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Chemical forms, occurrence, and speciation analysis of mercury

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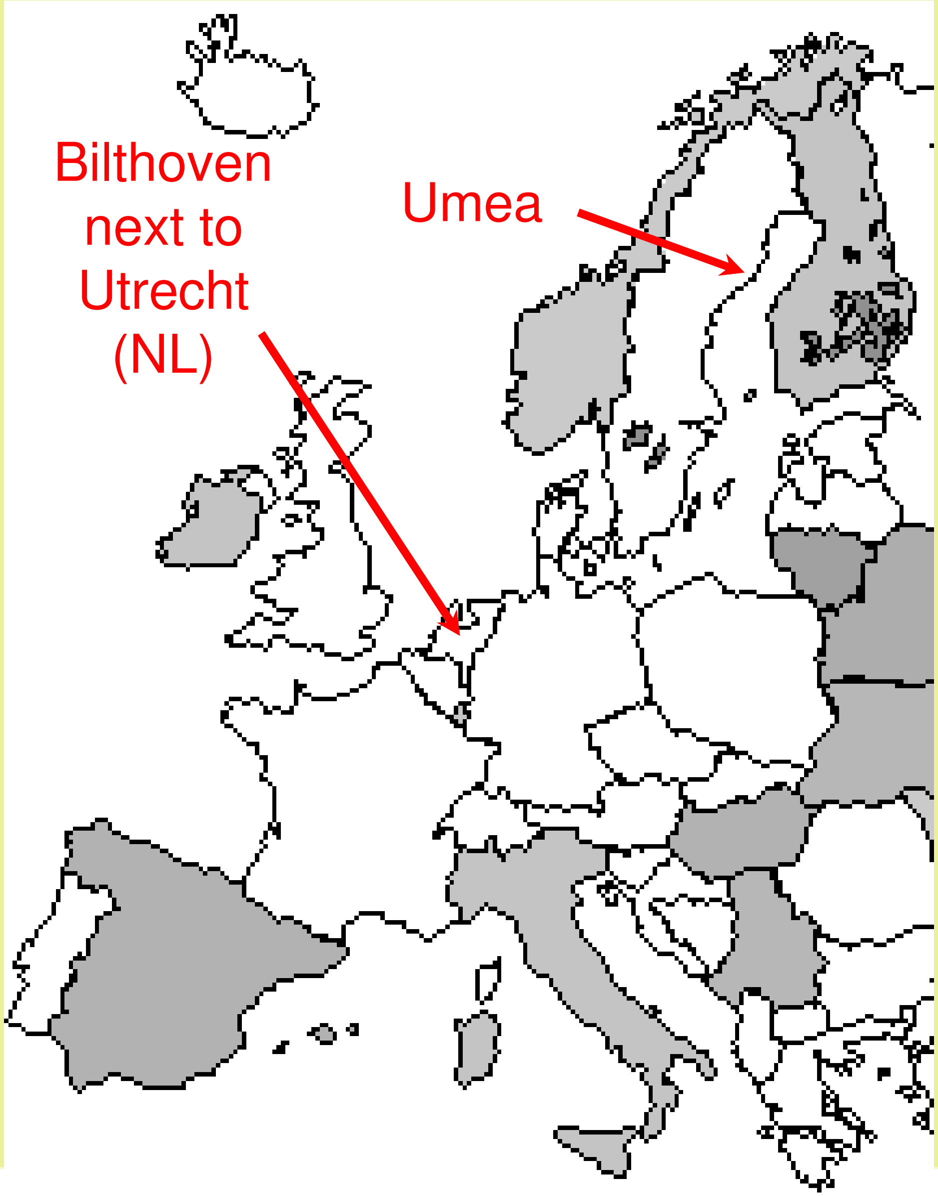
Research for men and the environment

National Institute for Public Health and the Environment (RIVM)

- Governmental knowledge center for Public Health and Environment in the Netherlands
- Around 20 centers + laboratories with 1 500 employees
- Customers: e.g. different national ministries, European Union, WHO
- National reports, international publications and advices



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Laboratory for environmental monitoring department analytical chemistry (LVM-AC)

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Mercury (Hg)

Latin language: hydrargyrum

Greek language: hydro = water

argyros = zilver

"water silver"

"History of Hg"
back to the alchemist age
combination of planets and mythology
-> the "moving & commercial god" MERCURY

Only liquid metal

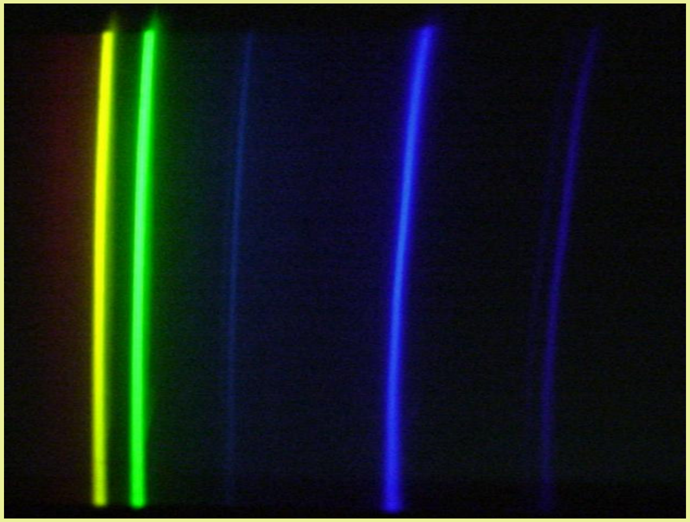
Hg: Physical & chemical properties

->Physical-chemical properties of
Hg and its compounds:
quite different from other metals

- Elemental Hg has a very high vapour pressure

7 isotopes

^{196}Hg	0.2%
^{198}Hg	10.1%
^{199}Hg	16.8%
^{200}Hg	23.1%
^{201}Hg	13.2%
^{202}Hg	29.8%
^{204}Hg	6.8%



Spectrum lines of Hg

Hg: States and Solubility

- Hg exists in 3 states

  Hg^0 (metallic)
  Hg_2^{++} (mercurous)
  Hg^{++} (mercuric)

- Solubility in water increases
  Elemental Hg < mercurous chloride < (methylmercury chloride) < mercuric chloride

- Solubility in non-polar solvents
  Elemental Hg and the halide compounds of alkylmercurials (e.g. methylmercury chloride, $MeHg^+Cl^-$) are soluble

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Hg: Occurrence

Cinnabar (mercury sulfide, HgS) is the most important ore

Native / pure Hg
- next to cinnabar
- in cinnabarit

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Hg: Important deposits

- The most important deposits are in the south of Spain

- Furthermore in

  other areas of Europe,
  Russia,
  Siberian (City of Aktash),
  China,
  Algeria,
  North and South of America

- Production in the world:
  5000 – 8000 tons per year;
  other source: about 10 000 tons per year

