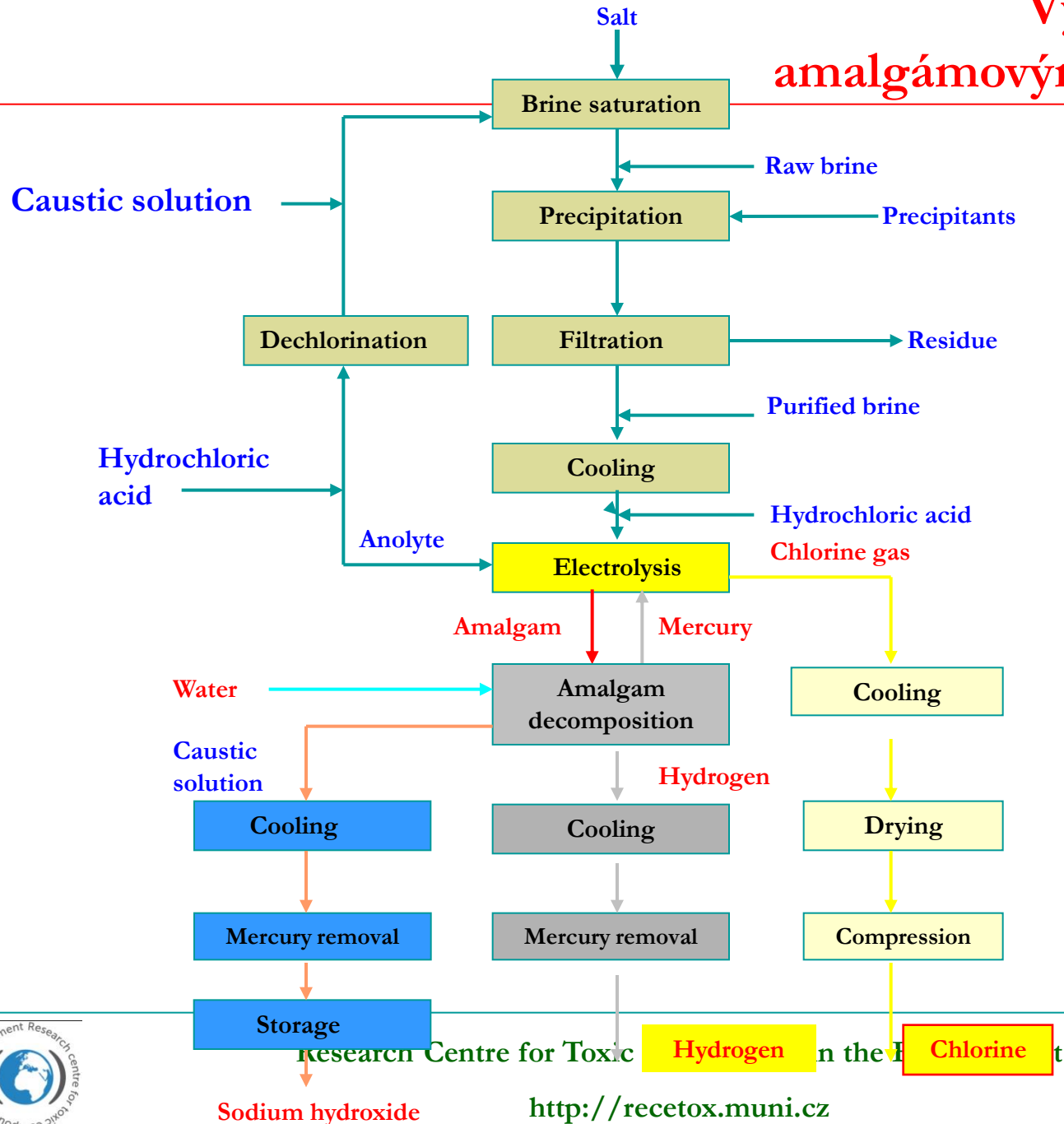


FIGURE 8.4 Mercury residues in the livers of Swedish birds. From Walker (1975).

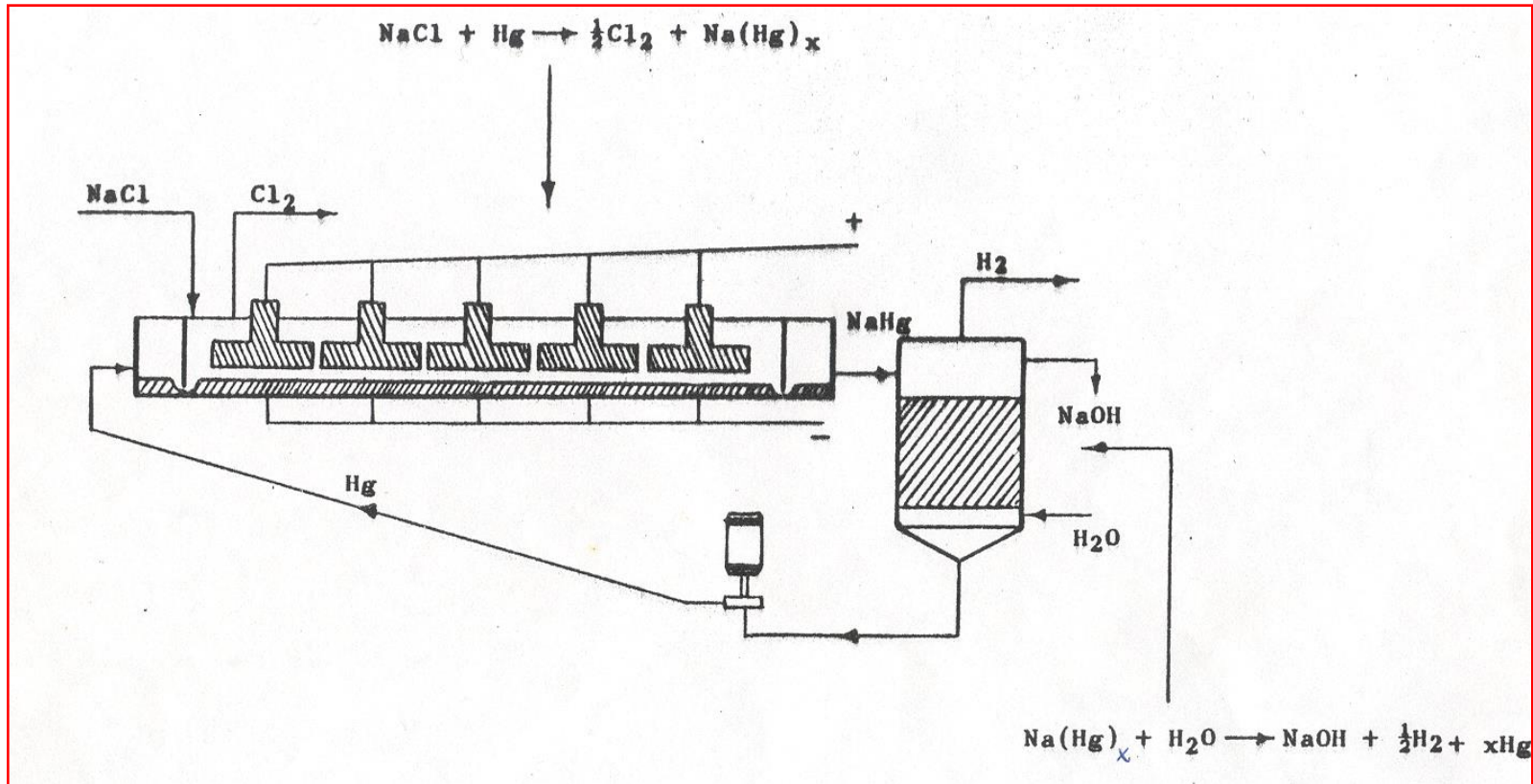
Výroba chloru  
amalgámovým  
způsobem v Itálii



