Analytical methodologies for mercury in environmental monitoring

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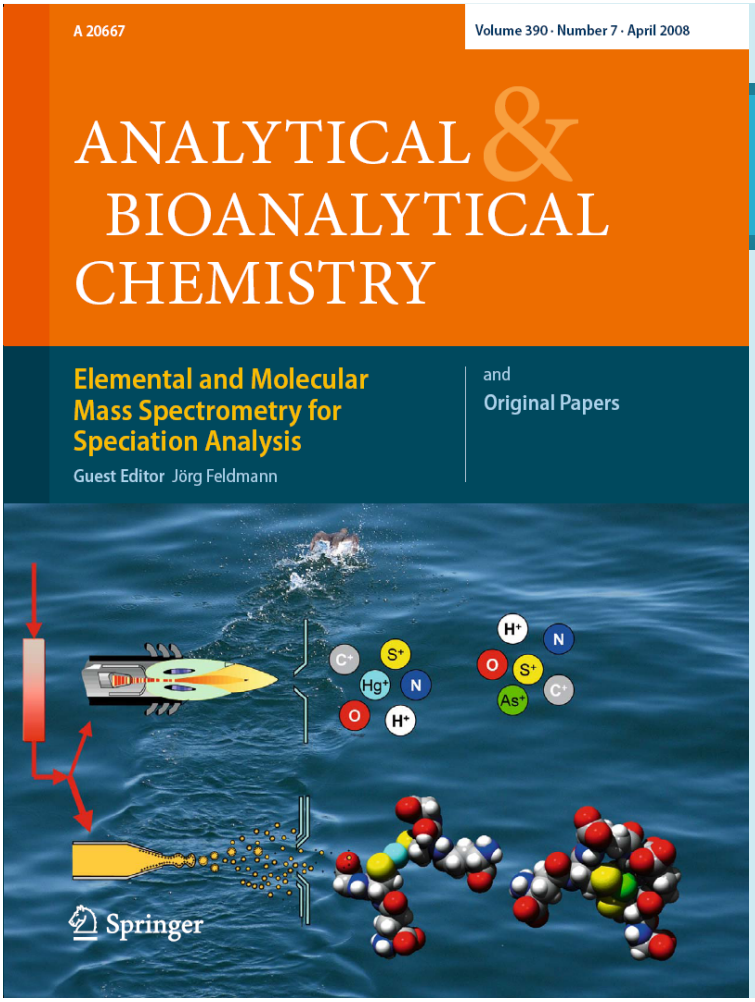
Special thanks to:

Instrumentation & lab

- 4 ICPMS (2 ICP-qMS, ICP-TOFMS, HR-ICPMS)
  - GC-ICPMS, HPLC-ICPMS,
  - Laser ablation-ICPMS
- 3 ES-MS (ES-qMS, ES-IT-MS, Orbitrap)
  - Coupled to HPLC and parallel to ICPMS
- AFS
  - GC-pyrolysis-AFS, HPLC-UV(ox)-AFS
- 3 AAS (2 FAAS, 1 GFAAS)
- GC-MS, 4 GC-FID
- Spring 2009 (clean lab, Cat II Microbiology, synthetic lab)
- (access to 400 & 600 MHz NMR)



- We try to understand environmental processes at a molecular level
- Molecular forms of metals in biota and in the environment.