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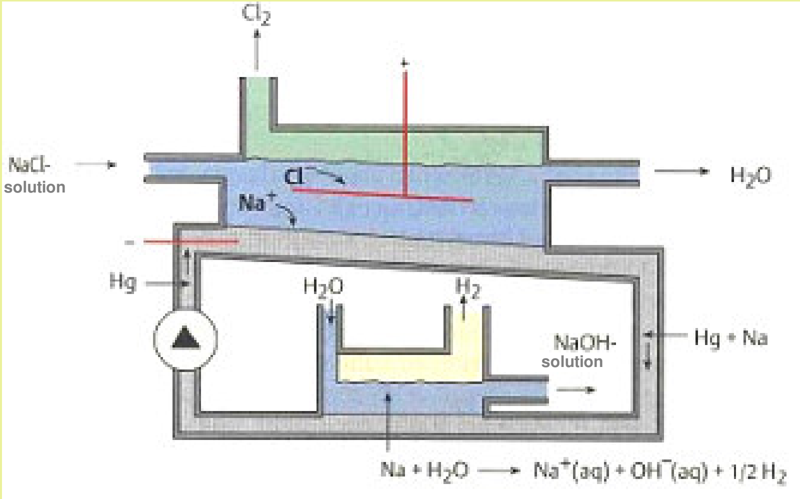
Hg: “Industrial uses”

- Electrolysis of sodium chloride (NaCl):
  “Chlor-alkali work”
  Hg is used as a cathode



- Effect:
  NaCl contaminated with Hg
  -> their use in other industrial activities
  leads to contamination of other products

- Hg in the electrical industry,
  in control instruments in the home and industry,
  in laboratory and medical instruments

- Extraction of gold / gold refining: very large amount of Hg is used

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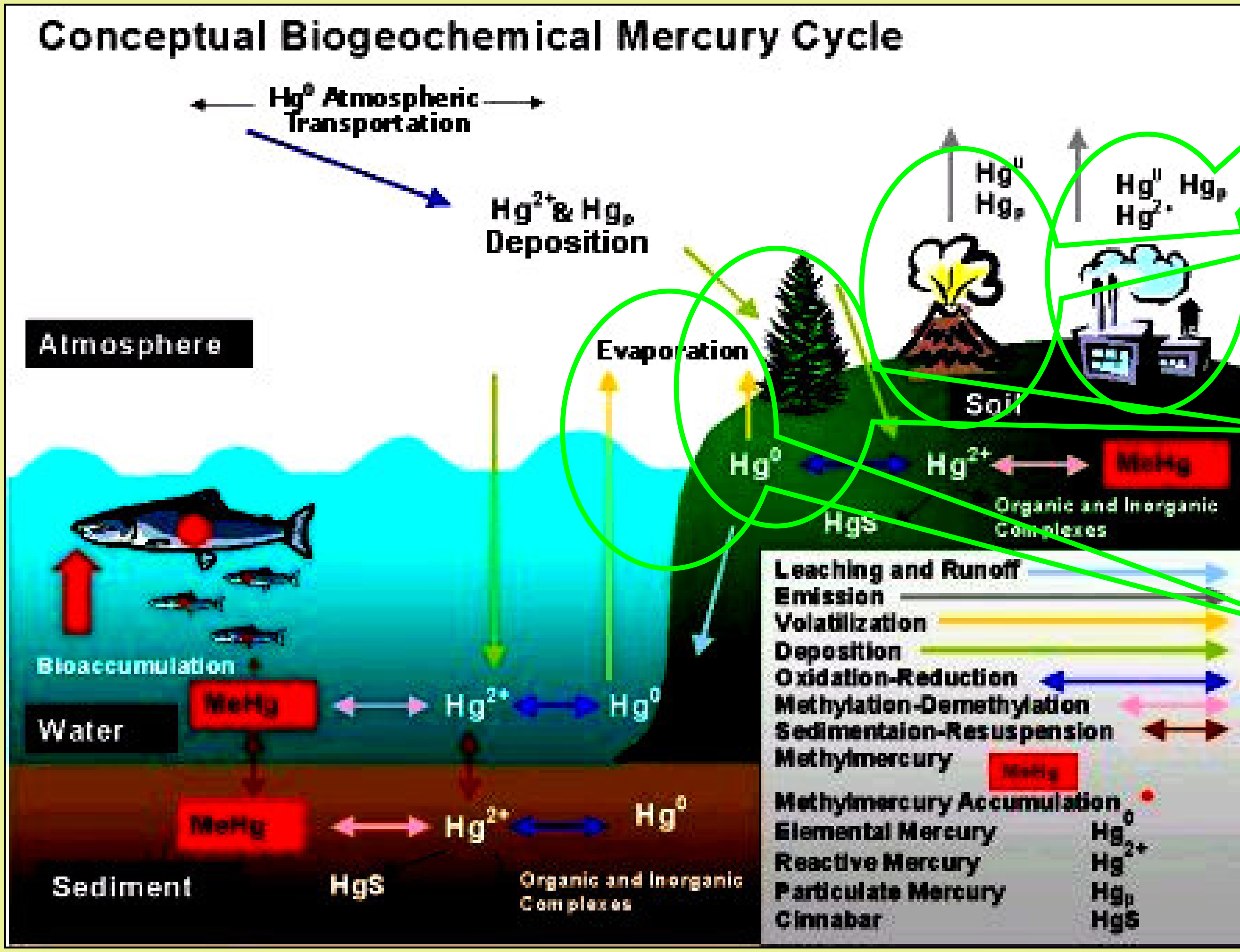
Anthropogenic sources of Hg in the environment

- Anthropogenic sources of Hg are numerous and worldwide
  Industrial activities: -> losses of Hg -> direct discharges with atmosphere
  E.g. specific normal emission from a chlor-alkali plant:
  about 450 g of Hg per ton of caustic soda produced
- Other important sources are, e.g.
  - fossil fuel combustion / coal fired power stations,
  - metal sulfide ore smelting,
  - gold refining,
  - cement production
- Total global amount and release of Hg, due to human activities, to the atmosphere: estimated up to 3 000 tons per year

Three major natural sources of Hg



1. Emissions from volcanoes
2. Emission from land / degassing of the earth's crust
3. Evaporation from natural water (low concentrations)

-> all: transport of Hg^0 in the atmosphere on a global scale

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Environmental compartments

soil <-> air <-> water <-> sediment <-> seafood/fish

Processes: transport <-> distribution <-> transformation

Levels of Hg in AIR

Hemisphere	1-2 ng/m^3
Indust. areas	10 ng/m^3

Atmospheric residence time
for Hg-vapour: up to 3 years
for soluble forms: only a few weeks

Levels of Hg in WATER

Rain water	
Natural water	5-100 ng/L
River water	1-3 ng/L
Drinking water	~25 ng/L

Abundance of $MeHg^{+}$ and Hg^{2+}
depends on geological origin
and pre-treatment (e.g. filtered)