# Výroba chloru amalgámovým způsobem



# Výroba chloru amalgámovým způsobem



Průměrné ztráty Hg  $\approx$  2,1 g Hg/t Cl<sub>2</sub>

- 0,1 g Hg/t Cl<sub>2</sub> ve vodách
- 0,5 g Hg/t Cl<sub>2</sub> v produktech
- 1,5 g Hg/t Cl<sub>2</sub> do ovzduší

# Nové trendy ve výrobě chloru

## Membránový proces

### Výhody:

↪ Bezrtuťový proces

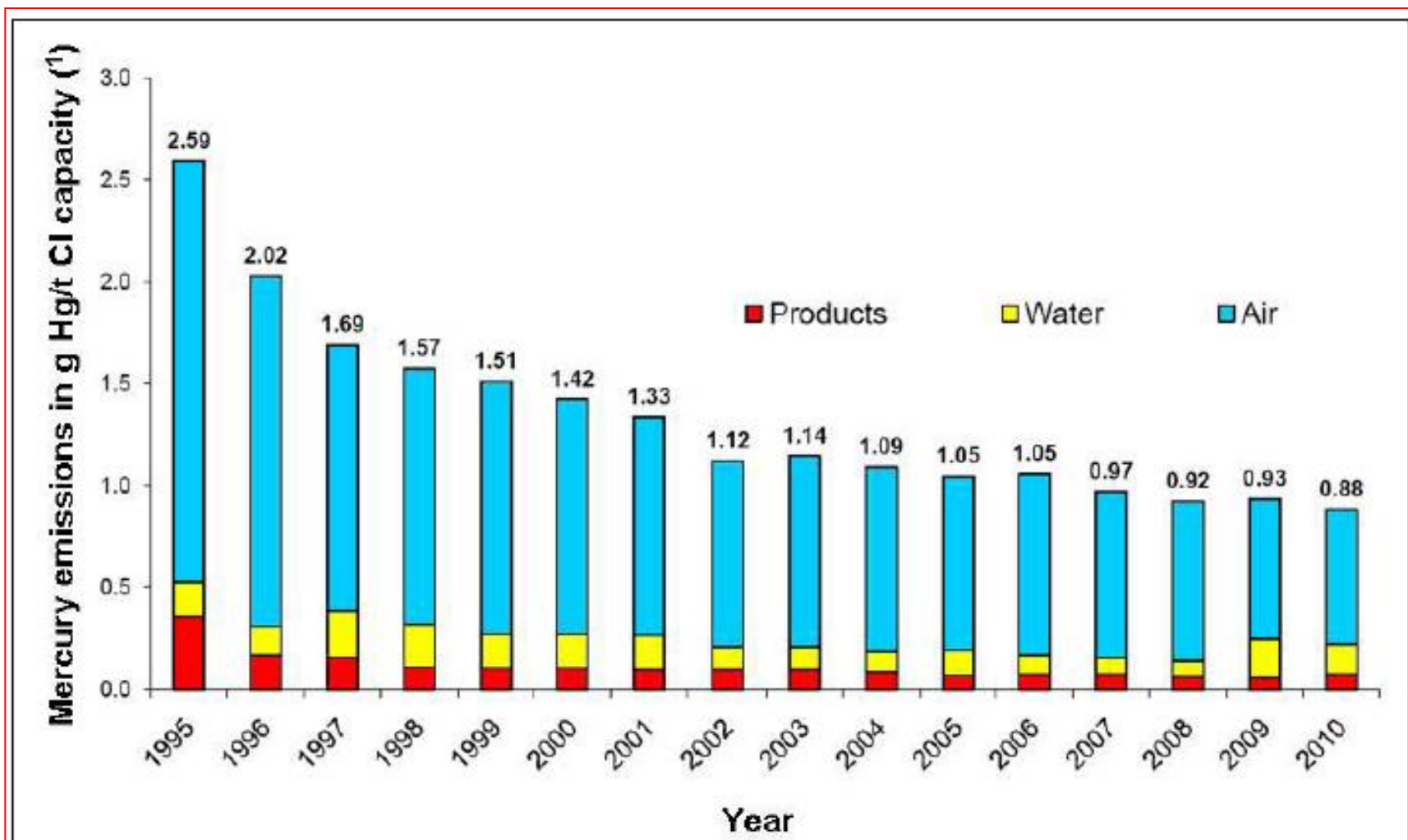
### Nevýhody:

