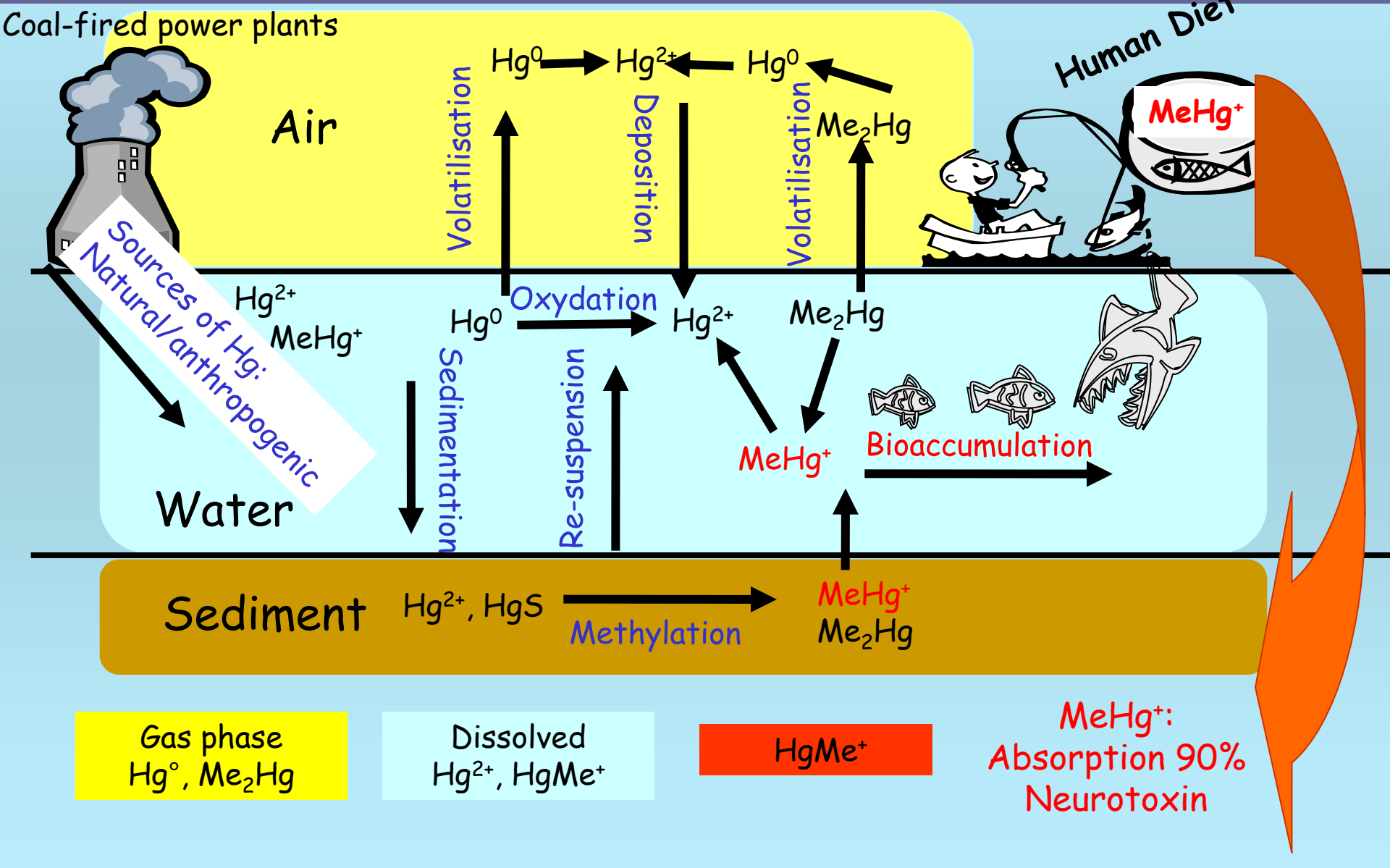
Mercury

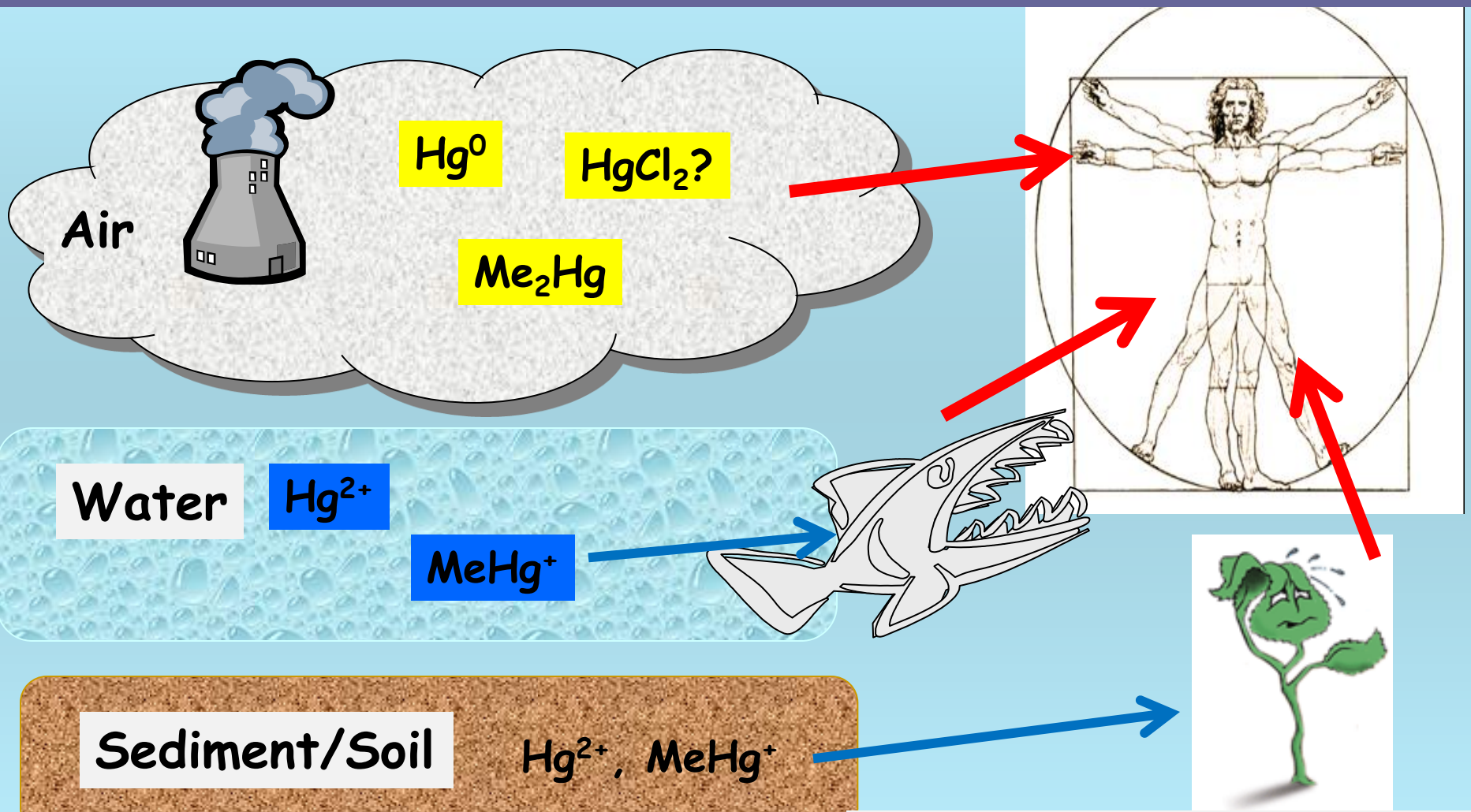
- No known essential biological function
- Industrial use: mercury switches, thermostats, thermometer, medications, preservatives (e.g. as *Thimerosal* in vaccines), antiseptics, pesticides…
- Amalgamates with gold and silver: use in mining and as a dental fillings
- Geogenic as ore (Cinnabar) and as trace element in coal: Partition of volatile Hg into air during coal combustion
- High-level Hg exposure produces serious neurological problems in adults and in children born to mothers with high mercury levels