outline

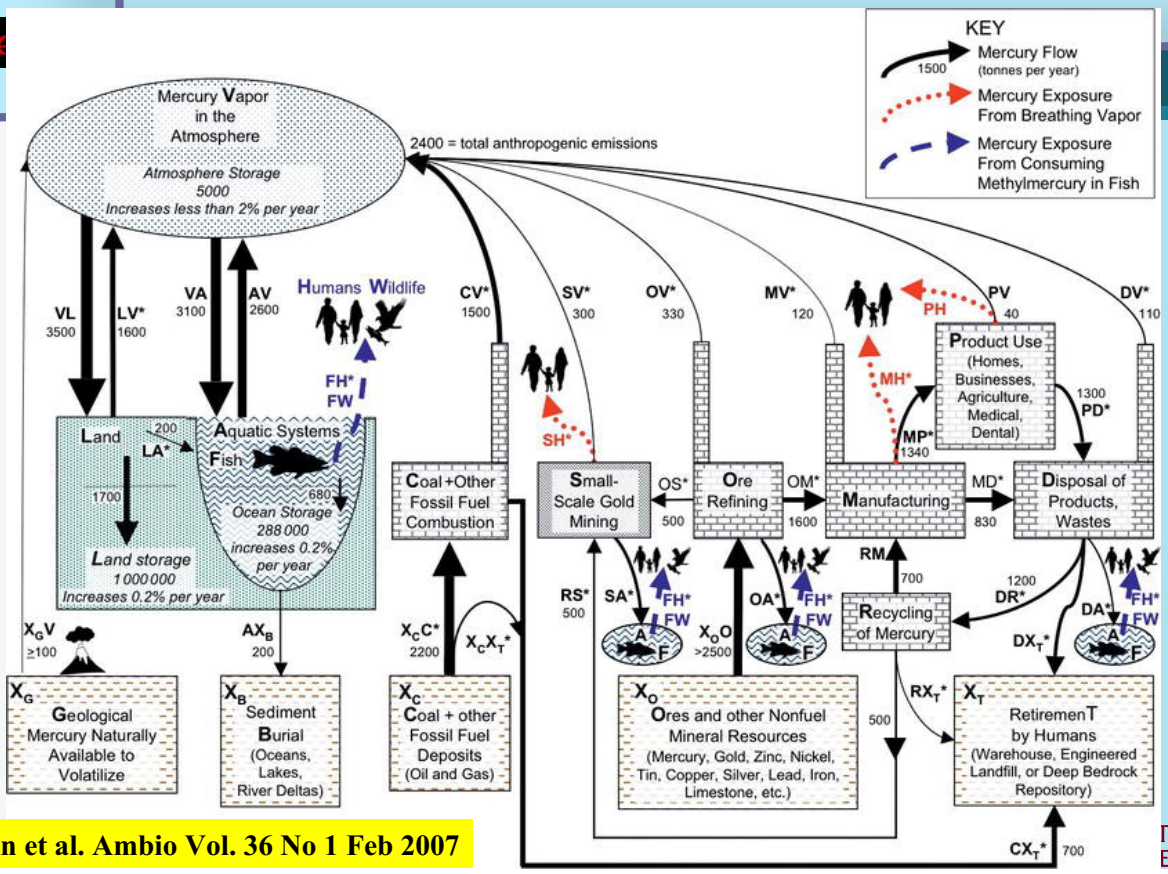
- Sources and sinks of mercury
- Analytical methodologies
- Target samples
  - Sampling, storage
  - Sample preparation
- Discussion points

Mercury

- No known essential biological function
- Industrial use: mercury switches, thermostats, thermometer, medications, preservatives, 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