↪ Vysoké pořizovací náklady

↪ Vysoké provozní náklady



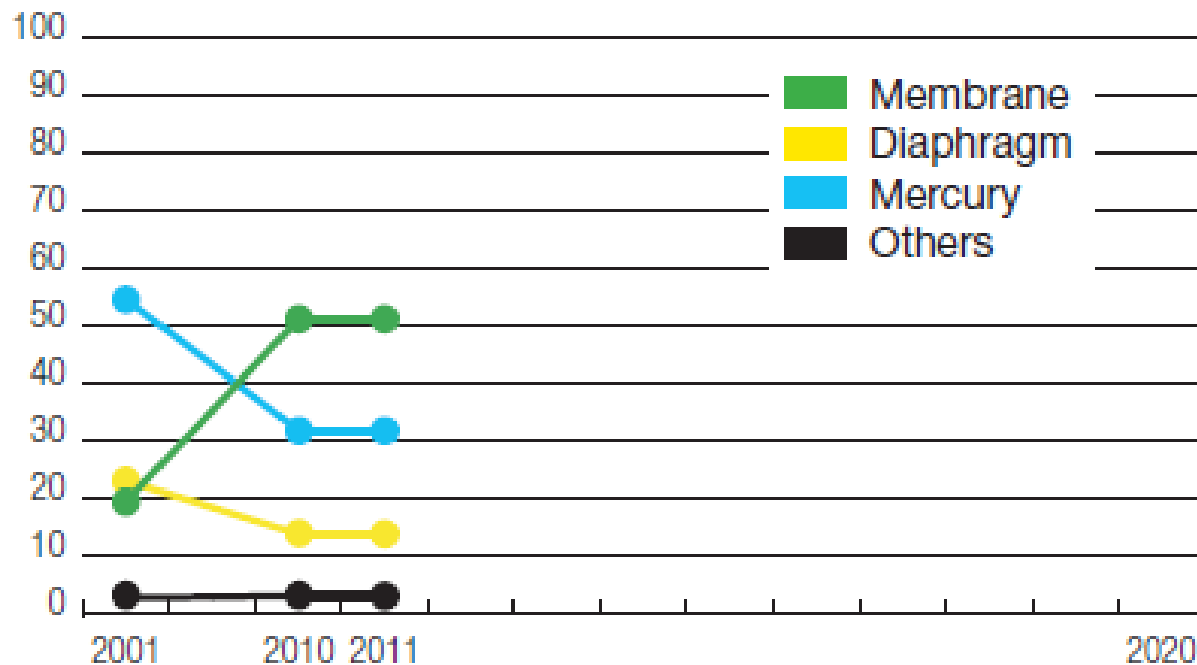
# Trend of mercury emissions (weighted averages) from mercury cell chlor-alkali plants in EU-27 and EFTA countries as reported by Euro Chlor



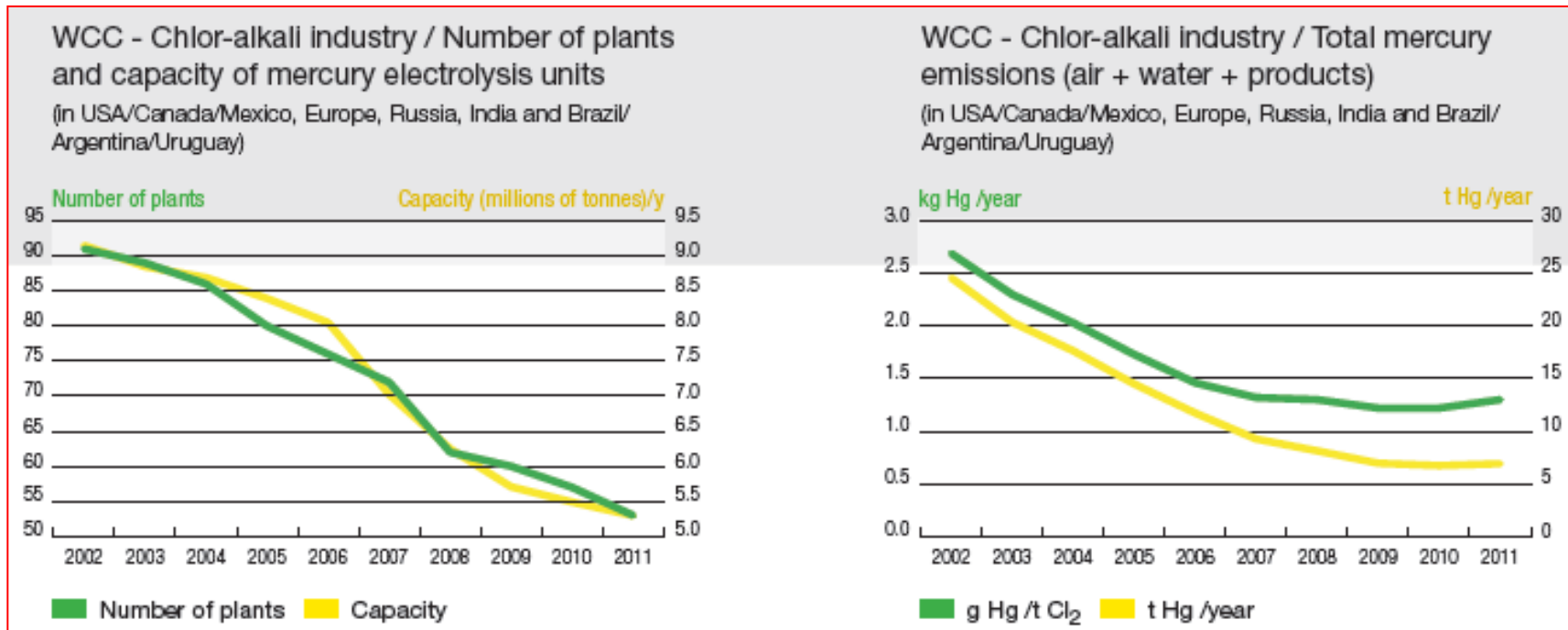
# Chlor-Alkali Production in Europe

## Chlorine manufacturing technologies

(% of total installed capacity)



# Chlor-Alkali Production - world



## WCC – World Chlorine Council

- ↪ The number of plants went down from 91 to 53 over the period 2002-2011 (-42%) and the mercury cell-based capacity from 9.1 million tonnes to 5.3 million tonnes (-42%).
- ↪ Global mercury emissions went down from 24.6 tonnes per year to about 6.9 tonnes, or 72 % decrease over the ten years of reporting by WCC. The emissions expressed in g mercury/ tonne annual chlorine capacity show a similar trend.