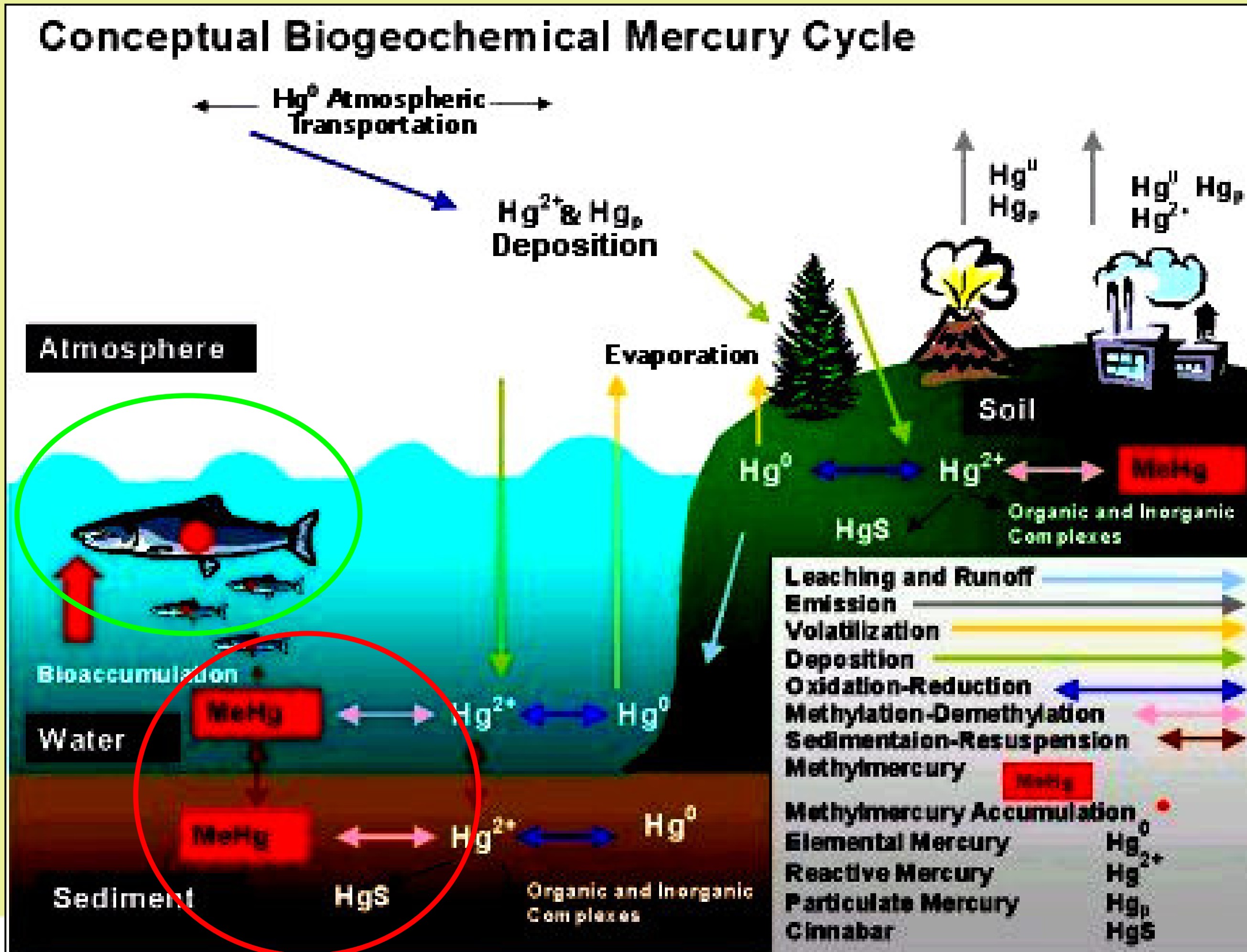
Aquatic bioaccumulation of Hg-species

- Change in speciation of Hg from inorganic to methylated forms
- This can occur non-enzymically or through microbial action
- $MeHg^{+}$ -> transfer to fish -> to food chain

Bioaccumulation factor:

$$= \frac{c(MeHg^{+} \text{ in fish tissue})}{c(MeHg^{+} \text{ in water})}$$

= 1 000 - 10 000



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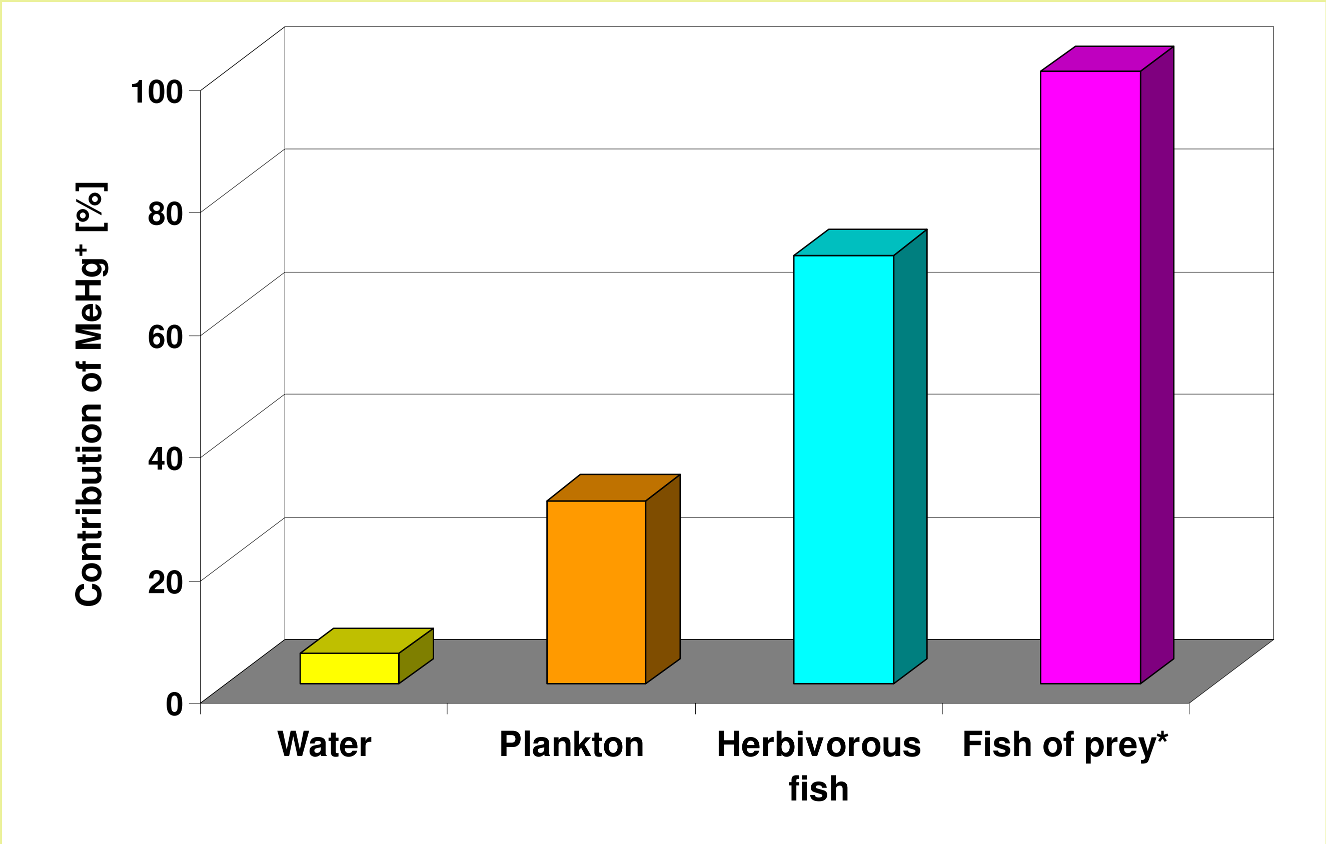
Ratio $Hg^{2+} \leftrightarrow MeHg^{+}$ in aquatic systems

