# Biogeochemistry of Hg unraveled by its isotopic signatures

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mass
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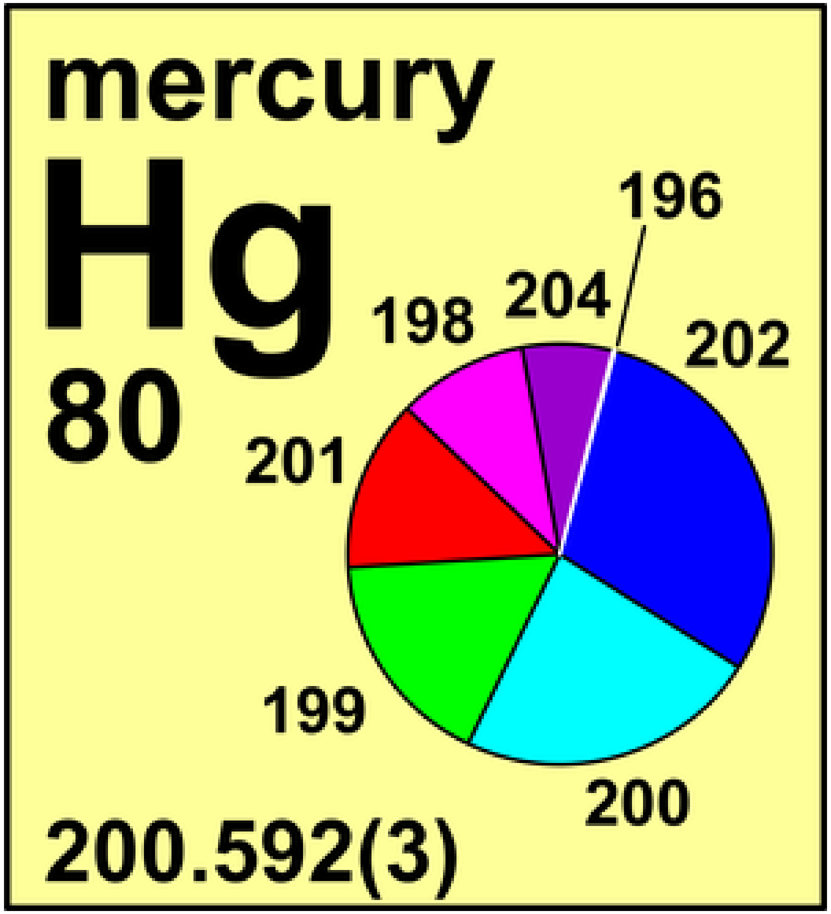
mercury
Hg
80
196
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198
202
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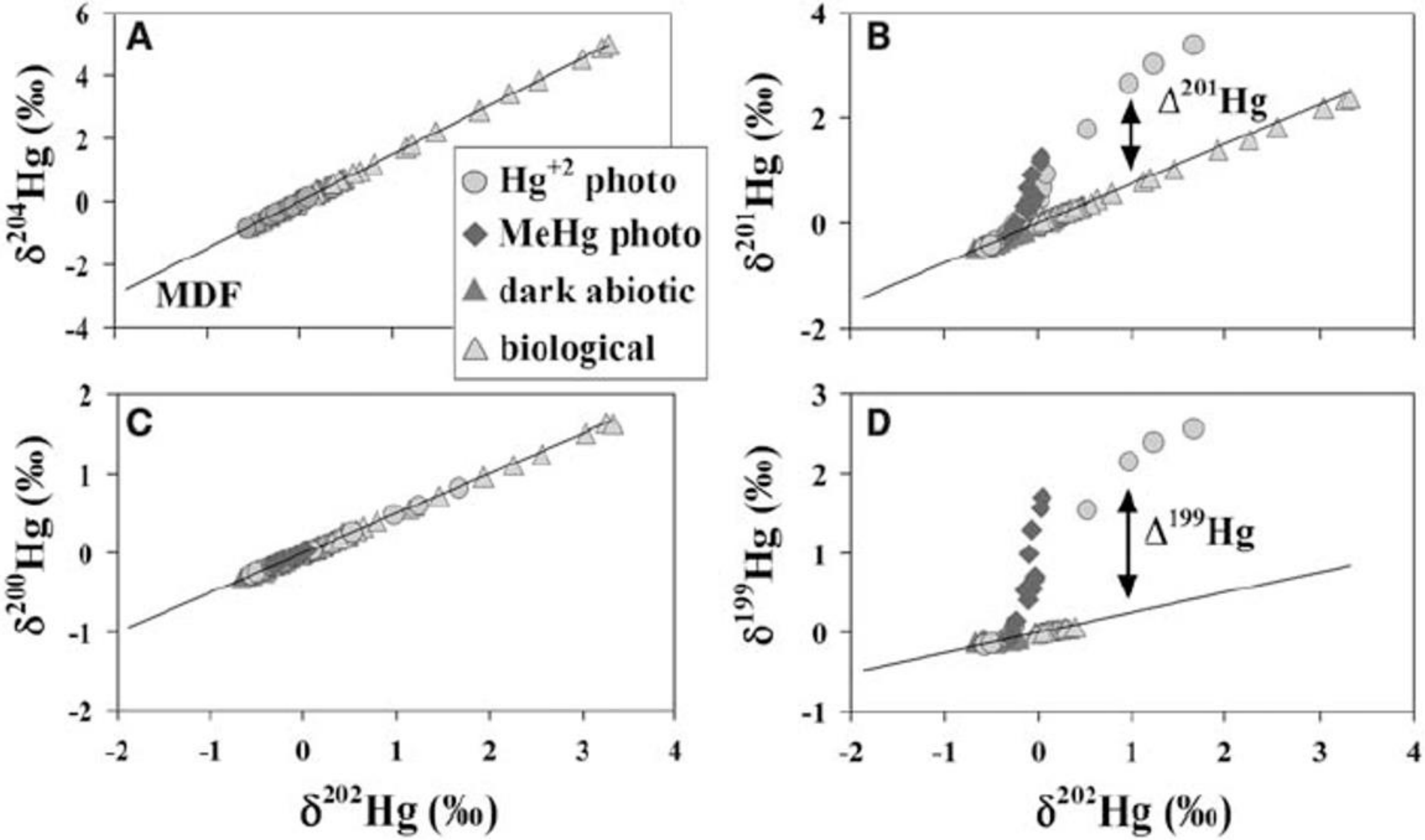
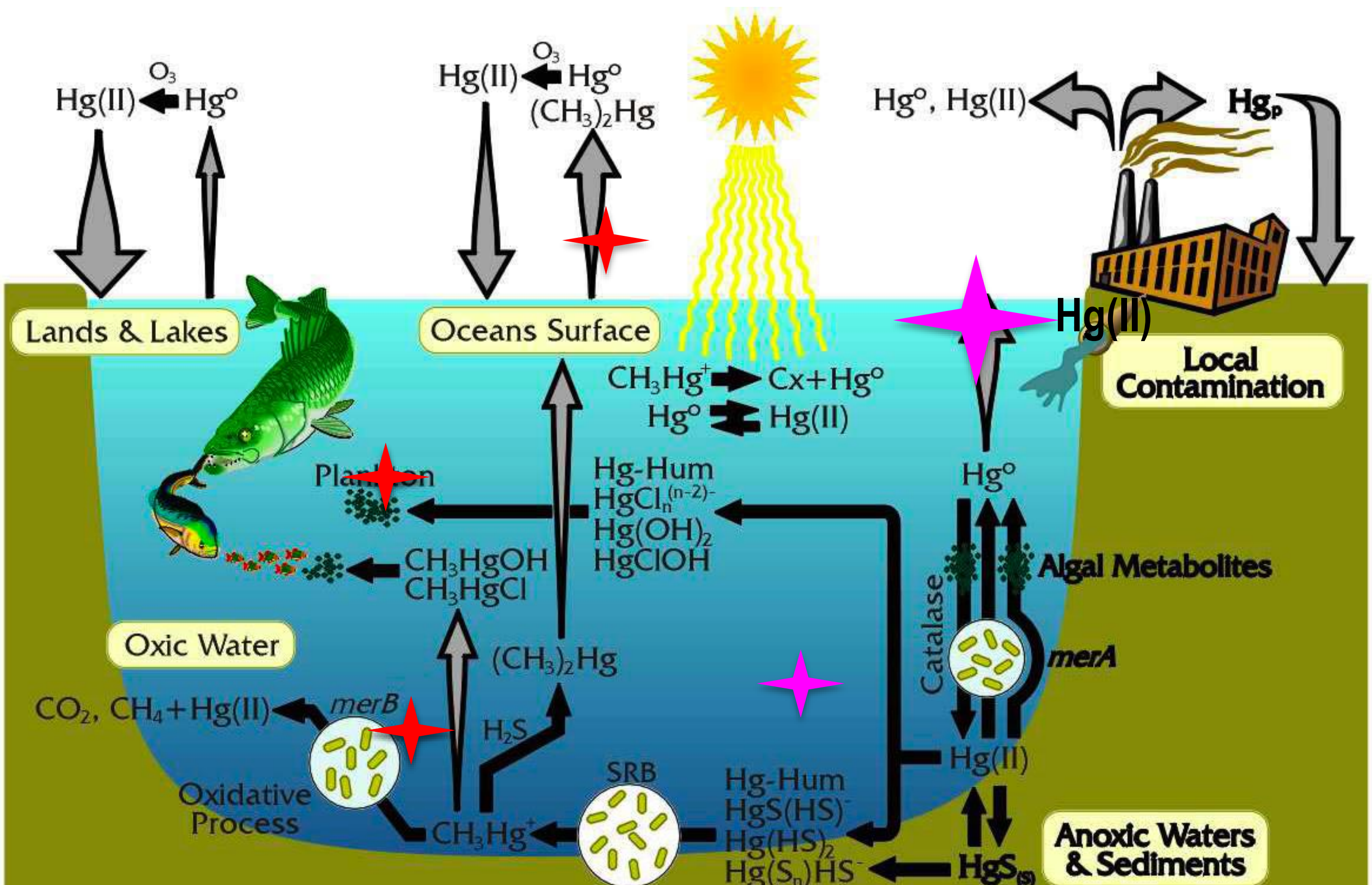