# Spolana Neratovice – former production of chlorine



# Life-cycle of Hg product or process

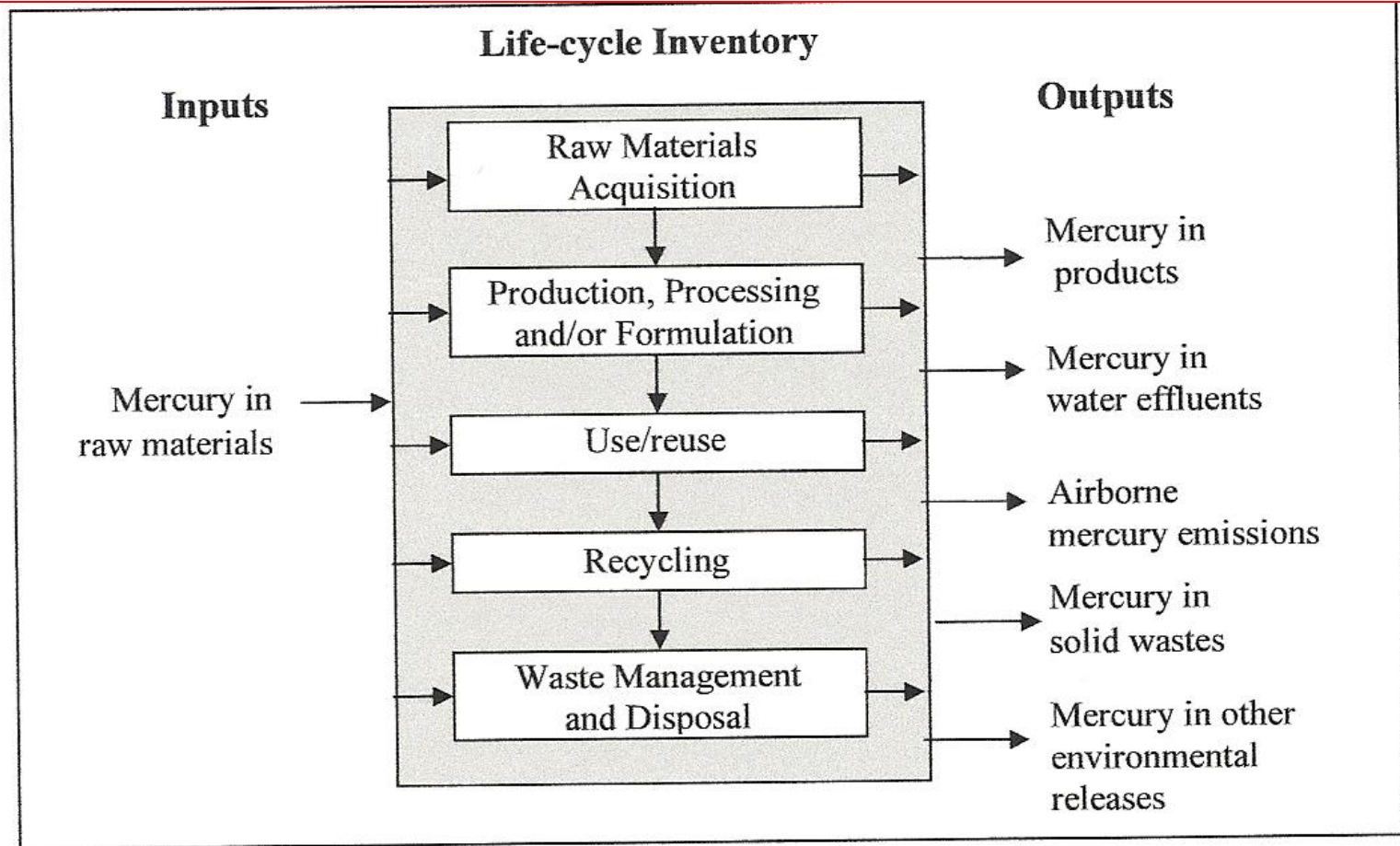


Figure 3-2 Illustration of a life-cycle inventory broken down into inputs and outputs for material as well as environmental releases

# Case Minamata (1953 – 1973), Japan

50's and 60's – Japan – mass poisoning by Hg and its compounds.

The first surrounding of Bay Minamata in 1953.

During the following three years was confirmed that the primary source is connected with the wastewaters from chemical company Chisso-Nippon Chemical Plant (production of acetaldehydes, vinylchlorides), which were released more than 30 years to this bay with high contents of Hg compounds, which were on water and sediments transformed to methylated form.

Mono- and dimethylmercury concentrated in plankton and via bioaccumulation in fish were transferred to human bodies.

# Case Minamata (1953 – 1973), Japan



# The UNECE Convention on Long-range Transboundary Air Pollution

- ↪ UNECE – Geneva Convention
- ↪ 8 protocols (POPs, Gothenburg P, Heavy Metals)
- ↪ Negotiations since early 70's
- ↪ 1998 HMP adopted, in force since 29.12.2003, 31 Parties
- ↪ Aims:
  - to control emissions of HMs caused by anthropogenic activities subject to long-range transboundary atmospheric transport, and
  - to reduce the significant adverse effects on human health and environment
- ↪ Basic obligations:
  - emission reduction compared to base year
  - emission limit values (ELVs) for dust
  - use of BAT
  - No lead in petrol
  - management measures for products
  - recommendation for reducing emissions from dental amalgam



# What is different for point sources in comparison to the future Hg Convention?

## Concerning point sources:

### ↪ Different Definition of BAT

...taking into account economic and technical considerations for a given party or a given facility within the territory of that party...

### ↪ Different source categories

### ↪ Higher capacity thresholds

### ↪ Different ways to reduce emissions

- ☞ adopt a [national] goal [or target or outcome] for controlling and/or reducing emissions to the atmosphere from these sources (either in aggregate or by source category;
- ☞ establish emission limit values (or equivalent technical measures to be applied to these installations),
- ☞ require the use of BAT/BEP at these installations.
- ☞ apply multi-pollutant control strategies

### ↪ Guidelines to assist Parties to reduce emissions are developed later

# Sampling of Hg emissions



Sampling of mercury emissions at the Kendal coal-fired power plant in South Africa, conducted under a UNEP project.

A probe with mercury traps is inserted into a sampling port in the stack to collect mercury present in the flue gas.

The mercury traps are subsequently analysed according to the US EPA Mercury Monitoring Toolkit sampling protocol.

# Atmospheric monitoring of Hg

Monitoring of mercury in air focuses on the three primary forms of mercury.

The measurement of gaseous elemental mercury is routine and robust.

Measuring gaseous oxidized mercury and particulate-bound mercury, however, is challenging.

Concentrations are typically very low, and these forms are chemically unstable, leading to high uncertainty in the measurements.

Nonetheless, these forms are critical for defining and modelling the fate and transport of airborne mercury.

In the past two decades, coordinated mercury monitoring networks and long-term monitoring sites have been established in a number of regions, measuring mercury concentrations in the air as well as deposition of mercury in precipitation.