Contribution of $MeHg^{+}$ increases significantly in the food chain



*depending on the part of the body

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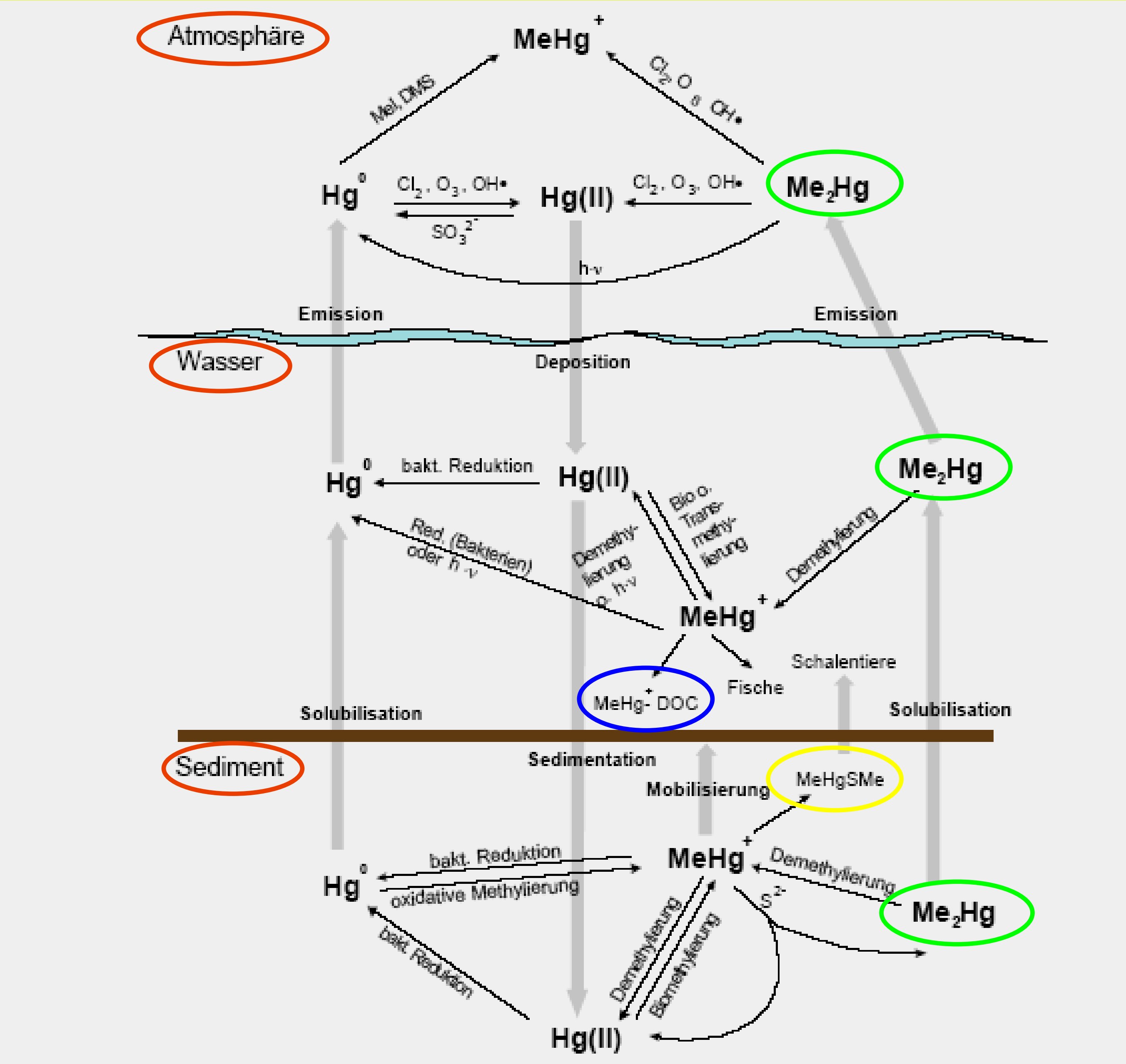

PhD thesis
Natascha Demuth
University of Mainz
Germany

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Hg: "Personal uses" and humane exposure (1)

- Some therapeutic agents contain inorganic Hg

- 1. SKIN-LIGHTENING SOAPS:
  Hg-containing soaps and creams:
  used by dark-skinned people to achieve a lighter skin tone

Soaps: up to 3% of mercuric iodine
Creams: up to 10% of ammoniated mercury

-> Since 1976: research for 2 main health concerns related to inorganic Hg:
skin-lightening soaps and dental amalgam

-> distribution of these products is now banned in Europe and in North America and in many African countries
-> but these products are still manufactured in several countries

Hg: “Personal uses” and humane exposure (2)

2. DENTAL AMALGAM

- Dental silver amalgam for tooth filling:
  contains large amounts of Hg;
  mixed (in the proportion of 1:1) with alloy powder (Ag, Sn, Cu, Zn)

- These uses can cause exposure of patients,
  dentist, and
  dental assistants.

- Experimental studies have shown that Hg is released from amalgam restorations in the mouth as vapour
  The release rate of this mercury vapour is increased, e.g. by chewing

Hg: Effects to humans

	Hg	Organo-Hg
Toxicity	• extremely toxic • can cause neurological + kidney damage, blindness • is associated with birth defects	• extremely high toxicity • safety precaution is absolutely necessary during handling • $MeHg^+$ is known as one of the five most toxic compounds • direct contact of $MeHg^+$ with skin can be lethal
Proper-ties	• Hg vapour dissolves only slightly in distilled water -> BUT is more soluble in whole blood and plasma	• are stable, although some are readily broken down by e.g. bacteria
Re-sorption	only 7% of ingested inorganic Hg-compounds	90% of ingested organic Hg-compounds

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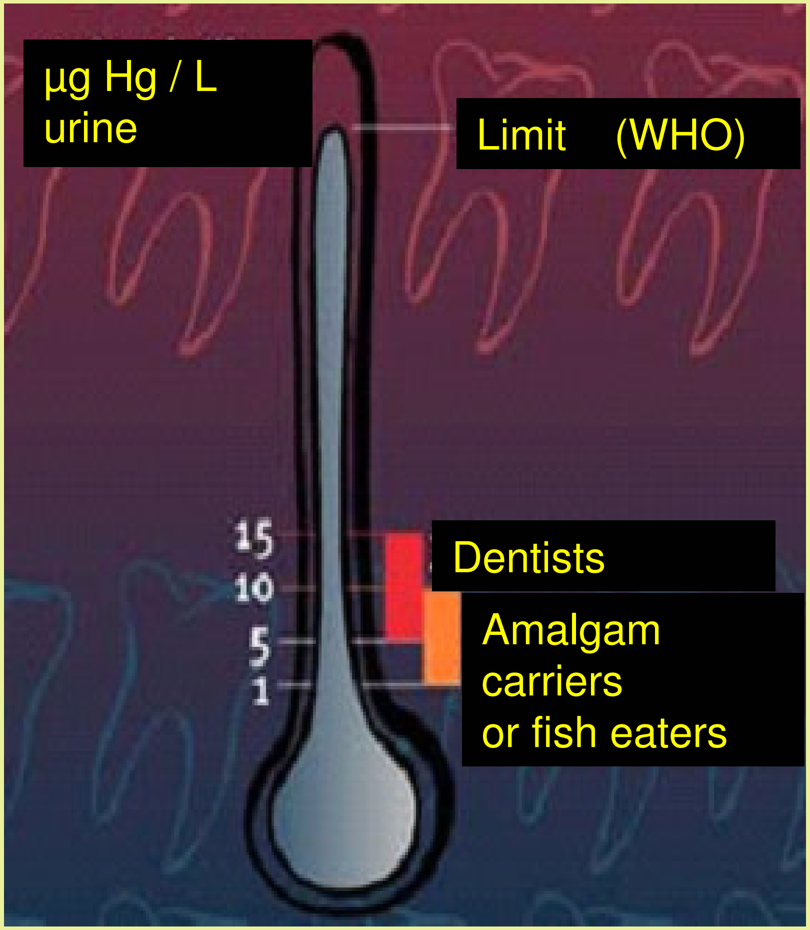
Hg: Indicators / matrices of humane exposure