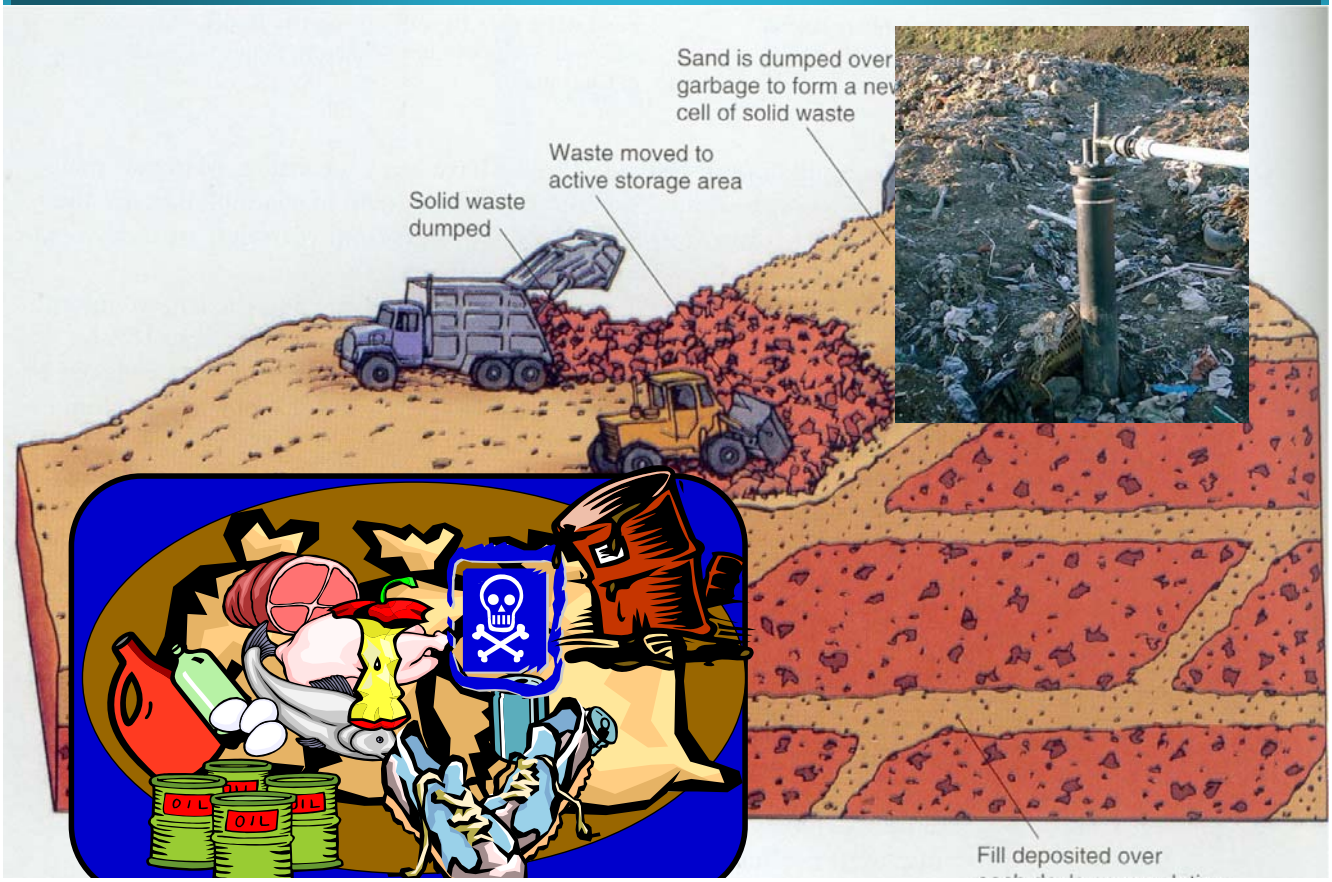
❖ **Mercury is a global pollutant!**

Mercury in the Environment

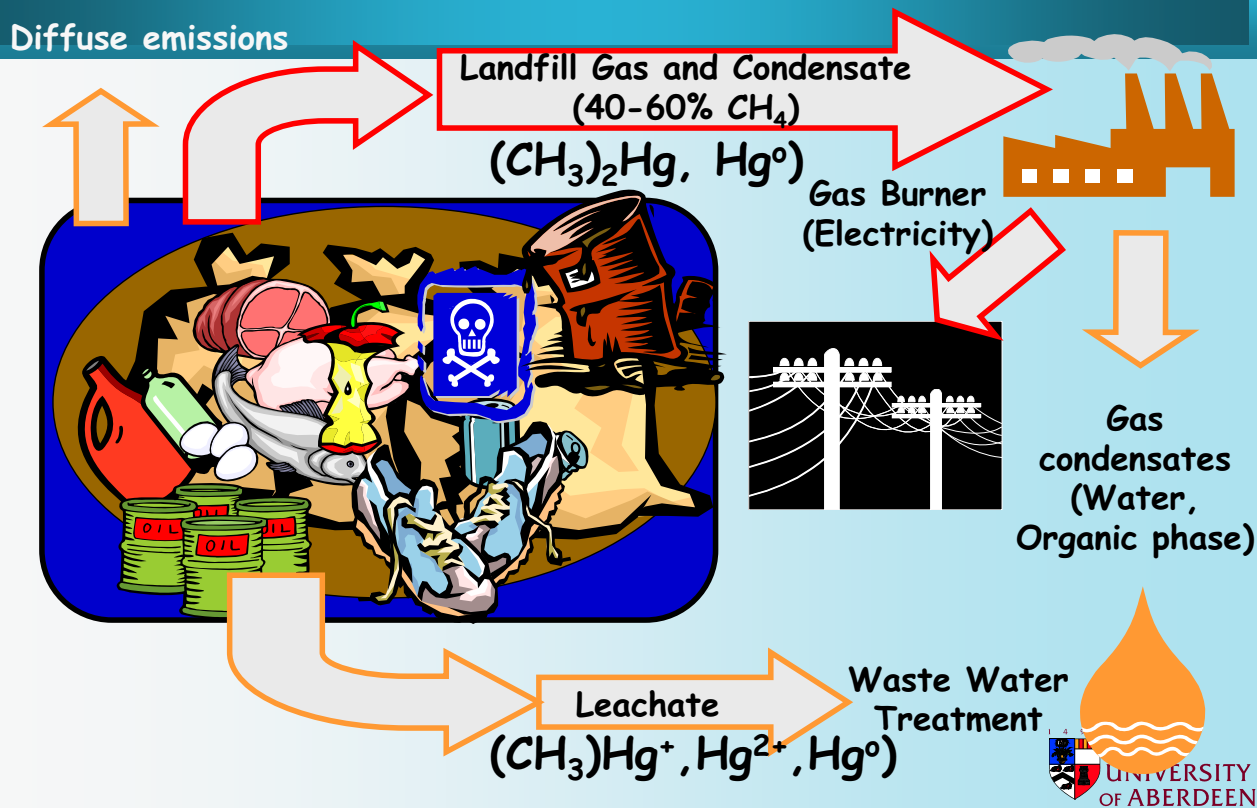


E.B. Swain et al. Ambio Vol. 36 No 1 Feb 2007

Waste Disposal on landfills



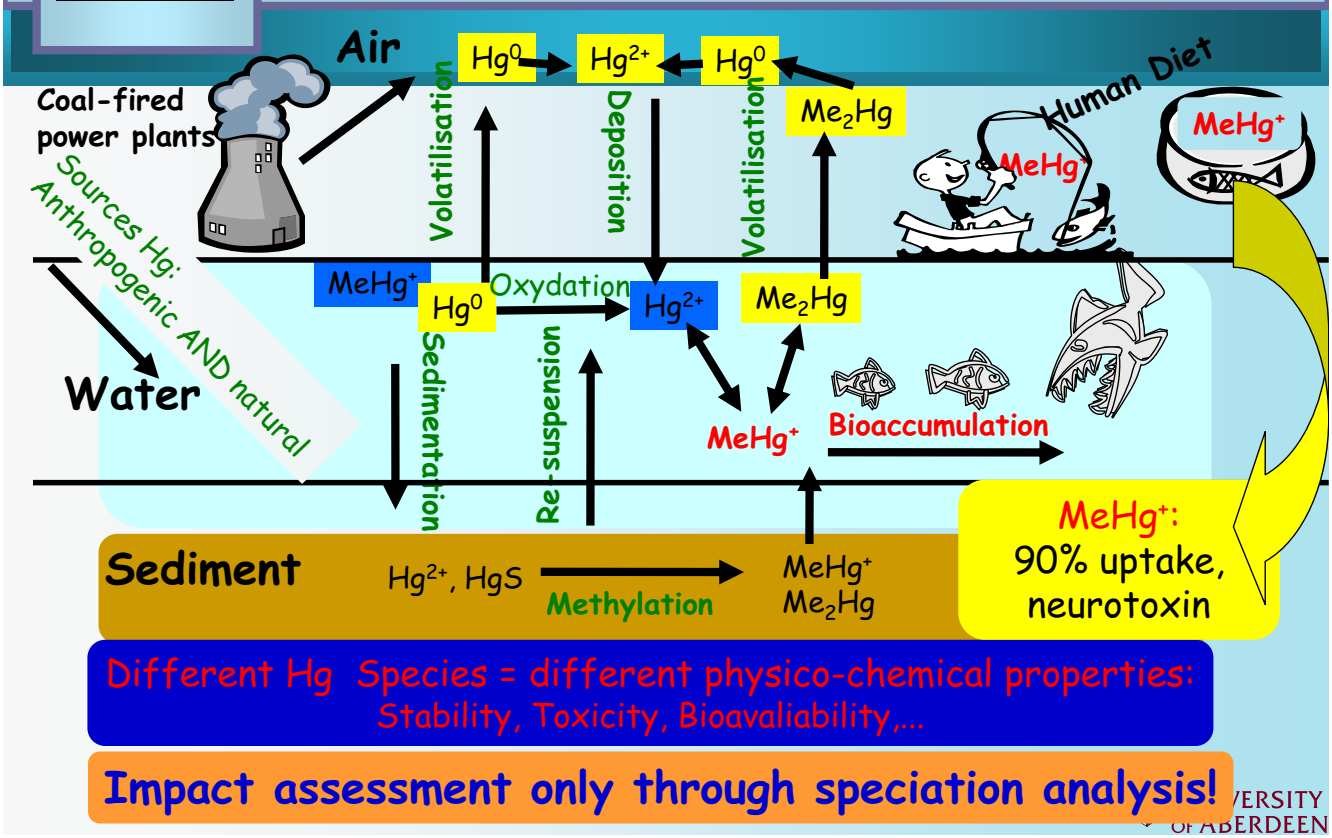
Emissions from Landfills



Waste streams which are potentially large diffuse mercury sources

- natural gas residues
  - Scales in pipelines
  - Dust from filters, charcoal, condensates
- Coal, sewage sludge and waste incineration waste products, furnace slags
- Waste products from mercury catalysts
- Paints, batteries, switches, light sources biocides, pharmaceuticals, cosmetics
- Amalgam fillings
- Thermometer, manometers,...

The Aquatic Mercury Cycle