In Europe and North America, high-quality, continuous monitoring has been going on for more than 15 years, especially in the Arctic. High quality monitoring has started more recently in East Asia and South Africa, as part of a global effort to expand the coverage provided by long-term monitoring sites.

# Atmospheric monitoring of Hg

Monitoring stations around the world have provided information about trends in atmospheric mercury, though the time periods vary depending on how long the site has been active.

Overall, a declining trend in background mercury levels over the past decade has been recorded from monitoring stations in many regions.

Other regions, however, show an increase in mercury levels.

The sites also provide information about geographical patterns, reflecting both background levels of mercury and local and regional influences.

Mercury concentrations at remote sites in Asia are higher than in other regions of the Northern Hemisphere.

Coastal cities in China have lower levels than inland sites, likely due to the influence of relatively clean air over the ocean.

# Atmospheric Hg trends

## *Trends in atmospheric measurements of mercury*

<i>Site(s)</i>	<i>Period</i>	<i>Measurement</i>	<i>Trend</i>
Mace Head, Ireland	1996-2011	Gaseous elemental mercury	Decrease of 1.4-1.8% per year
North America, rural sites	1995-2005	Total gaseous mercury	Decrease of 2.2% to 17.4% in total
High Arctic, sub-Arctic, mid-latitudes	Up to 20 years of records	Total gaseous mercury	Decreasing trend at some stations, increasing at others

# Atmospheric Hg monitoring programmes

## The European Monitoring and Evaluation Programme (EMEP)

Three monitoring networks currently operate in North America, providing good coverage of Canada and the United States: the Mercury Deposition Network, the Canadian Air and Precipitation Monitoring Network, and the Atmospheric Mercury Network. More recently, new sites have been established in Mexico, extending coverage on the continent. Monitoring of mercury in the air and in precipitation has been underway in Asia for nearly a decade.

The monitoring network of the Arctic Monitoring and Assessment Programme (AMAP) includes air and deposition monitoring sites located in Arctic regions of Canada, Greenland, Iceland, Norway, Russia, and Sweden.

# Atmospheric Hg monitoring programmes

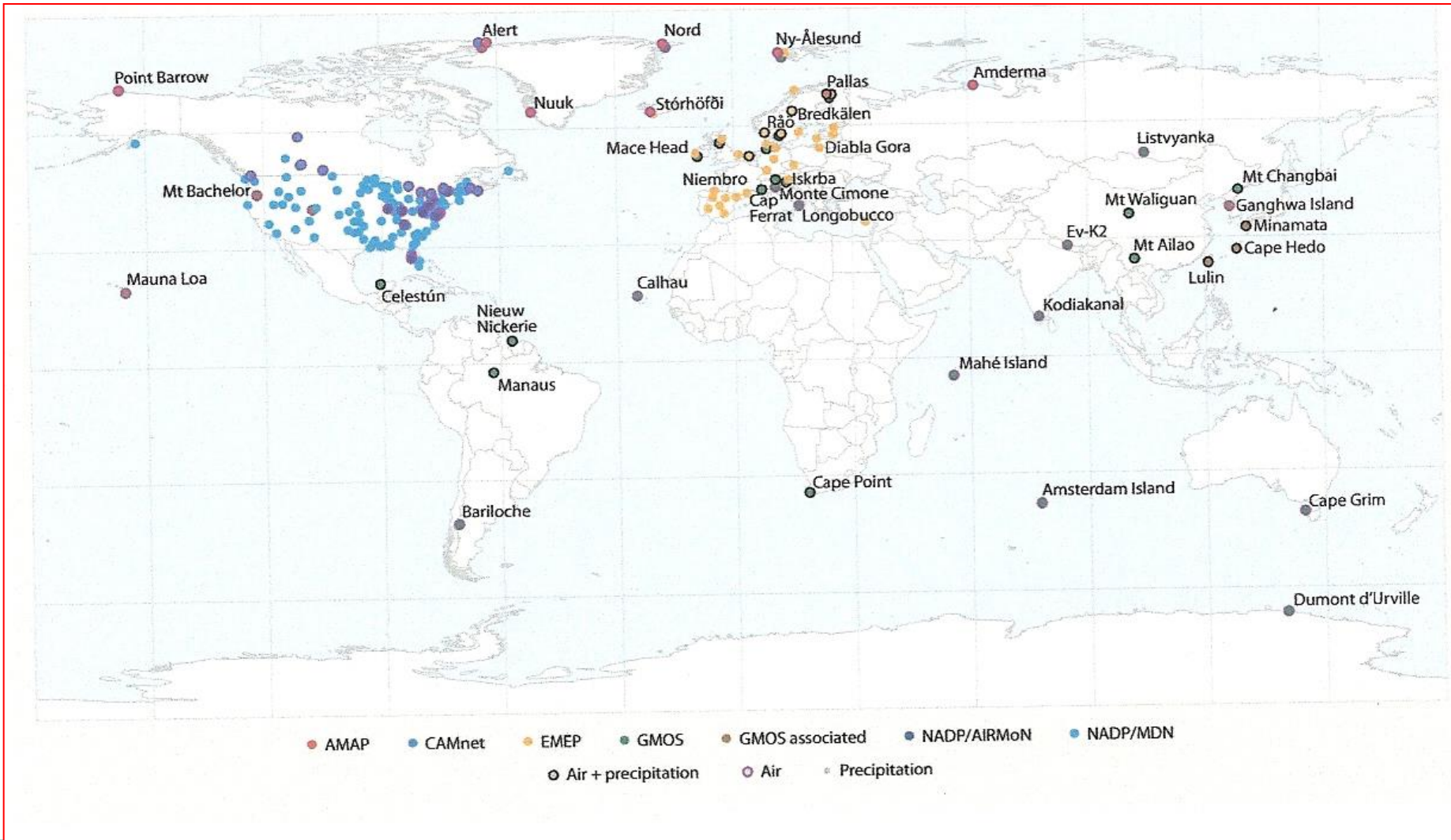
Building on existing national and regional monitoring networks, the European Union-financed project “**Global Mercury Observation System**” (GMOS) started in November 2010.

Its goal is to develop a coordinated global system for monitoring mercury, including a large network of ground-based monitoring stations.

New sites are being installed in regions where few monitoring stations exist, especially in the Southern Hemisphere.