❖ **Mercury is a global pollutant!**

The Aquatic Mercury Cycle



Hg Species of Interest – Occurrence, Exposure and Analytical Challenge

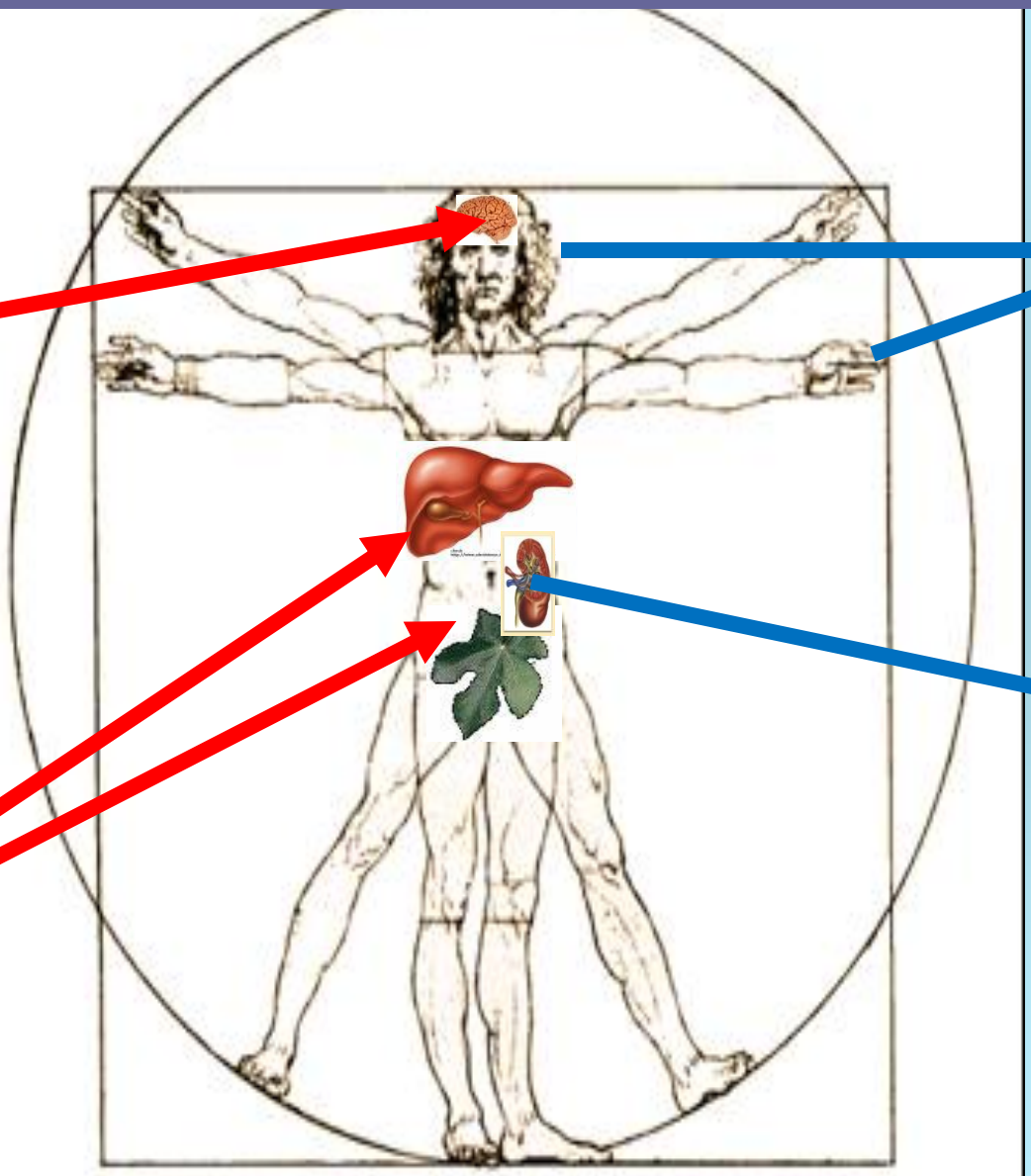


Toxicity of Hg species: Target Organs

IN

Hg (organic): HgMe, $HgMe_2$, HgEt…

Hg (inorganic)



OUT

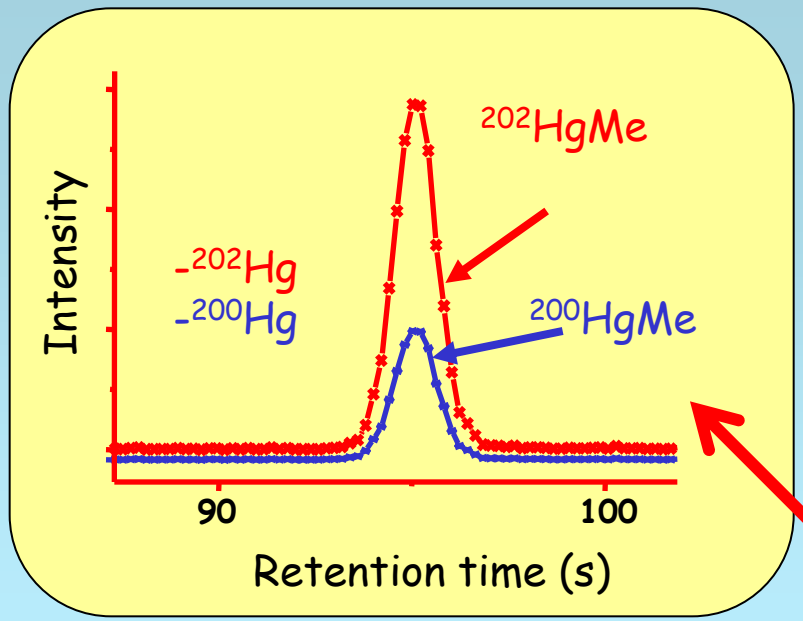