# MDF

# MIF

*Bergquist and Blum 2007*

# Mercury cycle and isotopic fractionation

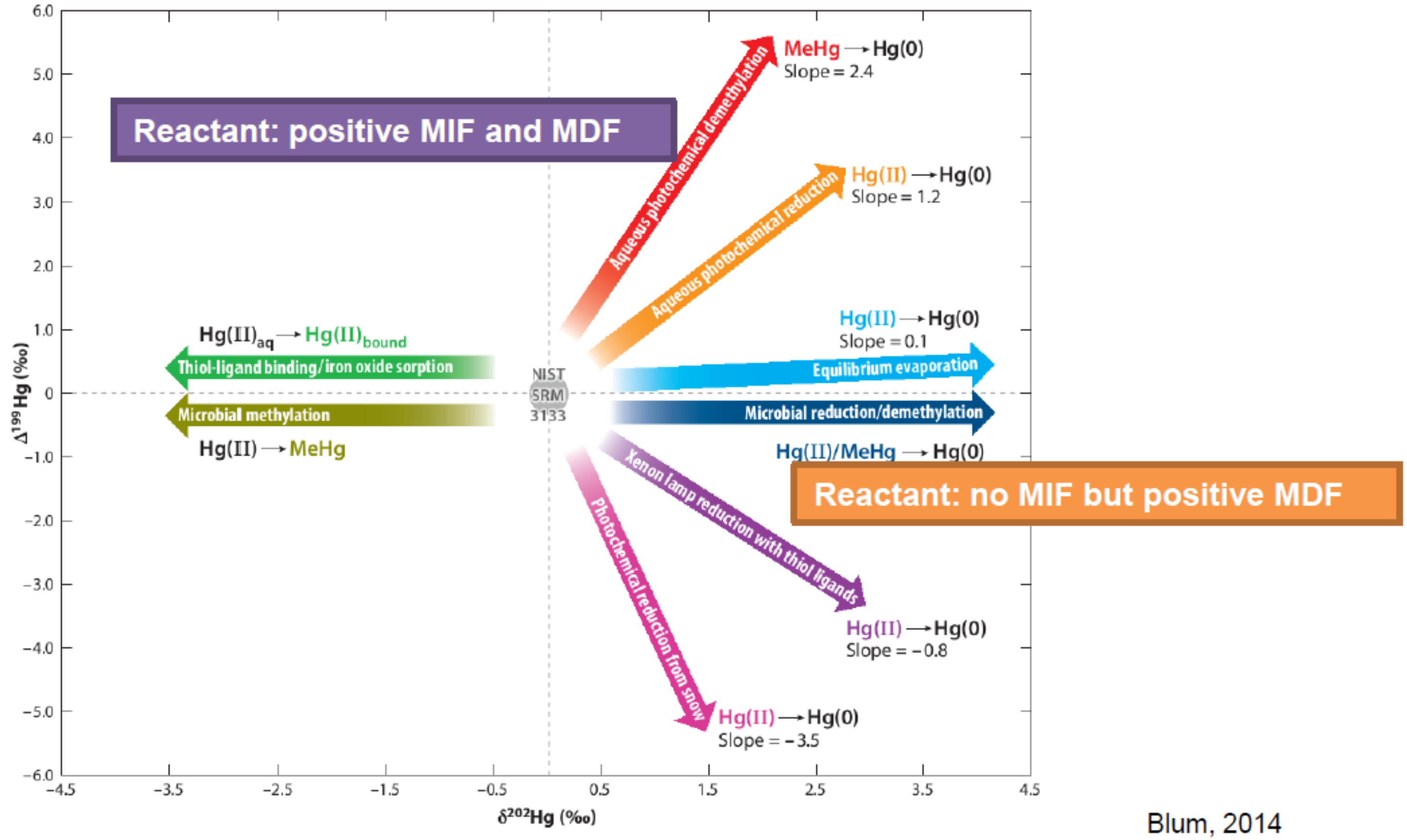



Based on Schaefer et al, Geomicrobiol. J. 2002

**Methyl-HgX Production**
Methylation
MDF (-)

**Methyl-HgX Degradation**
1) Photo-de-methylation MDF (+) & MIF (+)
2) Microbial de-methylation MDF (+)
3) Dimethyla-tion ?