- **BLOOD** and **URINE** can be used as indicators of exposure

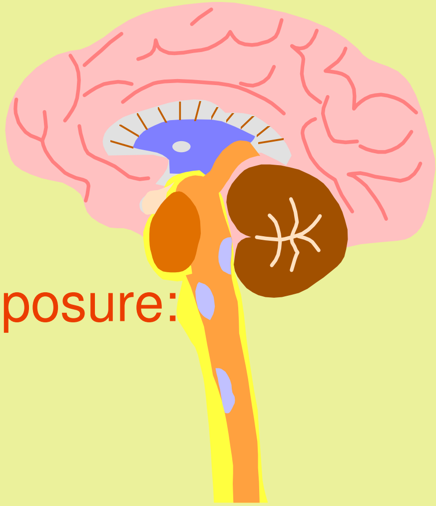
  -> Exposure must be "relatively constant"

Reference and normal values: urine



Hg: Indicators / matrices of humane exposure

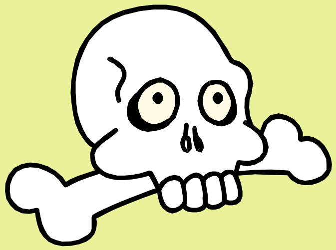
- **BRAIN** and **KIDNEYS** can be used as indicators of exposure
- Case nr. 1: With moderate number (about 25) of amalgam surfaces:
  -> increase of Hg in brain: by about 10 µg / kg
  -> corresponding increase in kidneys: probably 300 - 400 µg / kg
- Study based on a very limited number of analyses
  + individual variation is considerable !



- Case nr. 2: Deceased miners: years after cessation of exposure:
  -> increase of Hg in brain: several mg/kg
  (still higher values in some parts of the brain)
- Lack of quality control of the analysis -> uncertain data

$MeHg^+$ in the humane body and symptoms

Take-up via skin, inhalation and food
-> gastrointestinal track
-> via blood circulation
-> through the whole body



Partly elimination via urine, faeces, hair and mother's milk

Partly stored in brain:
Damage of the central nervous system:
-> "parts which are involved in the coordination"
-> not sharp eyesight
-> sense of hearing (deafness)
-> speech defects
Worst cases -> coma and finally death

"Freaks of baby's"

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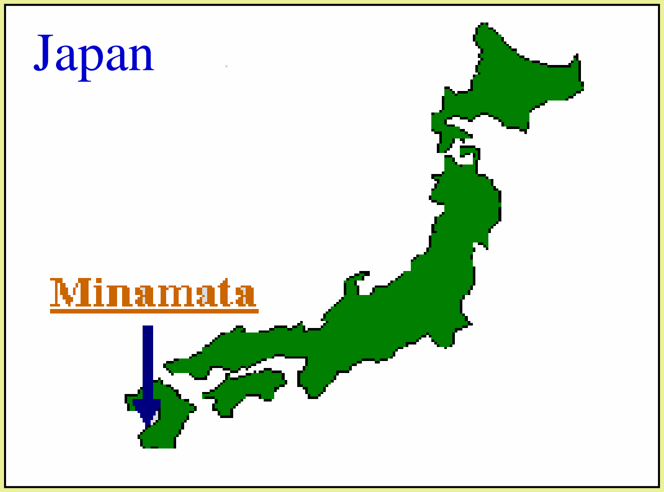
Minamata illness

- Inhabitants of Minamata: especially farmers and fishermen
- Since 1955: “strange” poisoning of persons
- >3000 victims



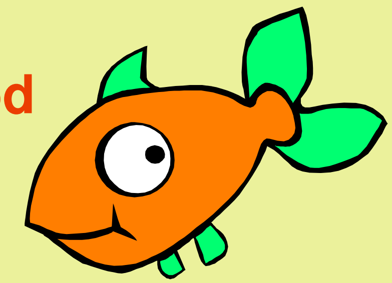
1932-1968: Chisso Coorporation: production of artificial fertilizer and carbide

dumped around 27 tons of Hg-compounds into the golf of Minamata

Hg: Humane exposure of general population (3)

3. DIET

Most human exposure by consumption of seafood / fish containing $MeHg^{+}$



Different guidelines for tolerable maximum intake via food

- WHO:
  300 µg Hg per week with a maximum of 200 µg $MeHg^{+}$

Advices for women who are or might become pregnant, nursing mothers and young children:

- EPA and FDA (2004):
  - Do not eat shark, swordfish, king mackerel, or tilefish
  - Eat up to 2 average meals a week of a variety of fish that are lower in Hg
- UK Food Standard Agency (2003):
  - Limited consumption of tuna to no more than 2 cans or 1 fresh tuna steak per week
  - Avoid eating shark, swordfish and marlin

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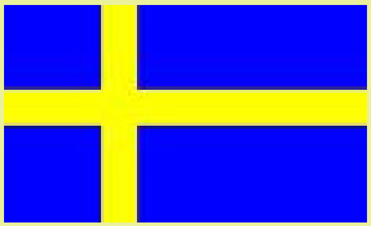
Example of an analytical method for Hg-speciation



fisk,fisk

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Hg-speciation of 3 shark-filets

Determination of $MeHg^{+}$ and Hg^{2+}
with GC-ICPMS
(gas chromatography inductively coupled plasma mass spectrometry)

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Sample pre-treatment: GC-ICPMS

Dissolution:

0.5 g shark fillet

+ tetramethylammonium hydroxide (TMAH)

10 - 12 h shaking, dilution with water

Derivatisation / ethylation and extraction:

Aliquot + HAc/NaAc-buffer

+ iso-octane as internal standard
(dibutyl-dipentyltin, ~ 2%)

2 x : + 1% $NaBEt_4$, 30 min shaking,
centrifugation

Furthermore: CRM 463, CRM 464 “tuna fish” / freeze-dried (0.1 g)