Hg (organic): Hair, fingernails

Hg (inorganic) Urine, Faeces

Focus on Hg speciation: MeHg

(Since Minamata in the 1950's)!

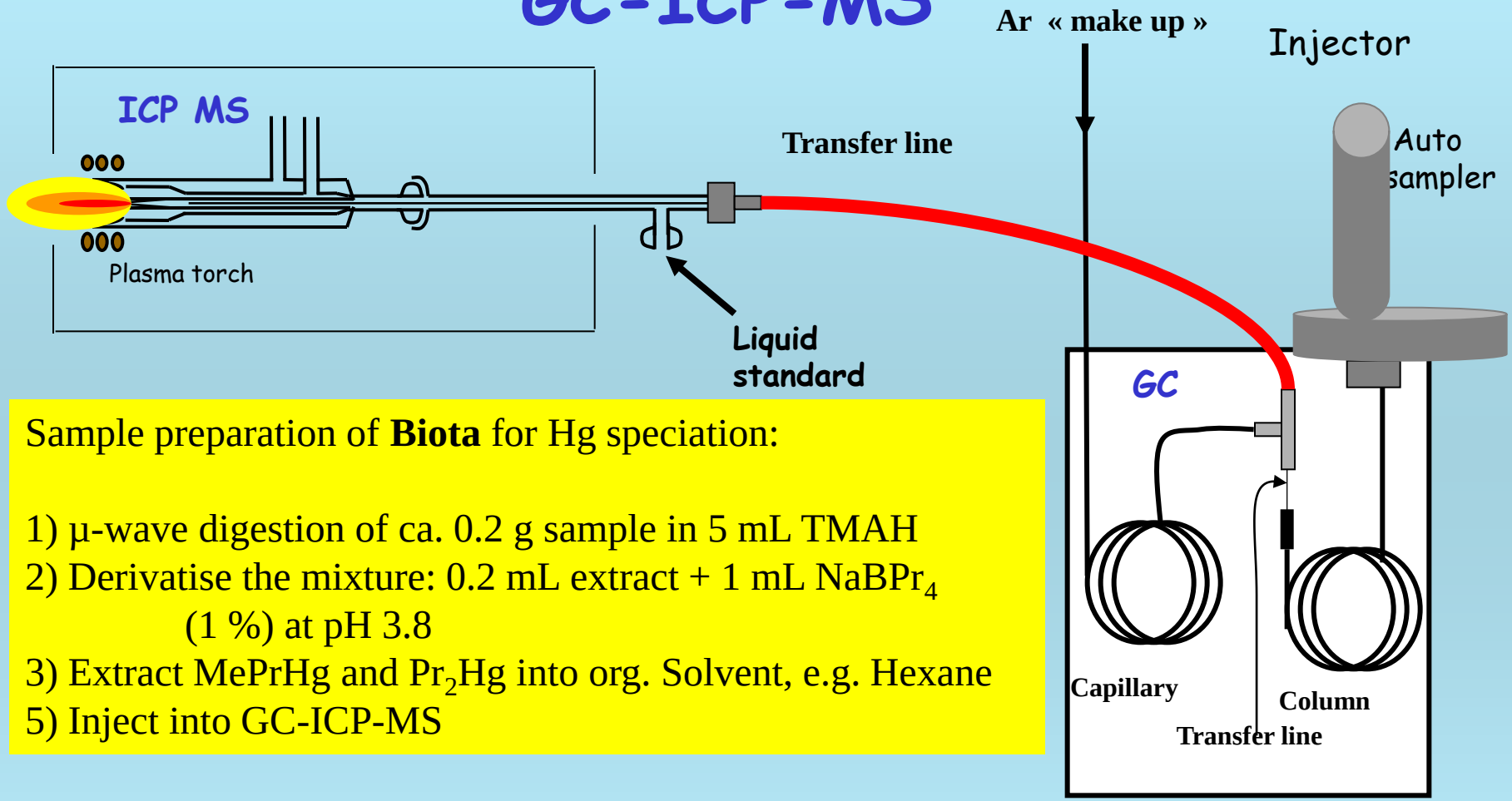
- Methylmercury speciation methods, eg:
  derivatisation with $NaBPr_4$ ($MeHg^+$ → MeHgPr)
  followed by Gas Chromatographic separation and
  Hg-specific detection (Pyro-AFS or ICP-MS)