**Ultimate sink of Methyl-HgX: food web bioaccumulation: no MIF, MDF (?)**




Blum, 2014

**MDF**

- Chemical processes
- Physical processes
- Biological processes

**MIF**

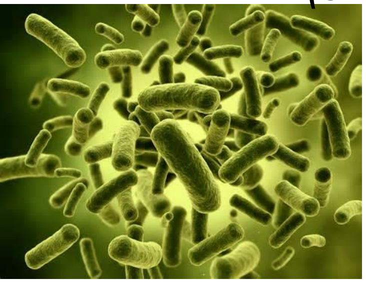
- Photo-reduction
- Photo-demethylation
- ~~Biological processes~~

# Mechanistic studies

## 2 Hg methylation pathways

**Biotic methylation**

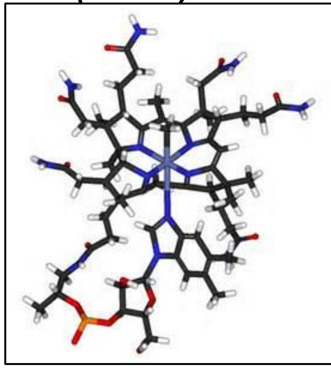
*by Sulphate-Reducing Bacteria (SRB)*



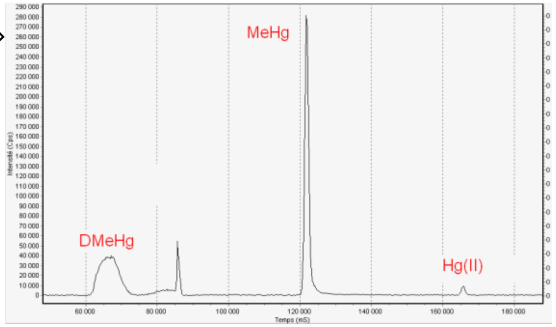
*Incubation of natural Hg(II) (NIST 3133)*

**Abiotic methylation**

*by methylcobalamin (MeCo)*



**Stop of the incubation at selected times (0, 0.5, 2, 8, 24h)**



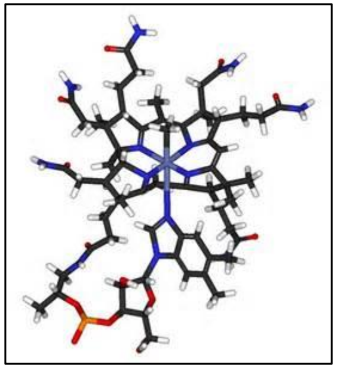

*Gas Chromatography – ICP/MS analysis*

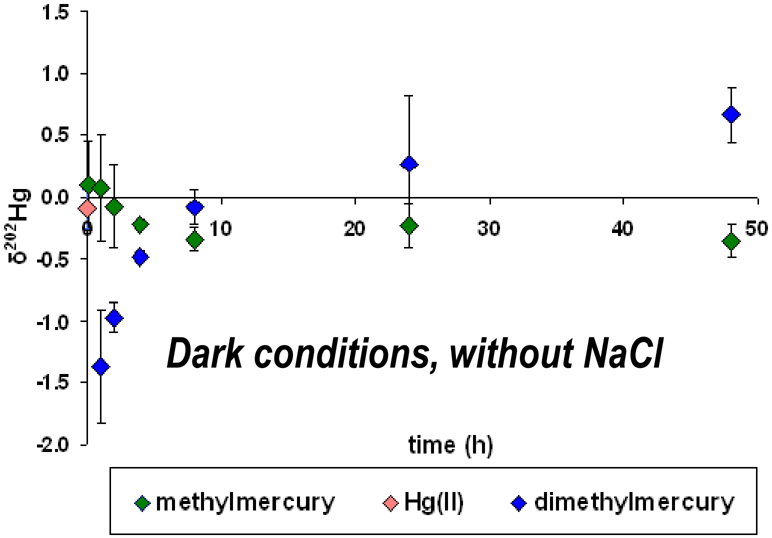
Quantification of Hg species (Hg(II), $CH_3Hg$, $(CH_3)_2Hg$) by isotopic dilution

*Gas Chromatography – Multicollector ICP/MS analysis*

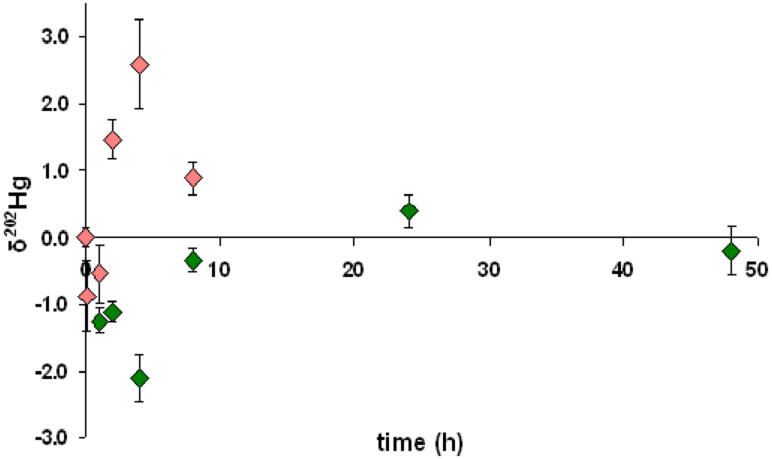
Measurement of of Hg species (Hg(II), $CH_3Hg$, $(CH_3)_2Hg$) specific stable isotopic composition