Speciation of mercury

- Toxicity: $MeHg^+$ >> inorg. Hg.
- Source: Coal burning and waste incineration.
- Bioaccumulation in the food chain.
- Biomethylation: Inorg. Hg -> $MeHg^+$
- ML: Tot Hg: 0.5 mg/kg (*1.0 mg/kg).

→ preditorial fish mainly MeHg

Seawater
0,005 µg/L (2% $MeHg^+$)

Plankton algae
11 µg/kg (25% $MeHg^+$)

Zooplankton
11 µg/kg (25% $MeHg^+$)

Anchovy
40 µg/kg (90% $MeHg^+$)

Ref: Bjerregaard, 1988

Hg speciation in biological and environmental samples

Table 1. Typical total and methyl mercury concentrations in environmental and biological matrices, compiled from US Environmental Protection Agency data (32).

	Hg_{Tot}	$CH_3Hg(II)$
Air	1–170*	0–40*
Precipitation	4–90†	0.04–0.6†
Fresh water	0.2–15†	0.04–0.8†
Sea water	0.3–15†	0.01–0.5†
Soil	8–406‡	0.3–23‡
Ocean sediments	2–2200‡	0.06–70‡
Lake sediments	10–750‡	0.3–30‡
Fresh water fish	30–330§	28–310§
Marine fish	10–1300§	10–1240§

* ng m^{-3}; † ng l^{-1}; ‡ ng g^{-1} dry weight; § ng g^{-1} wet weight

US Environmental Protection Agency. 1997. Mercury Study: Report to Congress, Vol. III, Fate and Transport of Mercury in the Environment. EPA-452/R-97-005. US EPA, Office of Air Quality Planning & Standards and Office of Research and Development.

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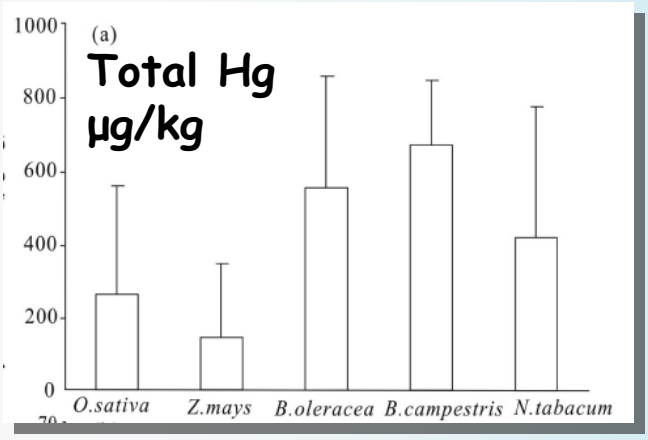
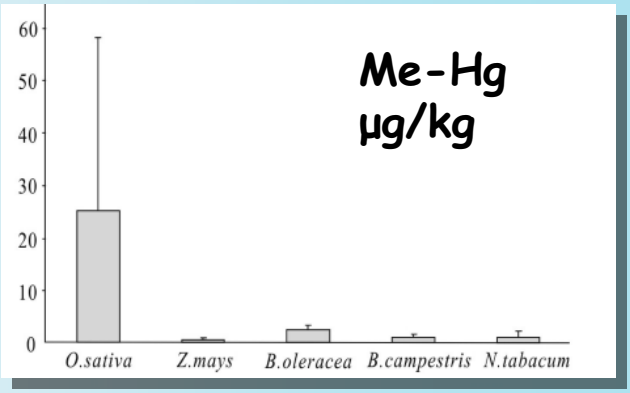
Rice: a methylmercury hyperaccumulator an emerging problem ?