- Highly selective
- Most sensitive
  (LOD in the
  femtogram range!)
- Highly precise
- Highly accurate

GC-ICP-MS

Useful method for Hg/HgMe speciation: GC-ICP-MS



Sample preparation of **Biota** for Hg speciation:

1) µ-wave digestion of ca. 0.2 g sample in 5 mL TMAH
2) Derivatise the mixture: 0.2 mL extract + 1 mL $NaBPr_4$ (1 %) at pH 3.8
3) Extract MePrHg and Pr_2Hg into org. Solvent, e.g. Hexane
5) Inject into GC-ICP-MS

Ethylation of mercury species with $NaBEt_4$:

$$MeHg^+ + NaBPr_4 \longrightarrow MePrHg$$

$$Hg^{2+} + NaBPr_4 \longrightarrow Pr_2Hg$$

Sample preparation for Hg speciation: Hg^{2+} vs $HgMe^{+}$ in soil/sediments

Challenge: High amounts of Hg^{2+} versus traces of $MeHg^{+}$ (1%) - artefact production of MeHg from Hg2+ due organic matter during sample preparation

Strategy:

Separation of Hg and HgMe by extraction

- **take 3 mL sample extract/digest**
- **add 1.5 mL CH_2Cl_2 and 100 µL HCl (conz)**
- **Shake 5 min**
- **Repeat once**
- **Derivatise and analyse the organic extract for MeHg**

Sample preparation for Hg speciation: Focus on Hg^{2+} vs $HgMe^{+}$

Extraction efficiency and species integrity?

- Aim: To transfer all Hg species from the sample matrix (water, biota, sediment...) into a "measurable form", i.e. a liquid for chromatographic species separation

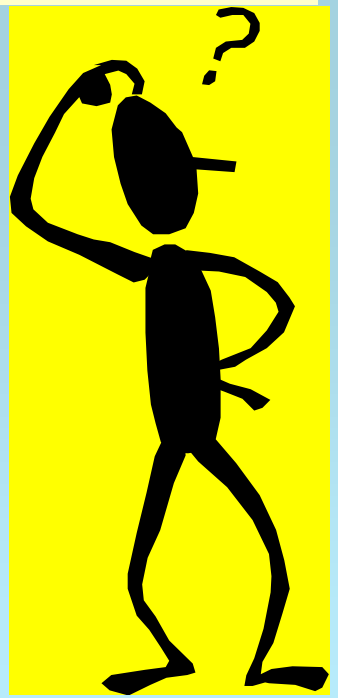
Questions:

- Does the species react quantitatively with the reagent ($MeHg^{+}$ → MeEtHg)?

- Is the derivatization matrix dependant ?

- Is all MeEtHg / Et2Hg extracted quantitatively into the hexane ?

- Is $MeHg^{+}$ stable or does it transform: demethylation of MeHg to Hg^{2+} or Hg^{0}, or formation of Me_2Hg?