# Isotopic fractionation of Hg species during abiotic methylation

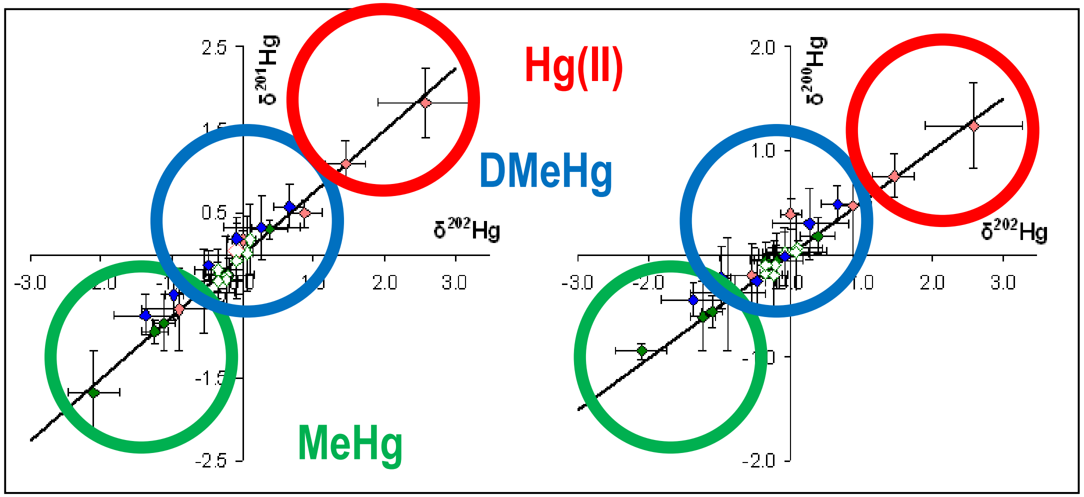





*Dark conditions, without NaCl*

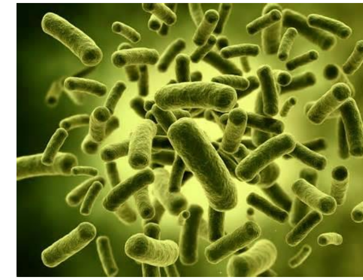


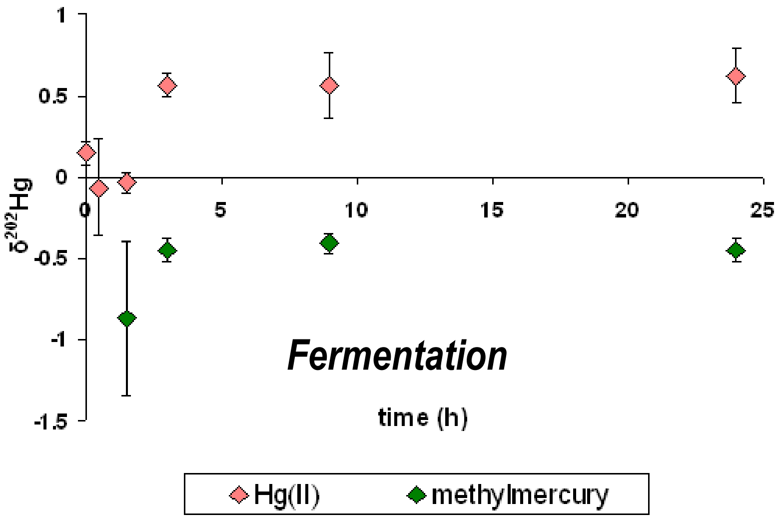

*Dark conditions, <u>with NaCl</u>*

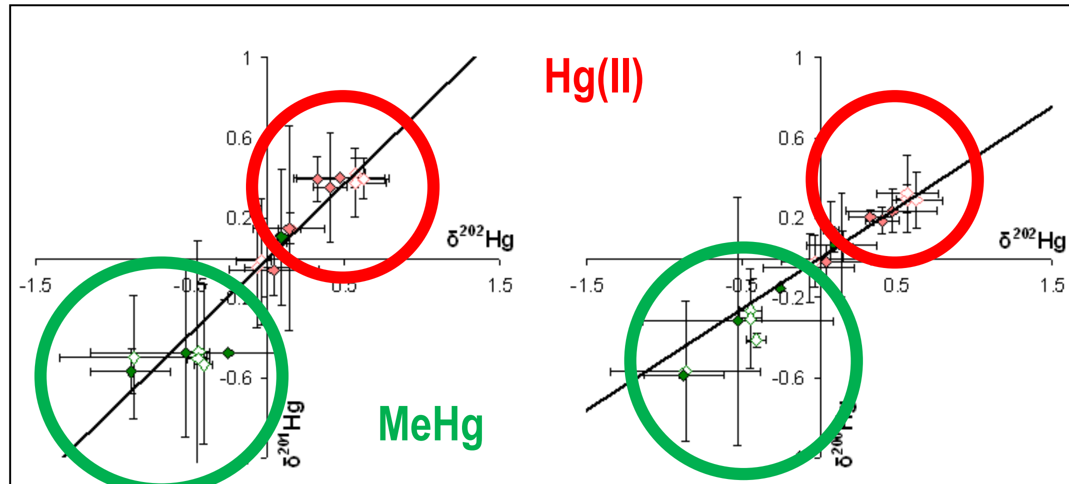


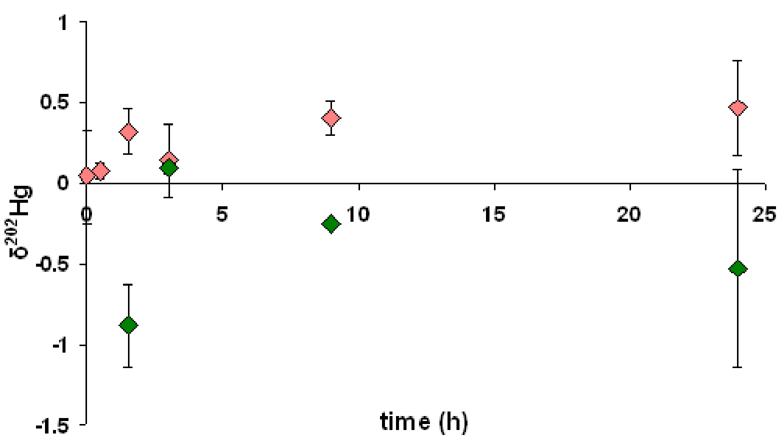

- **Pure Mass-Dependent Fractionation (MDF)**
- **$(CH_3)_2Hg$ become progressively enriched in heavier isotopes**
- **$CH_3Hg$ become progressively enriched in lighter isotopes**