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Measurement with GC-ICPMS

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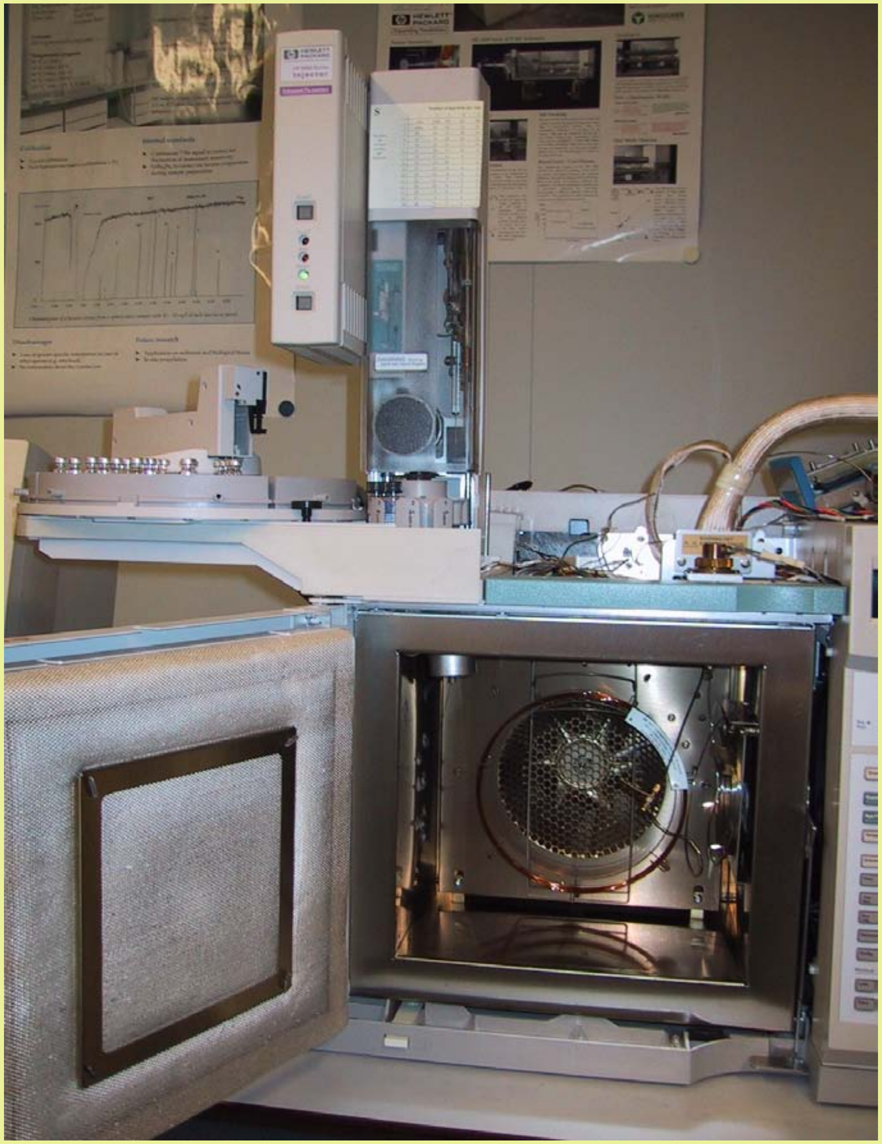
GC HP 6890

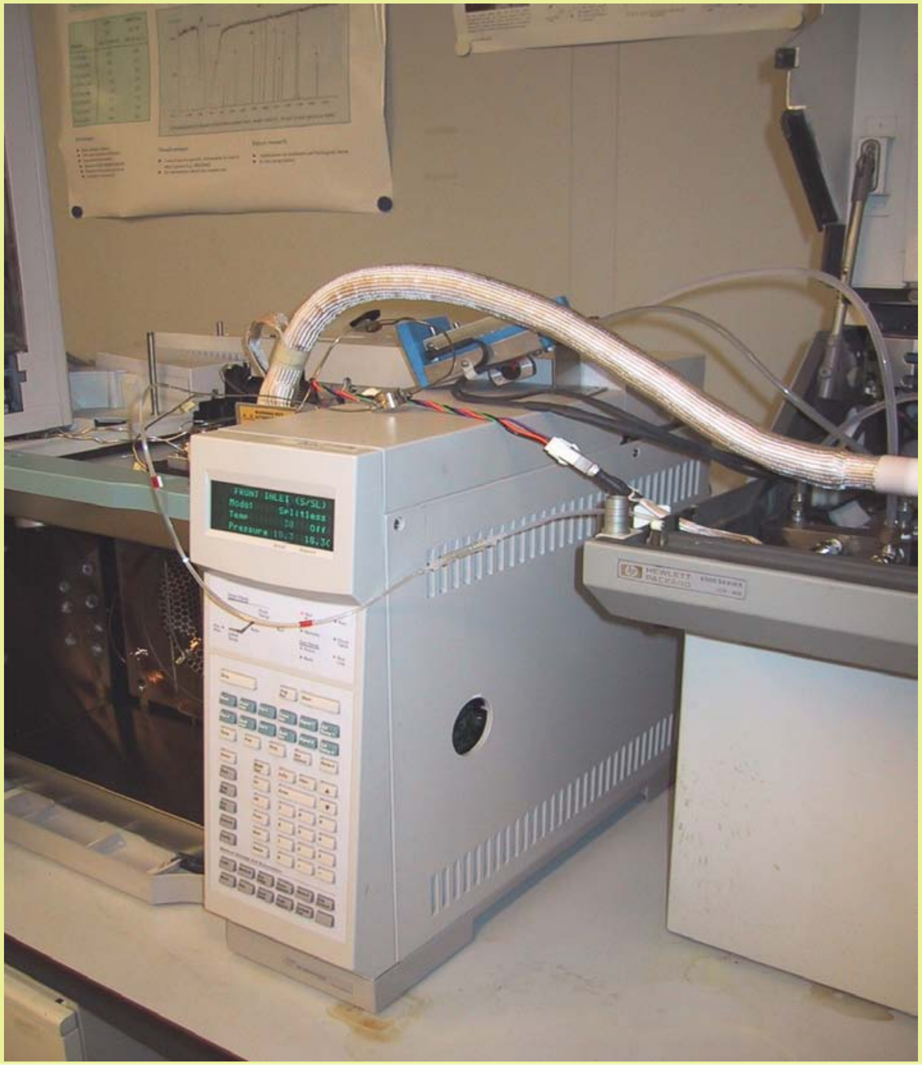
V(injection): 1 µL, splitless
T(injection): 250°C
Carrier gas: He
(+ 0.1% Xe - internal standard)
Flow rate: 6.5 mL/min (const. flow)
Column: HP-1 (polydimethylsiloxane)