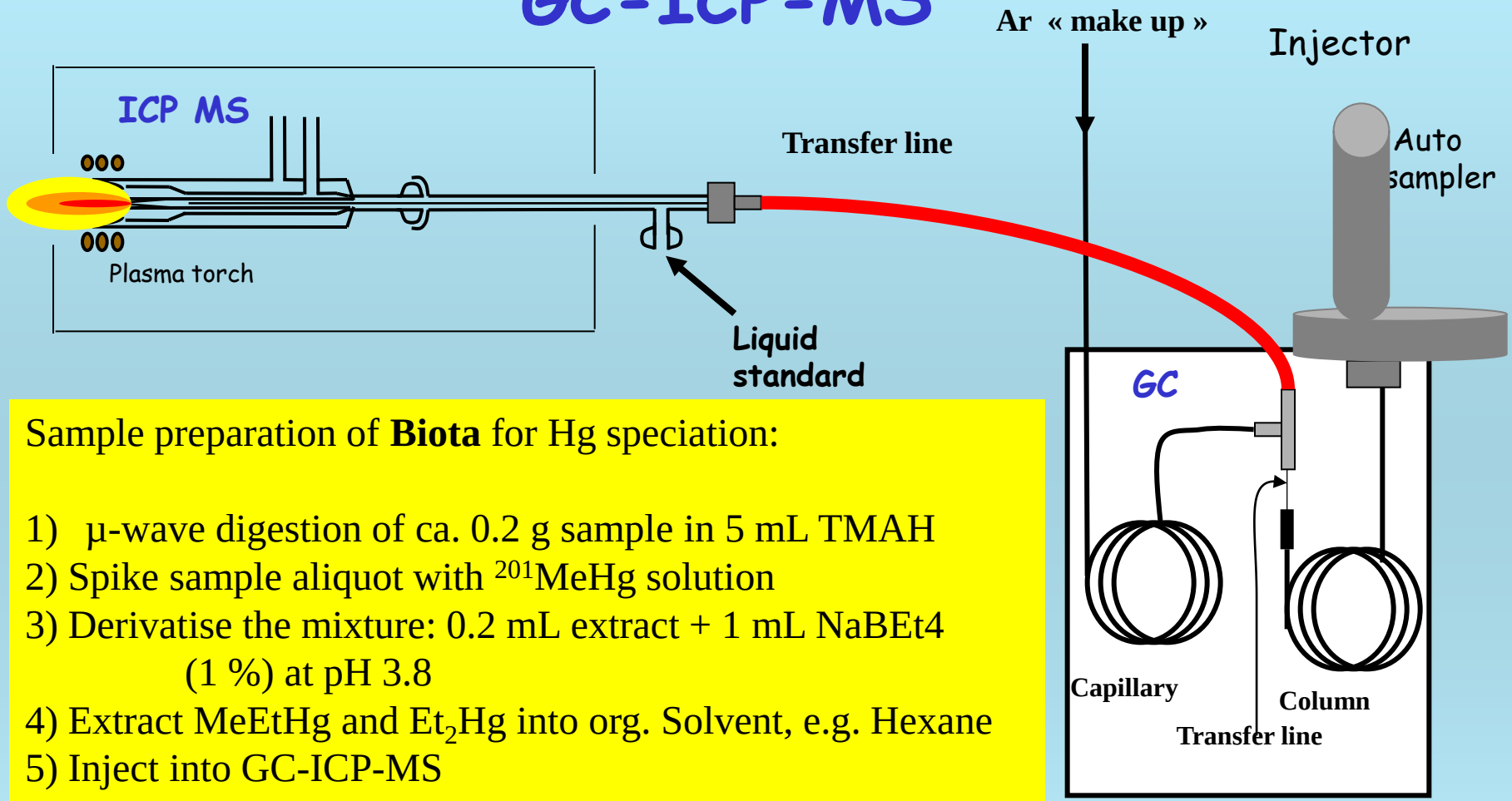


Sample preparation for Hg speciation: The use of stable Hg isotopes

Extraction efficiency and species integrity?

A species-specific isotope spike, i.e. *isotopically labelled* Hg species, can be used to determine and correct for species transformation during sample preparation and analysis

Useful method for Hg/HgMe speciation: GC-ICP-MS



Sample preparation of **Biota** for Hg speciation:

1) µ-wave digestion of ca. 0.2 g sample in 5 mL TMAH
2) Spike sample aliquot with ^{201}MeHg solution
3) Derivatise the mixture: 0.2 mL extract + 1 mL NaBEt4 (1 %) at pH 3.8
4) Extract MeEtHg and Et_2Hg into org. Solvent, e.g. Hexane
5) Inject into GC-ICP-MS

Ethylation of mercury species with $NaBEt_4$:

$$MeHg^+ + NaBEt_4 \longrightarrow MeEtHg$$

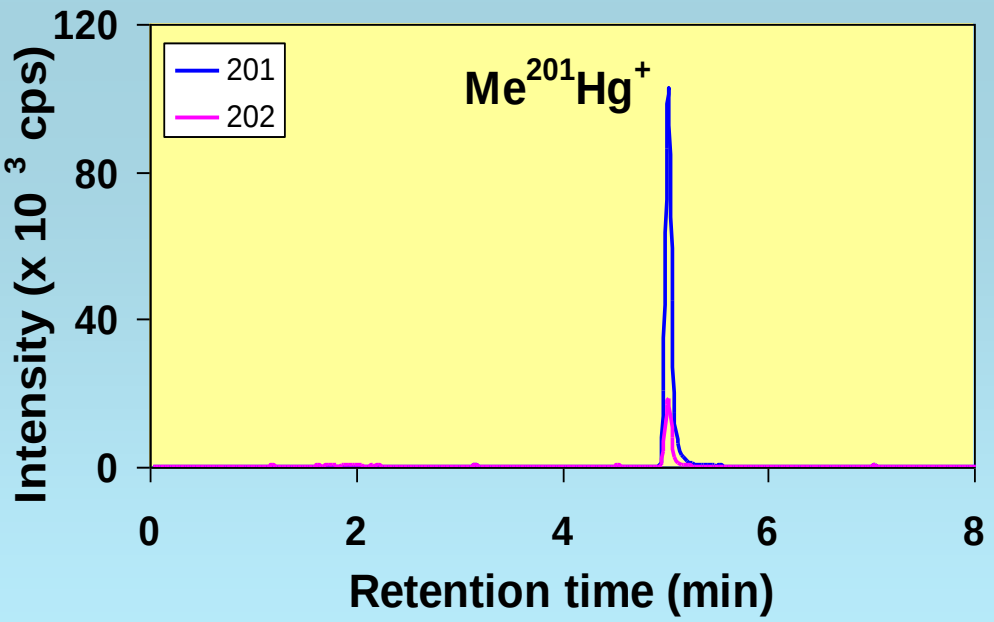
$$Hg^{2+} + NaBEt_4 \longrightarrow Et_2Hg$$