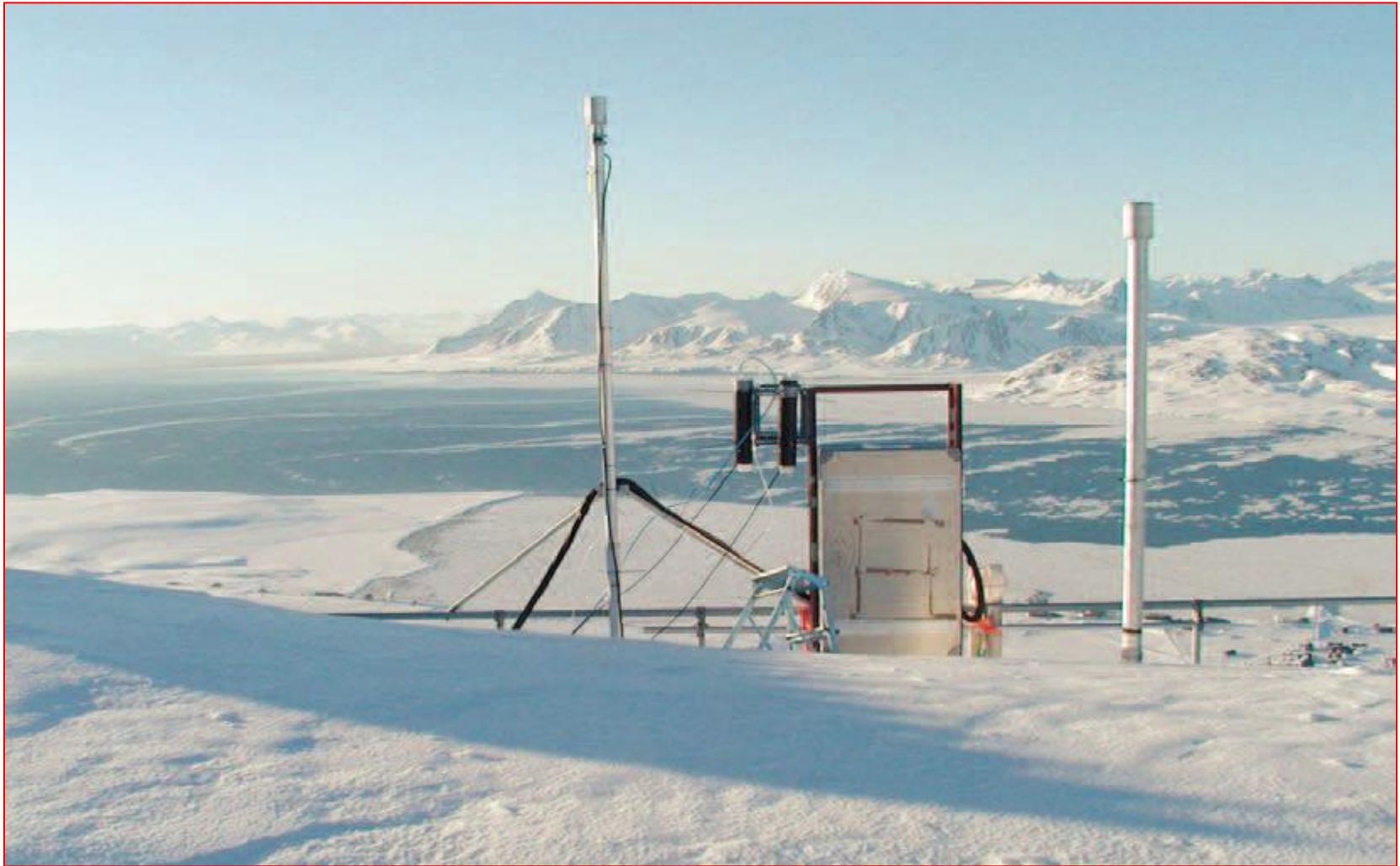
Two sites have been established in Antarctica, one on the Antarctic Plateau and one on the coast.

# Hg monitoring networks





# The mercury background air monitoring station at Zeppelin mountain, Svalbard



# Mercury Export Ban

**Regulation (EC) No 1102/2008 of the European Parliament and of the Council of 22 October 2008 on the banning of exports of metallic mercury and certain mercury compounds and mixtures and the safe storage of metallic mercury (Text with EEA relevance)**

# EU Chemical Policy - REACH

**Regulation (EC) No 1907/2006** of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

- ↪ Adopted on 30/12/2006
- ↪ Gradual entry into force
- ↪ REACH replaces about 40 pieces of EU legislation including some on mercury, specifically
- ↪ Applies to all chemicals
- ↪ Industry responsible to manage risks posed by chemicals
- ↪ European Chemicals Agency (ECHA) with a central coordination and implementation role in the overall process.

# Mercury in REACH

**Annex XVII** – refers to restrictions on the manufacture, placing on the market and use of 52 different groups of dangerous substances

- a) Contains **mercury compounds**
- b) As of 1 June 2009 will also contain provisions related to the EU Directive 76/769/EEC on restrictions on the marketing and use of certain dangerous substances and preparations as amended

# Control measures

- ↪ **Compliance with the requirements** – nationally (various bodies required to inspect (environmental inspections, hygiene institutes, COI) and evaluate national reports
- ↪ **EU level** – based on national reporting, verified by measurement and values from national and European registers – if not in compliance – infringements or fines
- ↪ **Directive 2007/51/EC** of the European Parliament and of the Council of 25 September 2007 amending Council Directive 76/769/EEC relating to restrictions on the marketing of certain measuring devices containing mercury (Text with EEA relevance)

# Unresolved issues by EU legislation

- ↪ **Dental amalgam** – review ongoing, phase down/ban in some cases of EU countries
- ↪ **Button cell batteries** – alternatives available, but collection scheme may be resource intensive