## Isotopic fractionation of Hg species during biotic methylation





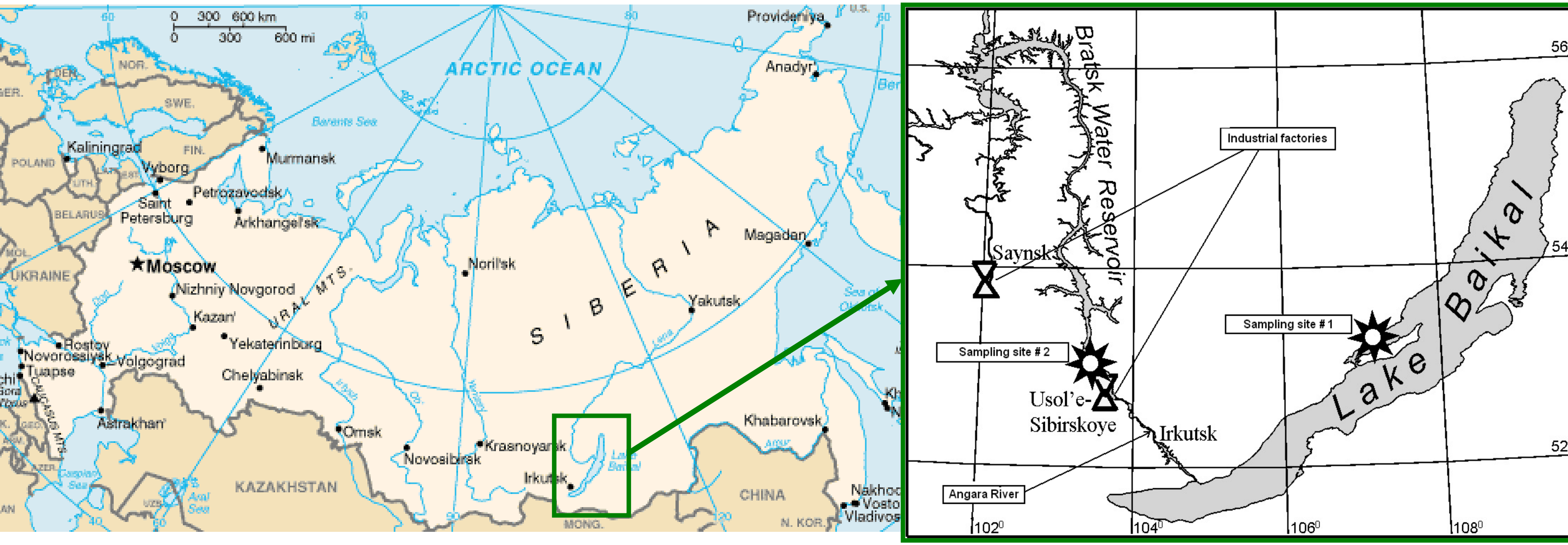




*Sulphate reducing conditions*

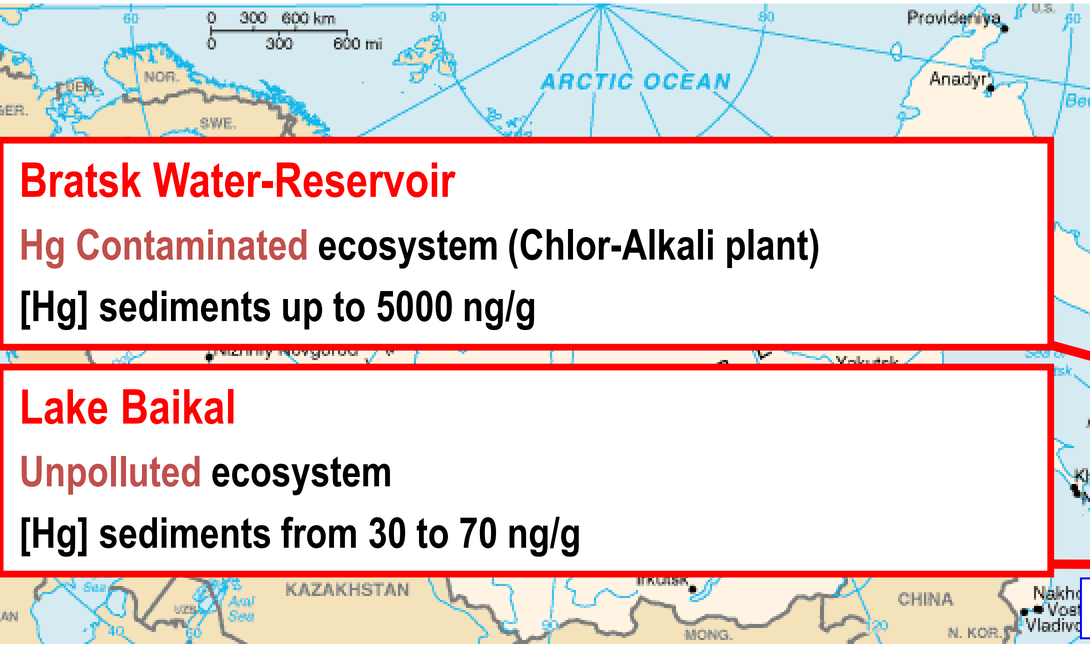
- **Pure Mass-Dependent Fractionation (MDF)**
- **$CH_3Hg$ after 24h enriched in lighter isotopes**

**➔in agreement with kinetic fractionation process**

# Comparing polluted & remote sites



# Comparing polluted & remote sites




**Bratsk Water-Reservoir**

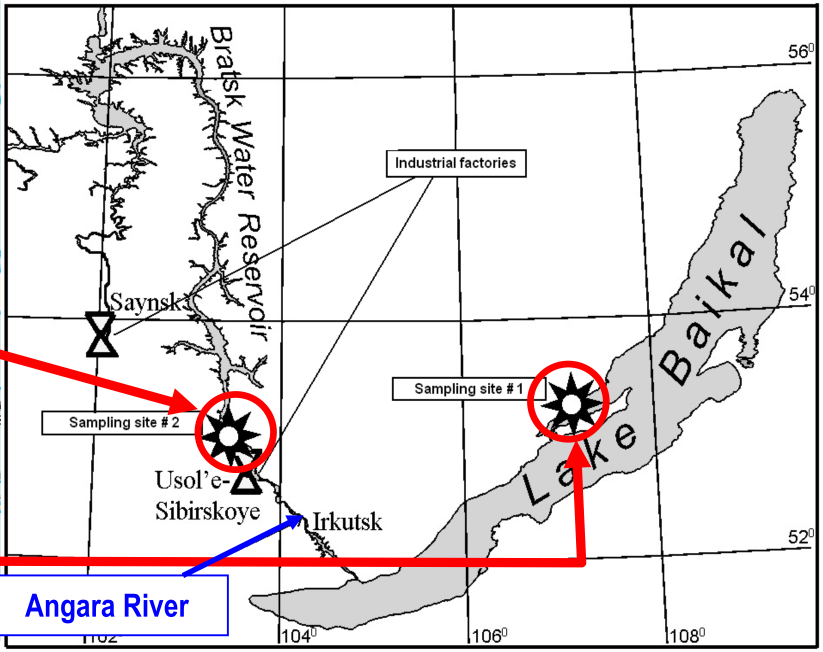
**Hg Contaminated ecosystem (Chlor-Alkali plant)**