How to produce isotopically labelled MeHg?

$^{201}HgO + 2\ HCl \rightarrow {}^{201}HgCl_2 + H_2O$

$^{201}HgCl_2 + Me\text{-}Co \rightarrow Me^{201}Hg^+$

Me-Co = Methylcobalamin



Spike isotope ratio:

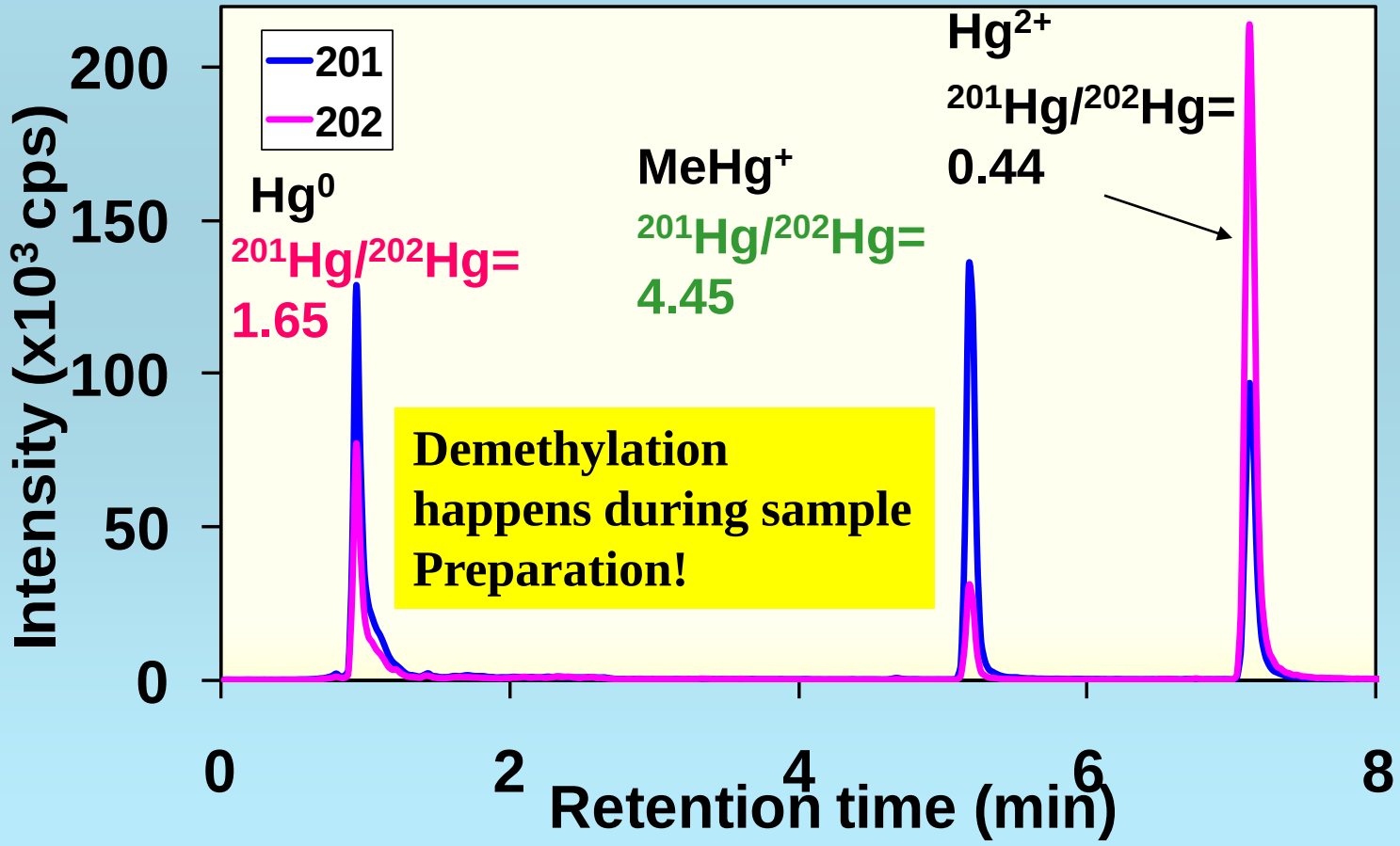
$^{201}Hg/^{202}Hg = 6.53$

(natural ratio = 0.44)

$MeHg^+$ analysis in seawater by CGC/ICP-IDMS using a $Me^{201}Hg^+$ spike

Spike isotope ratio:

$^{201}Hg/^{202}Hg$ = 6.53 (natural ratio = 0.44)



Species integrity during derivatization

- Does the species react quantitatively with the reagent ($MeHg^+$ → MeEtHg)?
- Is the derivatization matrix dependant ?
- Does all MeEtHg get into the hexane ?