Temperature program

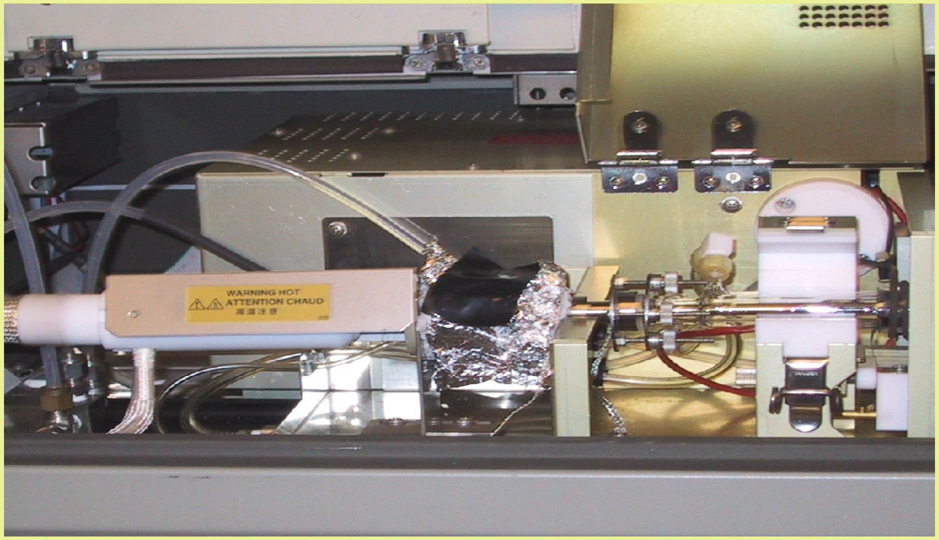
T rate [°C/min]	T [°C]	t [min]
	50	1
10	60	
80	140	
40	170	
120	270	1.5
	280	



Interface



Commercial interface from Agilent / type Sep. 2002



T(Aux. 1): 280^{o}C
T(Aux. 2): 280^{o}C

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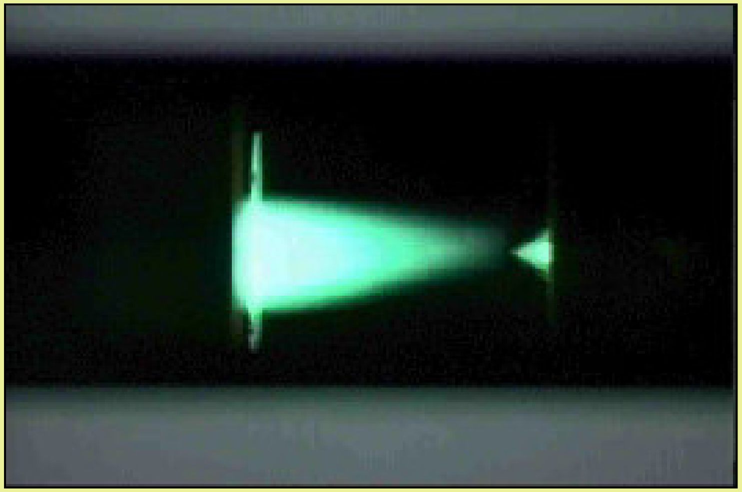
ICPMS HP 4500 with shield torch



Tune

RF power: 1220 W

Carrier gas flow: 0.9 L/min Ar

Addition. gas flow: 25 mL/min air

Method

isotope	integration time [ms/mass]
^{200}Hg	70
^{202}Hg	70
as internal standard:	
^{120}Sn	70
^{126}Xe	50

run time: 8 min

Balance of GC-ICPMS data

Sample	$c(MeHg^+)$ [mg/kg $MeHg^+$]	$c(MeHg^+)$ [mg/kg Hg]	$c(Hg^{2+})$ [mg/kg Hg]	$c(\Sigma Hg)$ [mg/kg Hg]	part($MeHg^+$) of ΣHg [%]
Shark 1	1.54 ± 0.08	1.43 ± 0.08	0.08 ± 0.02	1.52	94.0
Shark 2	1.01 ± 0.18	0.94 ± 0.17	0.01 ± 0.002	0.95	98.9
Shark 3	3.68 ± 0.30	3.42 ± 0.28	0.11 ± 0.02	3.53	96.9

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partly frozen /
partly thawed out

totally thawed out

“fresh”
fish material

several times
frozen and thawed out

??? EFFECTS ???

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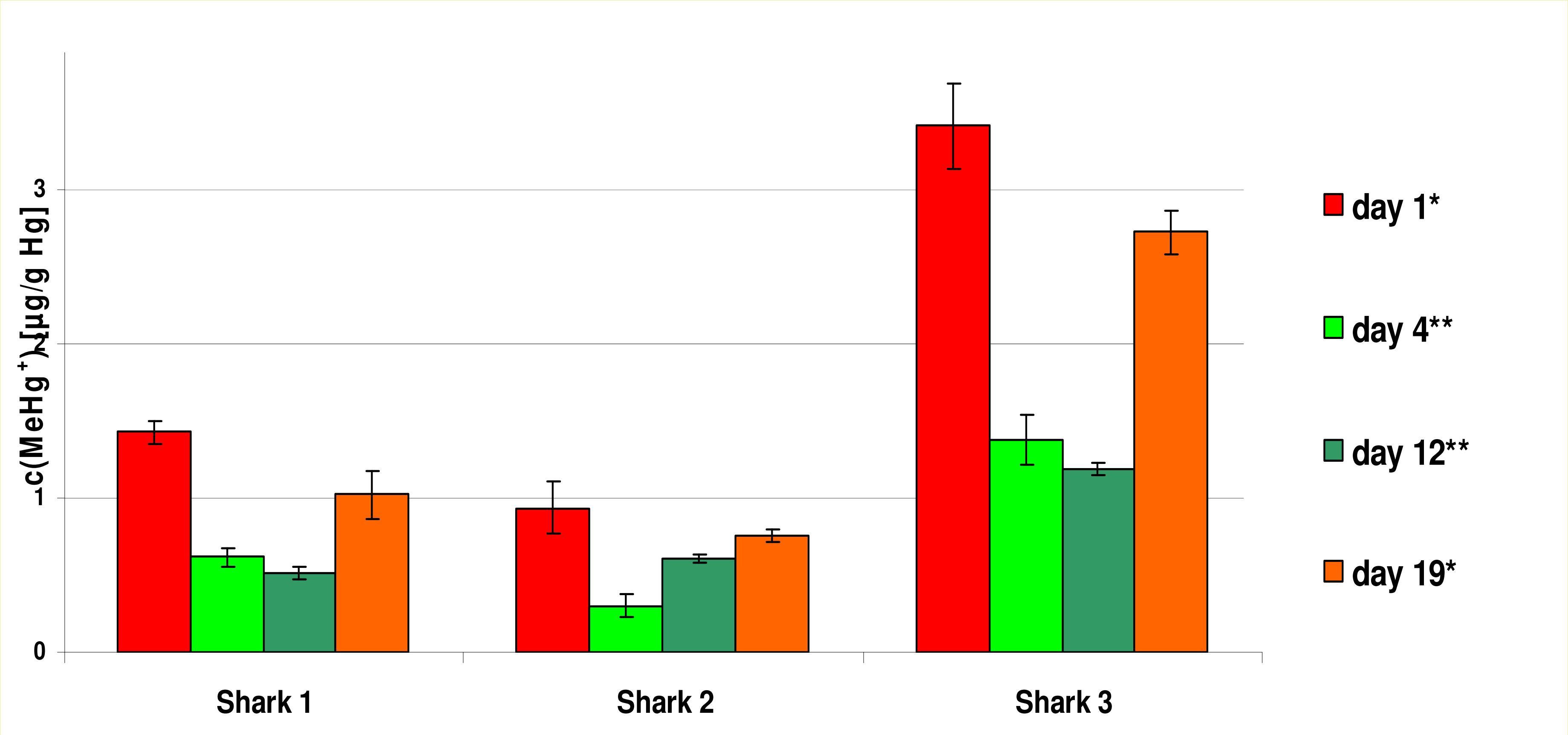
Influence from sub-sampling of "fresh" fish tissue