# Main sources of mercury releases and main control options

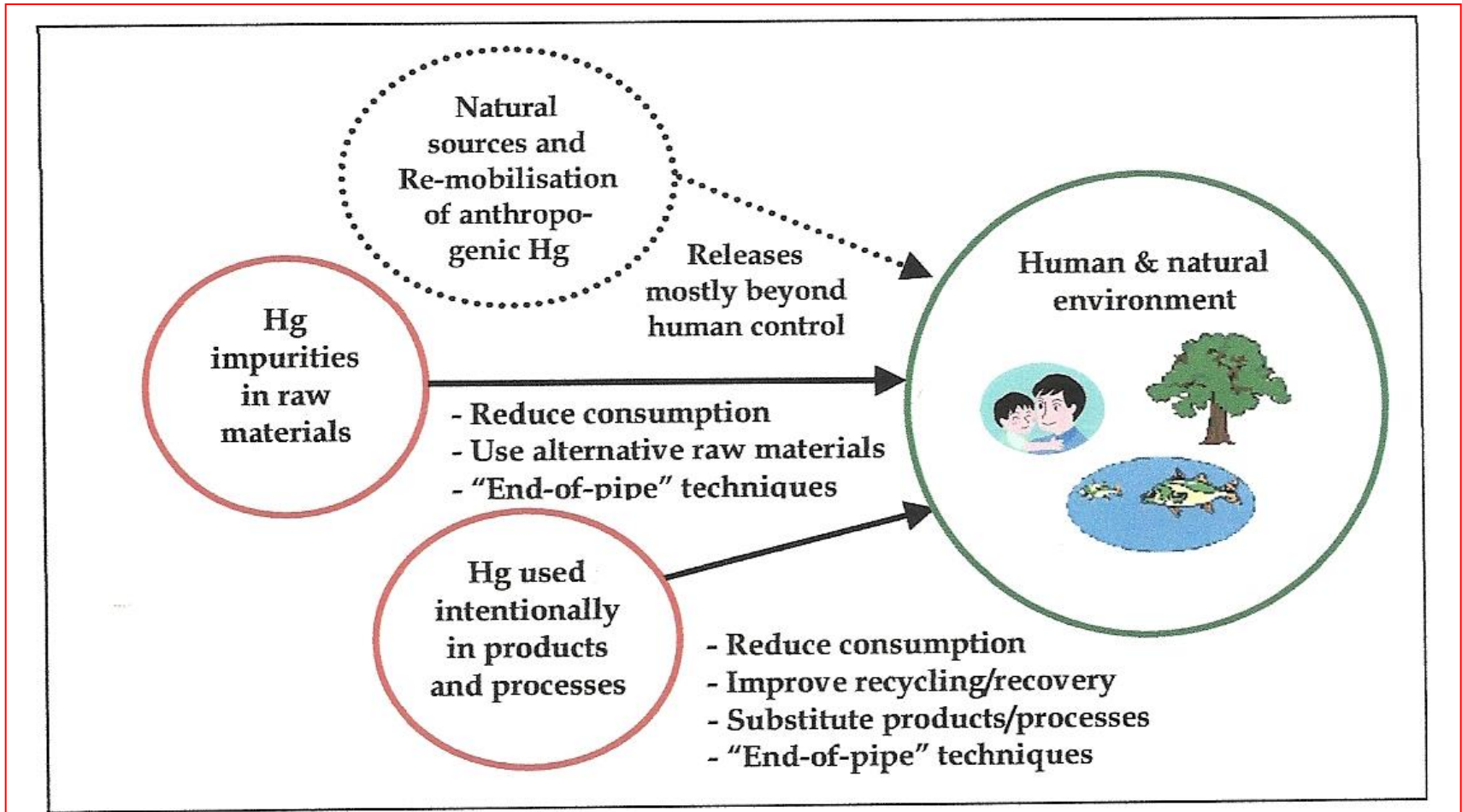
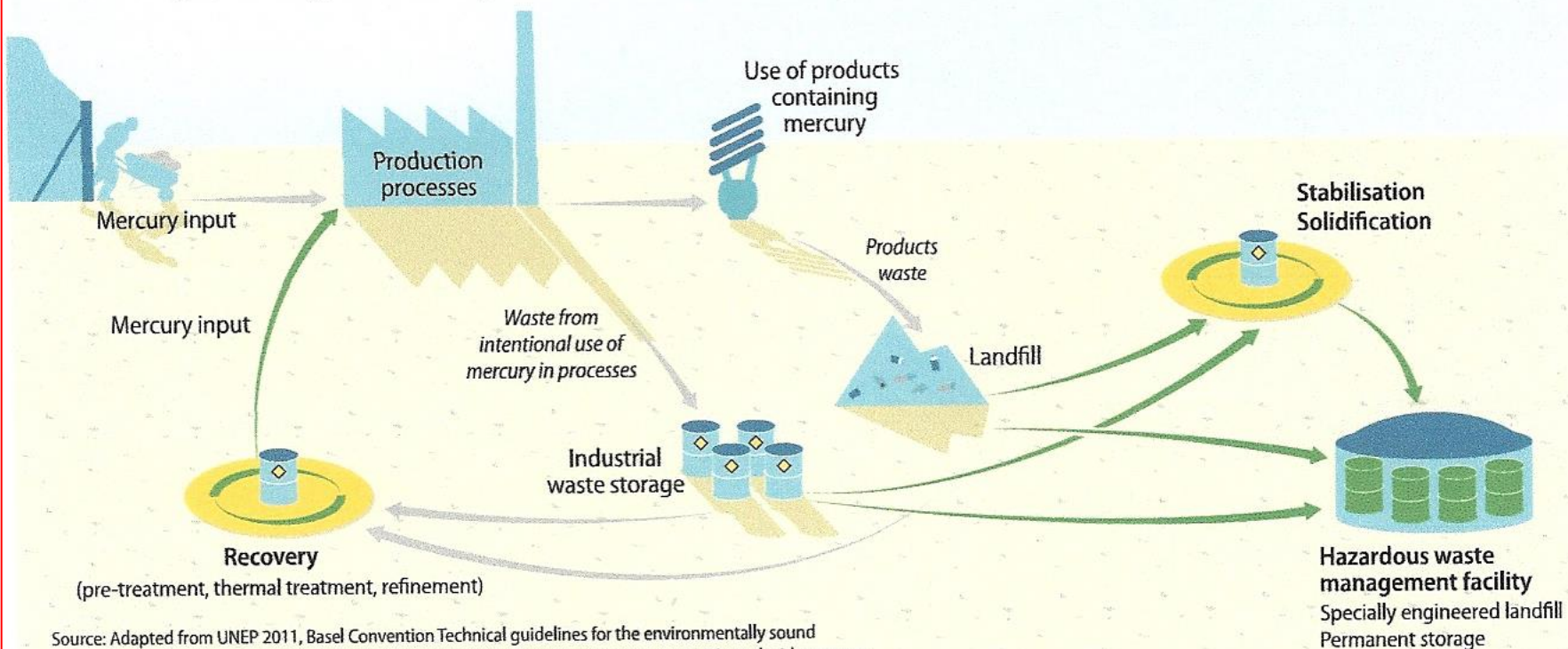


Figure 3-1 Main sources of mercury (Hg) releases to the environment and main control options

# Mercury management options

## Mercury management options



Source: Adapted from UNEP 2011, Basel Convention Technical guidelines for the environmentally sound management of wastes consisting of elemental mercury and wastes containing or contaminated with mercury  
Designed by Zoi Environment Network / GRID-Arendal, December 2012



# Chlor-Alkali Production - mercury

- ↪ Chlor-alkali industry largest EU user of mercury
- ↪ Chlor-alkali industry largest source of mercury exports
- ↪ Focus on mercury as a global pollutant
- ↪ Mercury process is not BAT

## Mercury in the chlor-alkali industry:

- ↪ Air and water emissions
- ↪ Site contamination
- ↪ Excessive concentrations off-site

# Mercury waste management

Waste containing mercury = hazardous waste – 9 catalogue nr.