→ **If the sample and the ^{201}MeHg spike are homogenised, these problems do not affect the analysis at all !!!**

- Is $MeHg^+$ stable or does it transform: demethylation of MeHg to Hg^{2+} or Hg^0, or formation of Me_2Hg?

→ **The ^{201}MeHg Spike will tell us!!!**

What did we learn from species-specific GC/ICP-IDMS of methylmercury ?

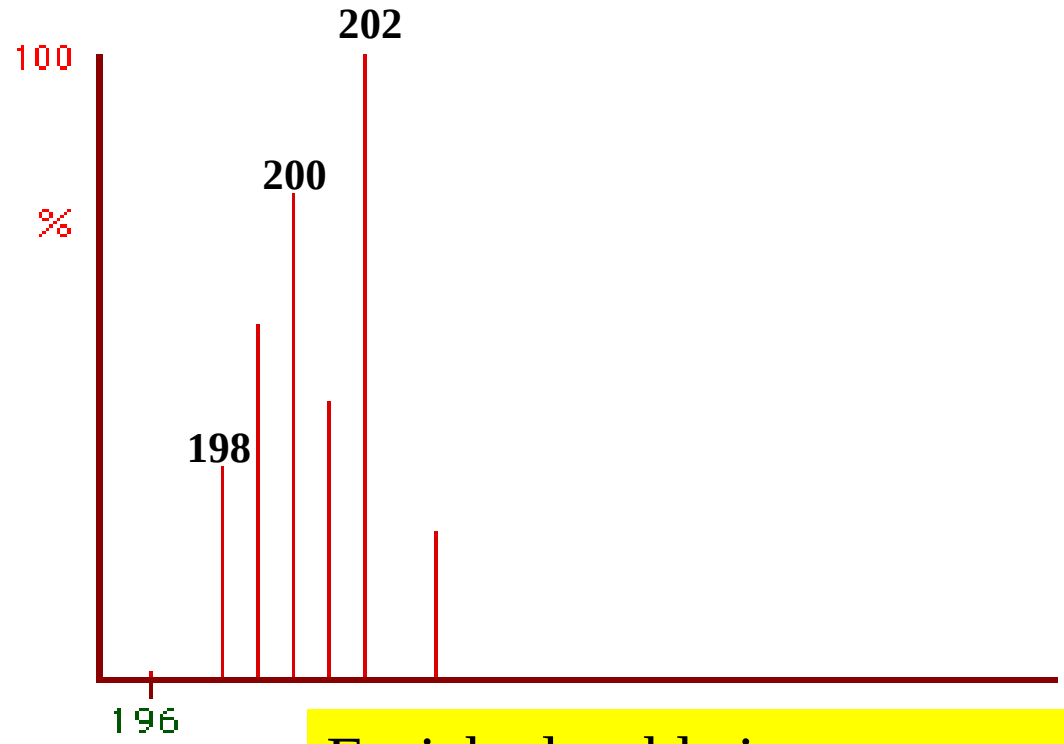
- ☺ The use of isotopically labelled species identifies species transformations
- ☺ Even if species transformation takes place, accurate quantification is possible by species-specific spiking

However, ICP-MS is mandatory!