**[Hg] sediments up to 5000 ng/g**

**Lake Baikal**

**Unpolluted ecosystem**

**[Hg] sediments from 30 to 70 ng/g**




**Hg total concentration ?**

**MeHg? Hg(II)?**

**Trophic level ?**

**Feeding strategy ?**

**Water chemistry ?**

**Hydrologic parameters ?**

**SAMPLES**

**Relationship ?**

- Fishes muscles
- kidney, …
- Plankton, amphipods
- Sediments

**Anthropogenic sources**

**Biogeochemical processes**

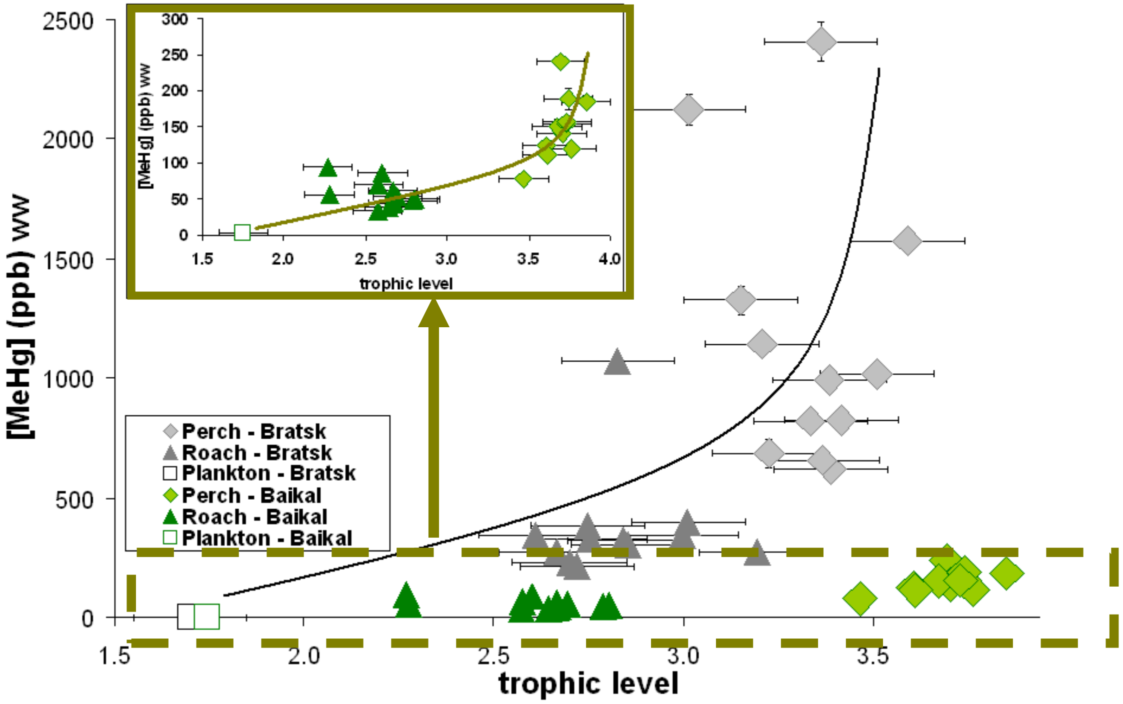
**Isotopic composition ?**

**Hg Total ?**

**Hg Compound specific ?**

*MC-ICPMS*

# Comparing polluted & remote sites




- MeHg > 85% total Hg in fishes
- MeHg from 20 to 50% in plankton
- [MeHg] increase with TL

Hg speciation at various fishes trophic level:

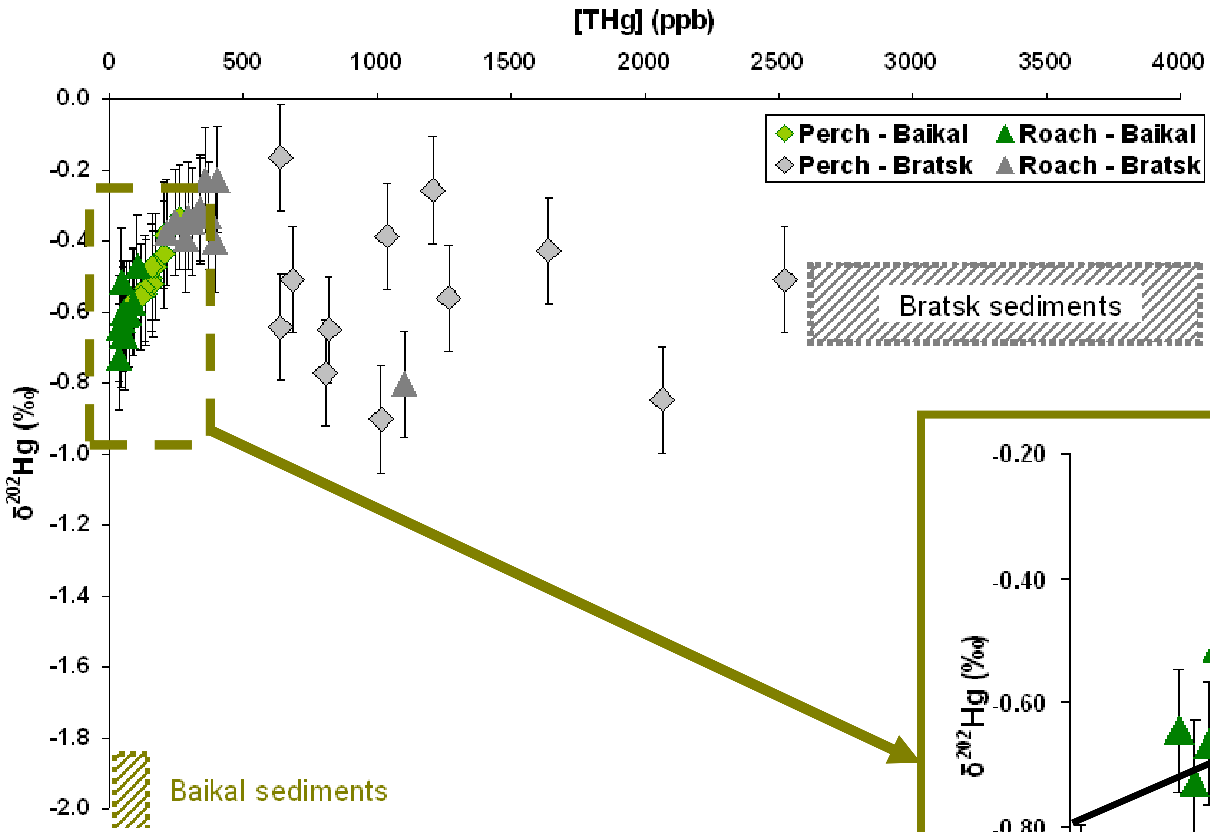
➔ MeHg bioaccumulation and biomagnification within food webs of both areas