## Production of specific waste containing mercury

Type of waste	Ton - 2010
Construction and demolition waste containing mercury	150
Waste from inorganic chemical processes	135
Fluorescent tubes and other mercury-containing waste	135
Amalgam waste from dental care	2

## Mercury waste production

year	2009	2010	2011
ton	454,8	440,1	675,8

Research Centre for Toxic Compounds in the Environment

<http://recetox.muni.cz>

# Collection in the Czech Republic



Compact fluorescent lamps



Straight fluorescent lamps



+ Gas discharge lamps



# Collection in the Czech Republic



- ↪ Mercury is included in a white CaO powder
- ↪ Lapms are collected in cardboard boxes, which are specially designed to prevent smash of lapms



# Treatment - feeding



Inside special machines



Staff feeds lamps into special grips by lamp cap



Straight fluorescent lamps



Gas discharge lamps

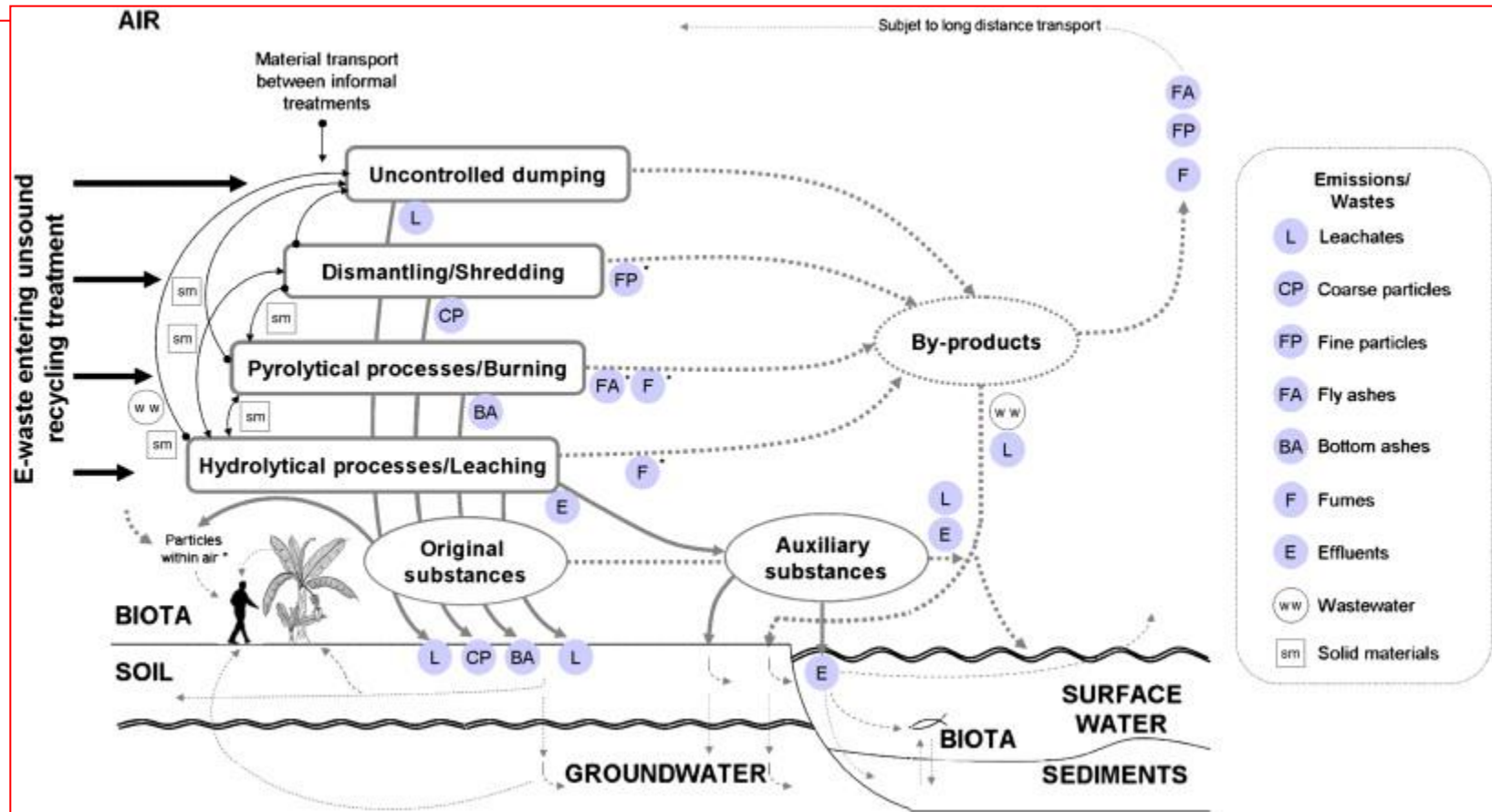
# Treatment - depollution



- ↪ The machine breaks off lamp caps
- ↪ Shredding of glass, milling



- ↪ Milled glass is feeded into furnace, mercury is converted into gas, exhausted into condenser and cooled
- ↪ Glass is afterwards cleaned
- ↪ Viable market for mercury: producers of fluorescent lamps
- ↪ In line with Basel guidance



Principal WEEE recycling activities in China and India, types of produced emissions and general environmental pathways. Ovals: types of substances contained within emissions. Continuous bold lines: fate of original and auxiliary substances. Dotted bold lines: fate of by-products such as dioxins and furans. Black arrows with a bold dot: material transport fluxes between treatments. Fine dashed arrows: general environmental pathways. Environmental fluxes are driven by processes as atmospheric deposition (dry/wet), leaching, adsorption–desorption, complexation (by which heavy metal and cyanide secondary products can be formed), uptake, degradation (chemical/biological) and volatilization. In addition, the environmental fate of pollutants depends on the physico-chemical properties of the media.