Isotopic properties of Hg

WebElements

Isotope pattern of mercury

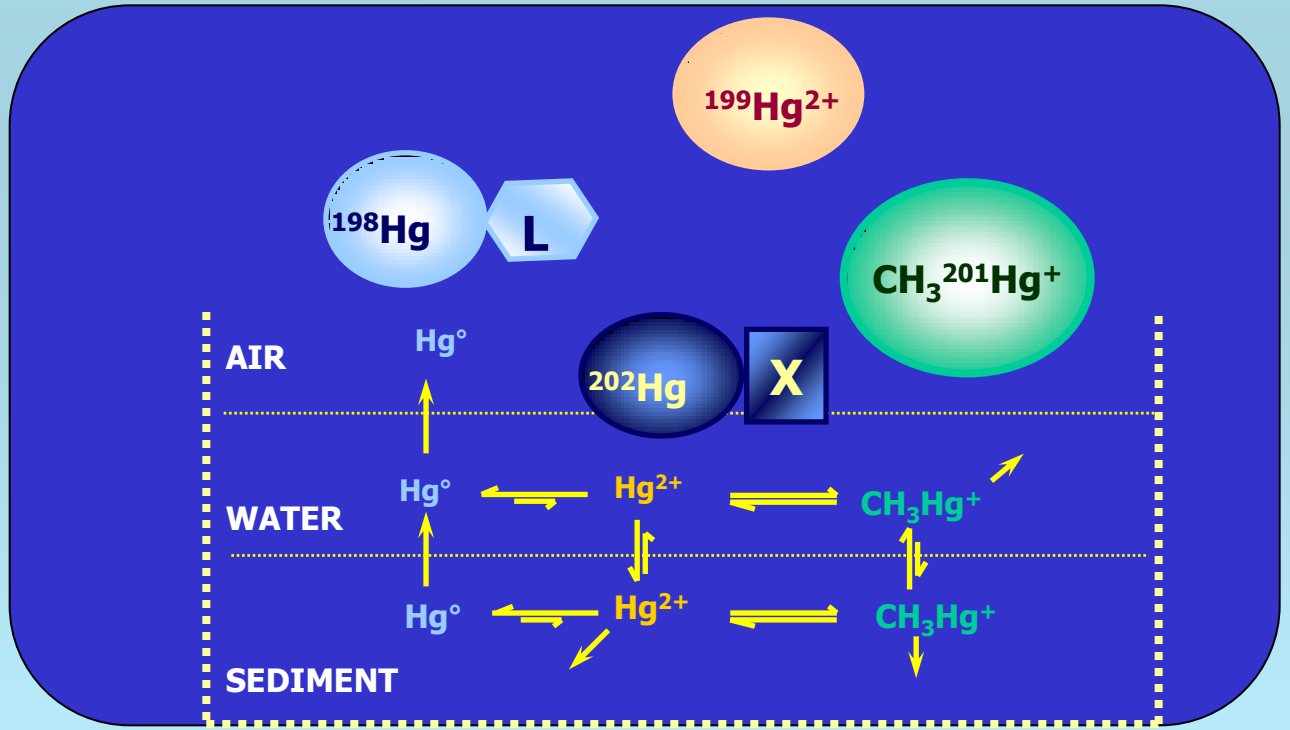


	Mass %
196	0.5
198	33.4
199	56.5
200	77.4
201	44.1
202	100.0
204	23.0

Enriched stable isotopes are available!

Use of Hg stable Isotopes

Detection of transformation reactions using stable Hg isotope tracers, for e.g. Demethylation/Methylation rate determination in sediments



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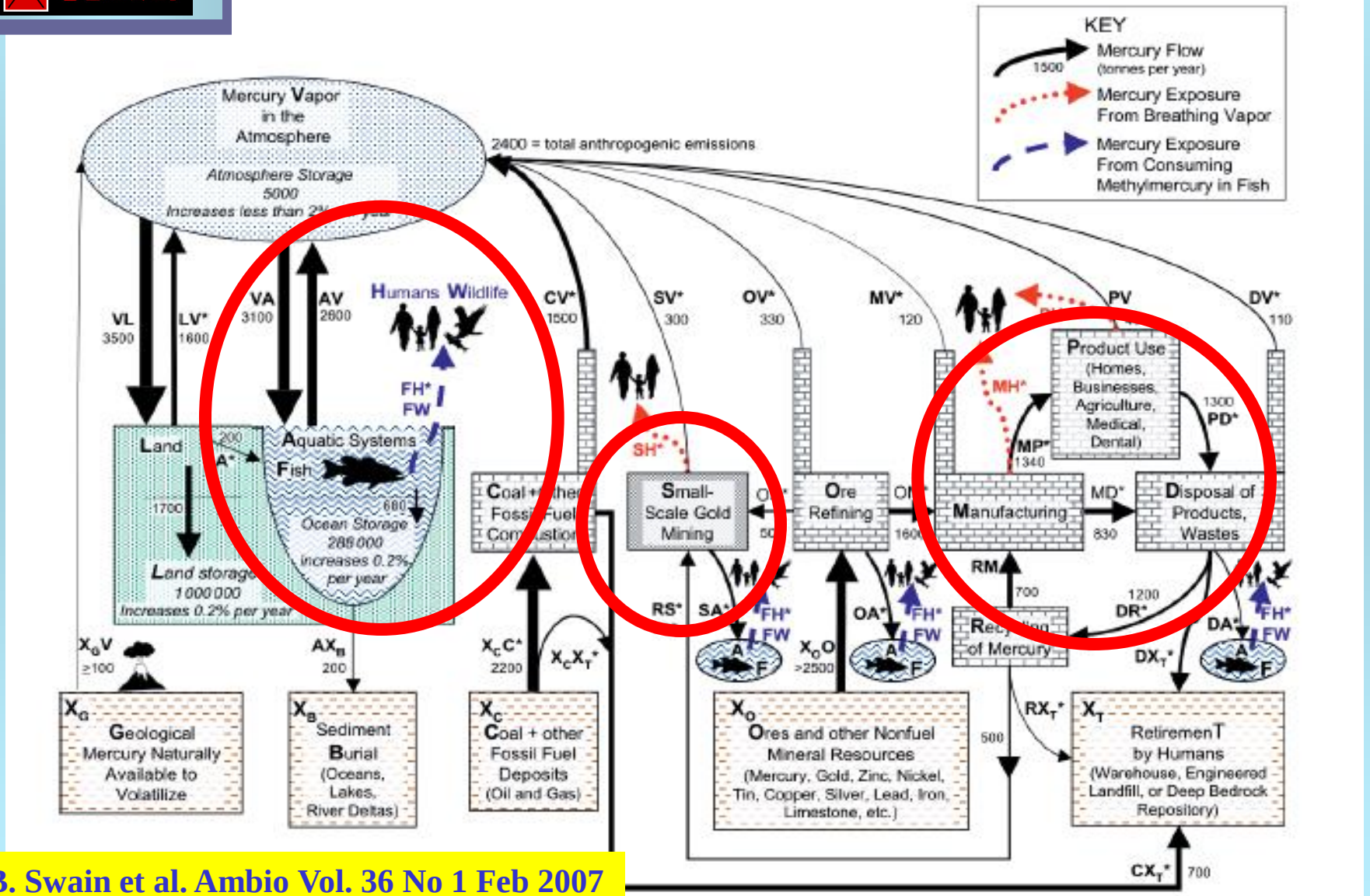
Mercury in the Environment



E.B. Swain et al. Ambio Vol. 36 No 1 Feb 2007