→WHO RfC 1.6 µg/kg bw/week → 0.23 µg/kg bw/d →14-16 µg/d





→US-EPA: 0.1 µg/kg bw/d → 6-7 µg/d
25 µg/kg rice with 300 g rice daily = 7.5 µg/d

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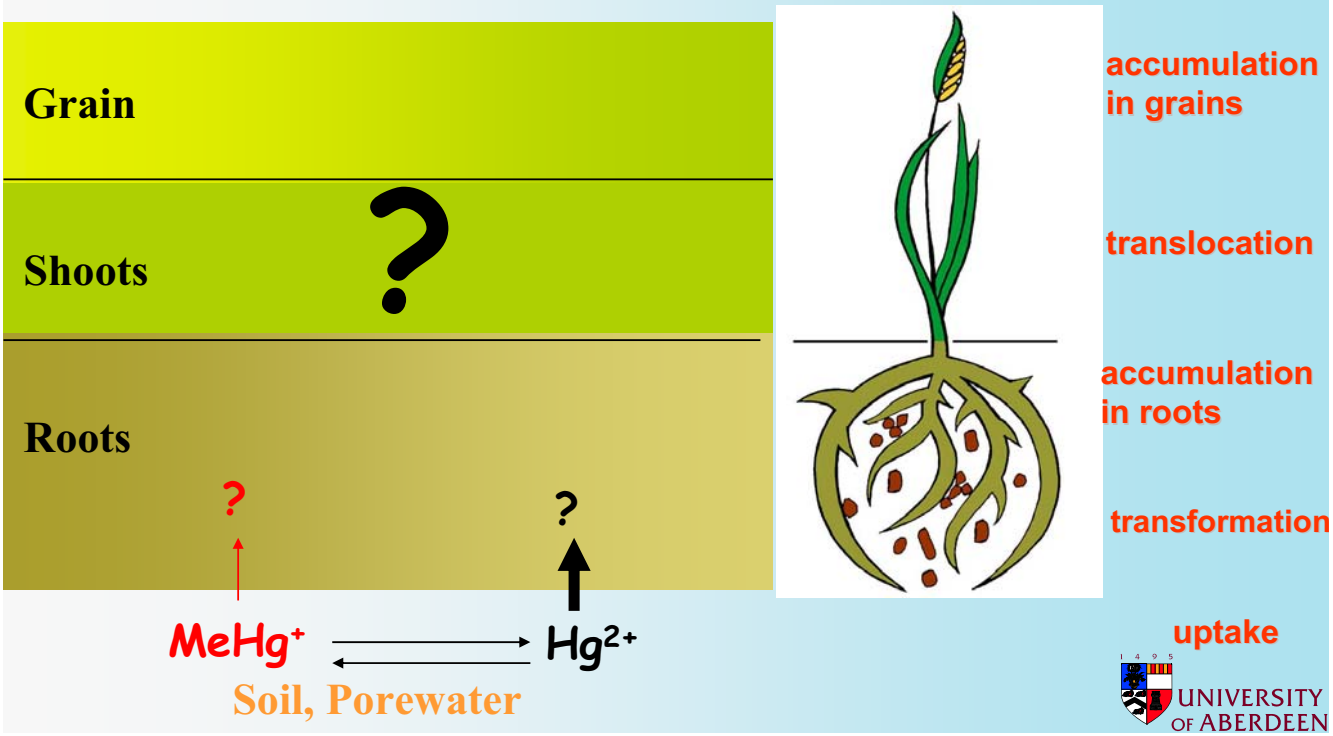
Preferential accumulation of MeHg in rice



Why do we find MeHg in rice?

Hg^{2+} and $MeHg^{+}$ in roots, shoots and grains by GC-ICP-MS after derivatisation with $NaBPr_4$