➔ highly Hg contaminated fishes in Bratsk reservoir

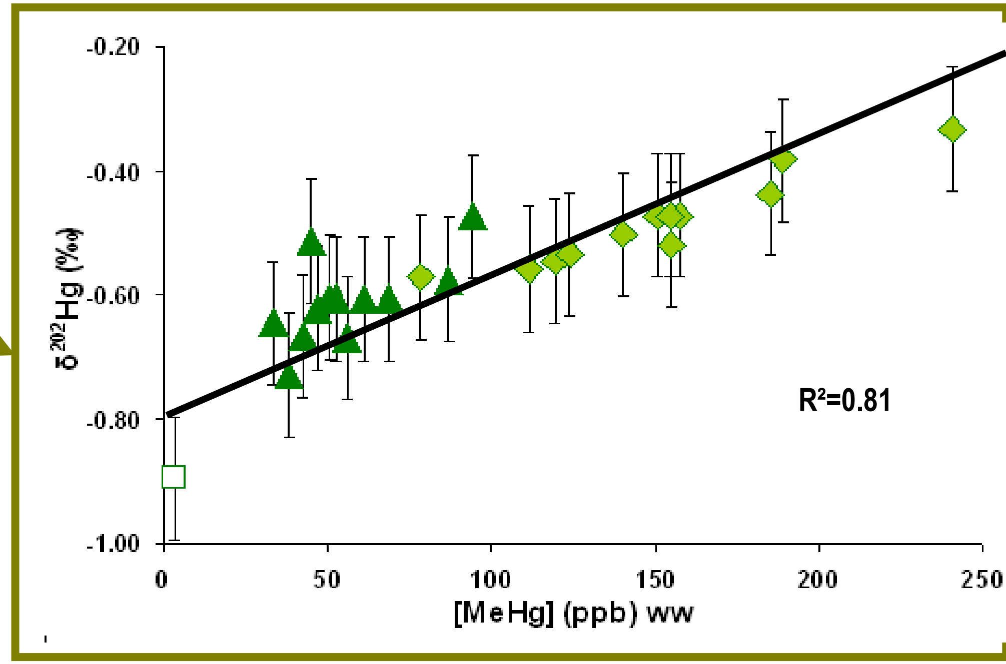
(5 to 20 times more concentrated than Lake Baikal)

**WHAT ABOUT ISOTOPIC COMPOSITION ?**

# Comparing polluted & remote sites




## MDF vs [Hg]




**BRATSK RESERVOIR**

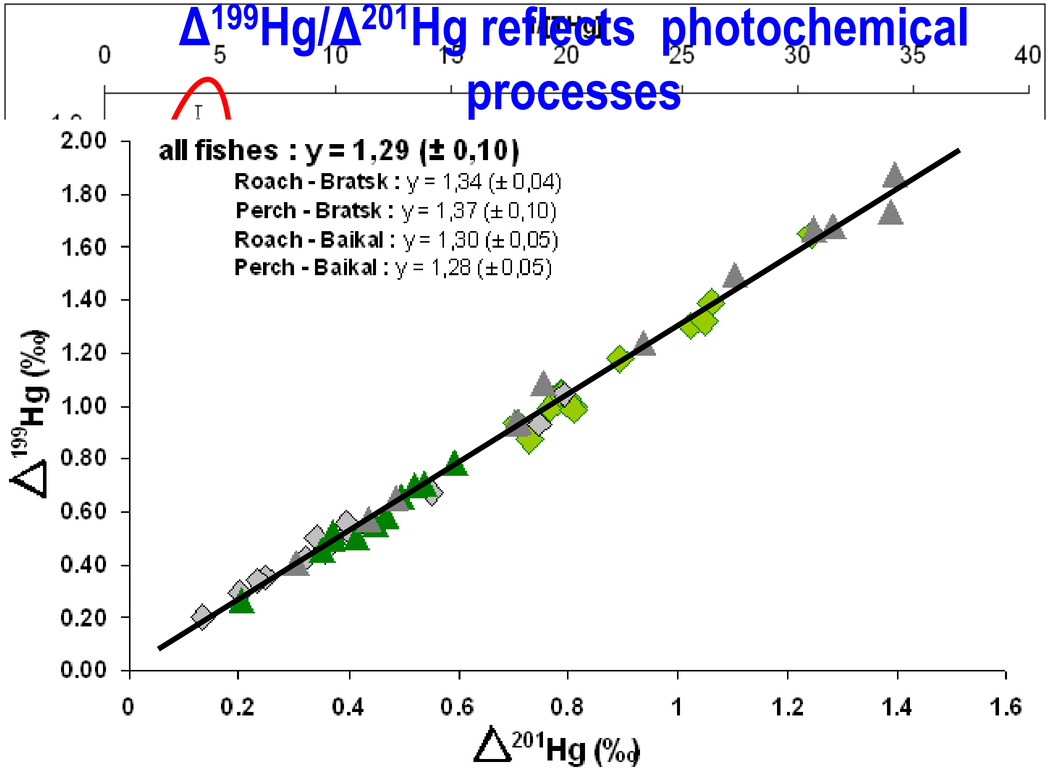
➔ No trend for $\delta^{202}$Hg

**LAKE BAIKAL**

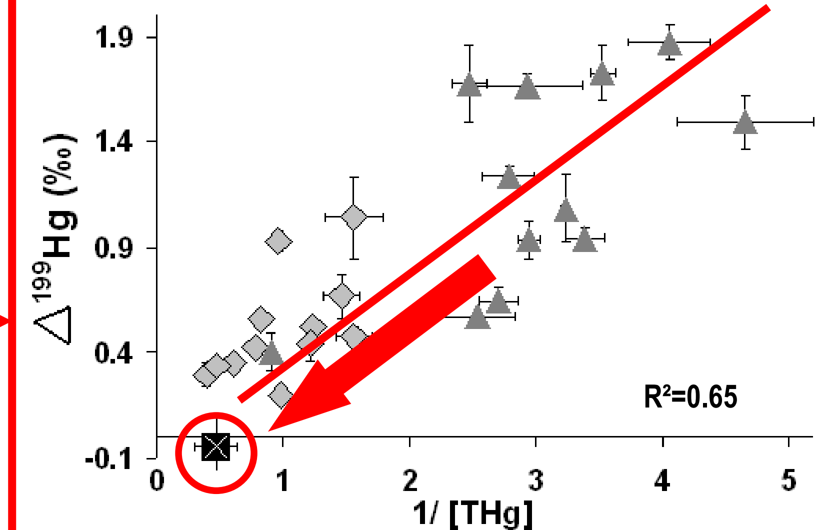
➔ increasing $\delta^{202}$Hg due to Hg bioaccumulation and/or trophic transfer

# Comparing polluted & remote sites

## $\Delta^{199}Hg/\Delta^{201}Hg$ reflects photochemical processes




**MIF vs [Hg]**




**LAKE BAIKAL & BRATSK RESERVOIR**

LAKE BAIKAL

➔ MIF signature ($\Delta^{199/201}$=1.3)

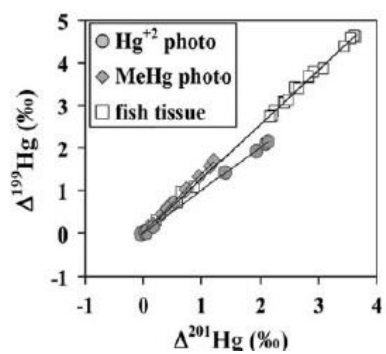
➔ Higher MIF extent higher trophic le

- photodemethylation in the water column

Bioaccumulation? Source effect?