* red colours = **totally thawed out** fish tissue

** green colours = partly frozen fish tissue

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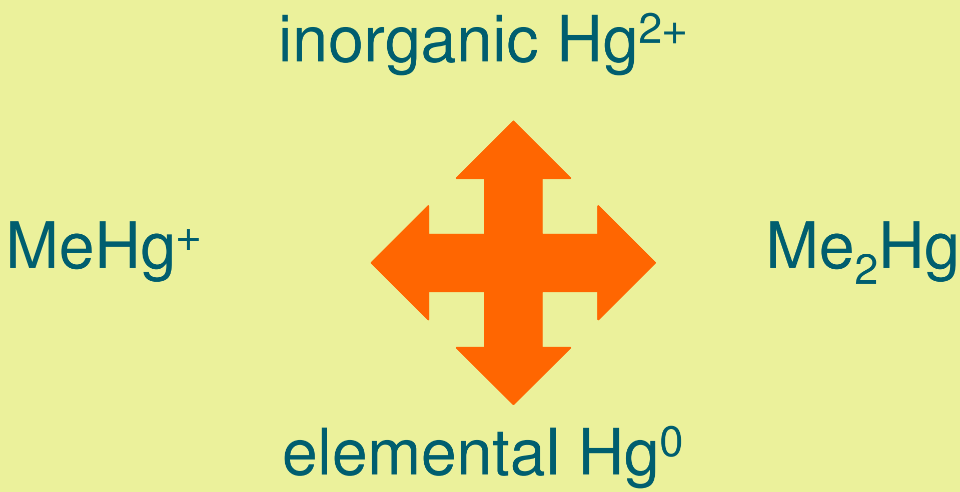
Other possible effects which may influence the analytical results?

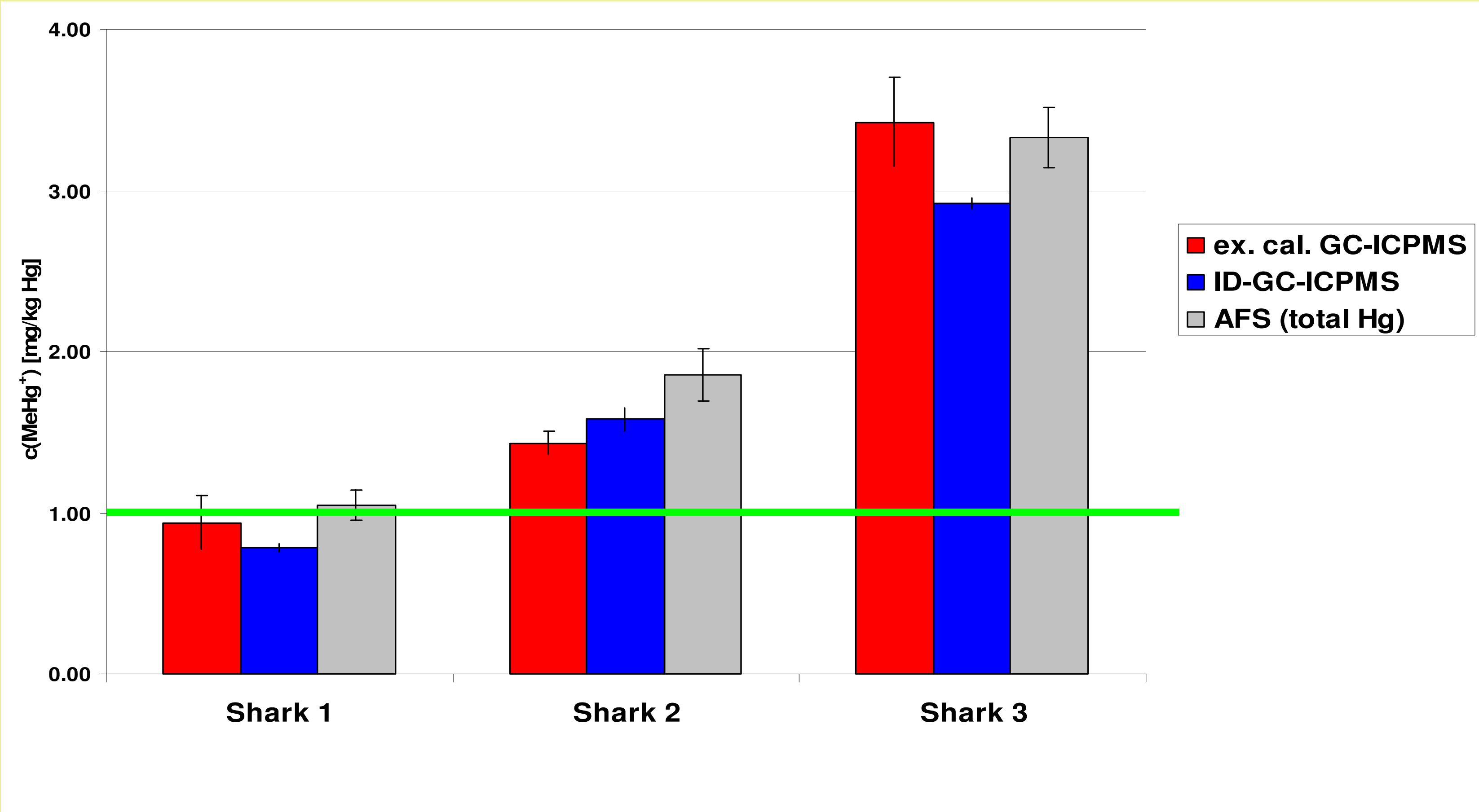
Species-transformation:



Species-transformation ... during ...

- Storage of the samples?
- Thawing out?
- Dissolution?
- Derivatisation?
- Extraction?
- Measurement?

Results of $MeHg^+$ determined by two GC-ICPMS procedures as well as total Hg-concentrations in fresh shark samples



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Results from a Dutch "market study"*

- From each kind of fish 15 specimens were bought
- Eatable part was selected + pre-treated by cutting
- Mixture was analysed once

Specimen	c(total Hg) [mg/kg]	c($MeHg^+$) [mg/kg]
Limit of Detection	*0.002*	*0.03*
Pollack	0.008	< LOD
Tilapia	0.010	< LOD
Salmon conserve	0.018	< LOD
Salmon fresh	0.026	< LOD
Salty herring	0.032	< LOD
Cod fish	0.045	< LOD
Sole	0.049	< LOD
Plaice	0.050	< LOD
Shrimps	0.060	< LOD
Bass	0.066	< LOD
Mussels	0.034	0.03
Mackerel	0.035	0.03
Eel	0.138	0.09
Tuna	0.153	0.09
Tuna	0.427	0.19

* Study was carried out by order of the Dutch "consumentenbond"

Shark 0.95-3.53

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Thank you for your attention

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