- Assimilation of Residual MeHg

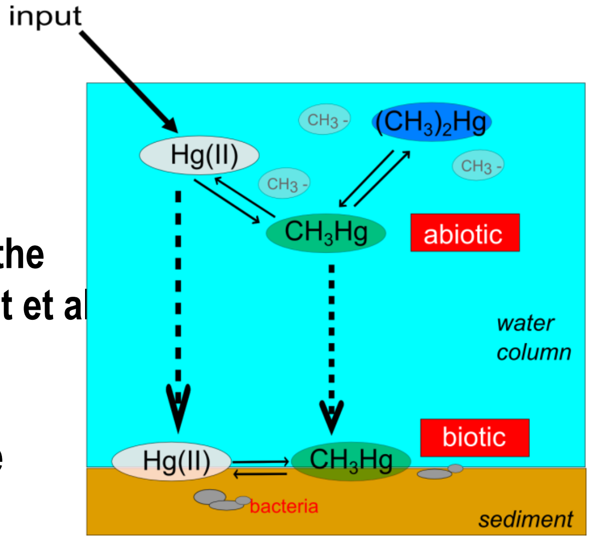
*(Bergquist and Blum, 2007)*




**BRATSK RESERVOIR**

➔ **MIF extent tracks sediment contamination source in fishes**

# Hg stable isotopes in nature




- **Variations of Hg isotopic composition in the environment**

  **➔ Isotopic signature of Hg in environmental samples helpful to identify the source of Hg contamination (ex. Foucher et al. (2009) in sediments, Perrot et al (2010) in fishes, …)**

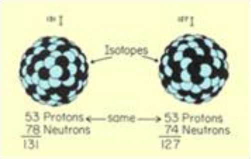
- **Several biogeochemical reactions involving Hg in nature produce isotopic fractionation of Hg**

| | | |
|---|---|---|
| **reduction** | **➔ microbial** | (Kritee et al., 2008) |
| | **➔ photoreduction** | (Zheng et al., 2009; Bergquist and Blum, 2007) |
| | **➔ abiotic** | (Zheng and Hintelmann, 2010) |
| **demethylation** | **➔ microbial** | (Kritee et al., 2009) |
| | **➔ photodemethylation** | (Bergquist and Blum, 2007; Malinovsky et al., 2010) |
| **methylation** | **➔ microbial** | (Rodriguez-Gonzalez et al., 2009) |
| | **➔ abiotic** | (Malinovsky and Vanhaecke, 2011) |

***Modification of Hg source isotopic signature***

***≠ pathways of reaction*** → ***≠ fractionation processes and extent***

**Are Hg species (Hg(II), $CH_3Hg$) fractionation dependent both on methylation/demethylation kinetics and environmental conditions?**



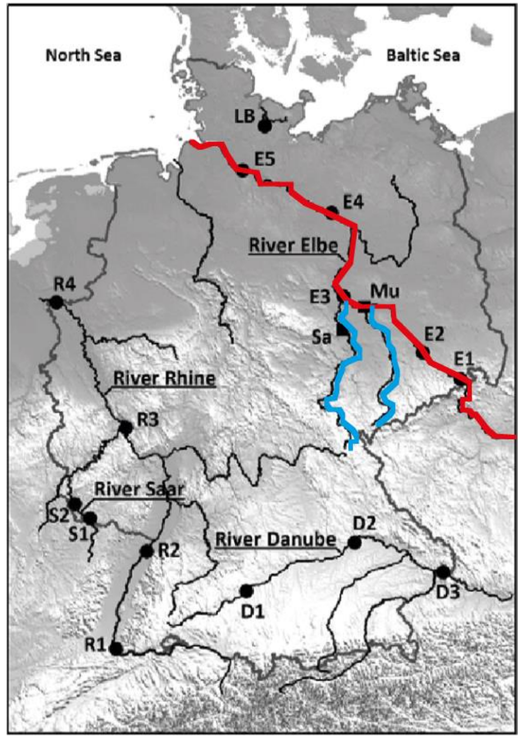

# Assessing historical Hg contamination of main German rivers using Hg isotopes

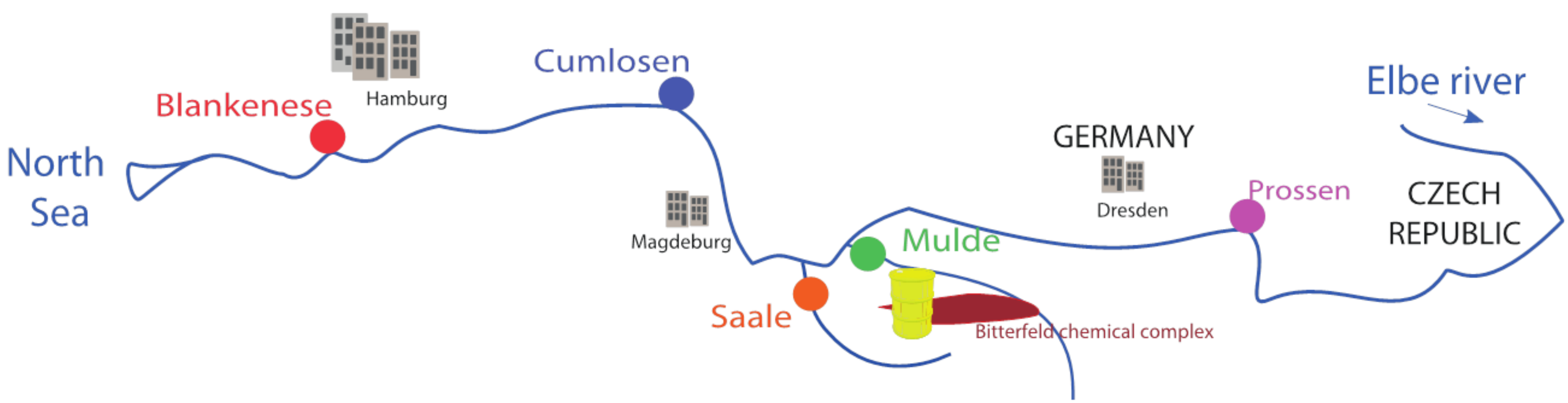
Umwelt Bundesamt

Fraunhofer IME

UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR

Umwelt Bundesamt



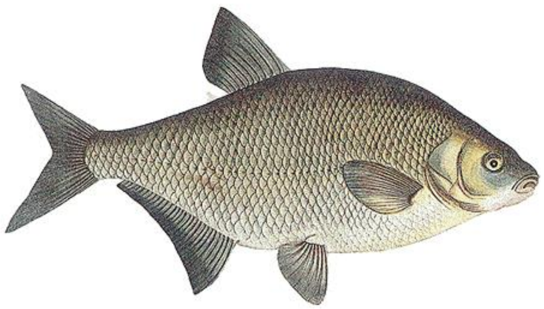

cnrs

Fraunhofer IME

The **Water Framework Directive (WFD)** 2000/60/EC requires that EU countries achieve good chemical status of waters within regulated limits

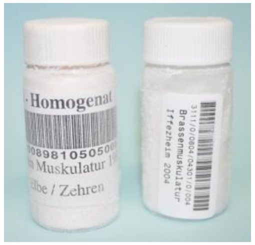
Directive 2013/39/EU on environmental quality standards (EQS) specifies that the mercury (Hg) level of fish is below the **EQS of 20 µg/kg wet weight (ww)**

**Protection goal:**
secondary poisoning of predators



# Concept of the German ESB

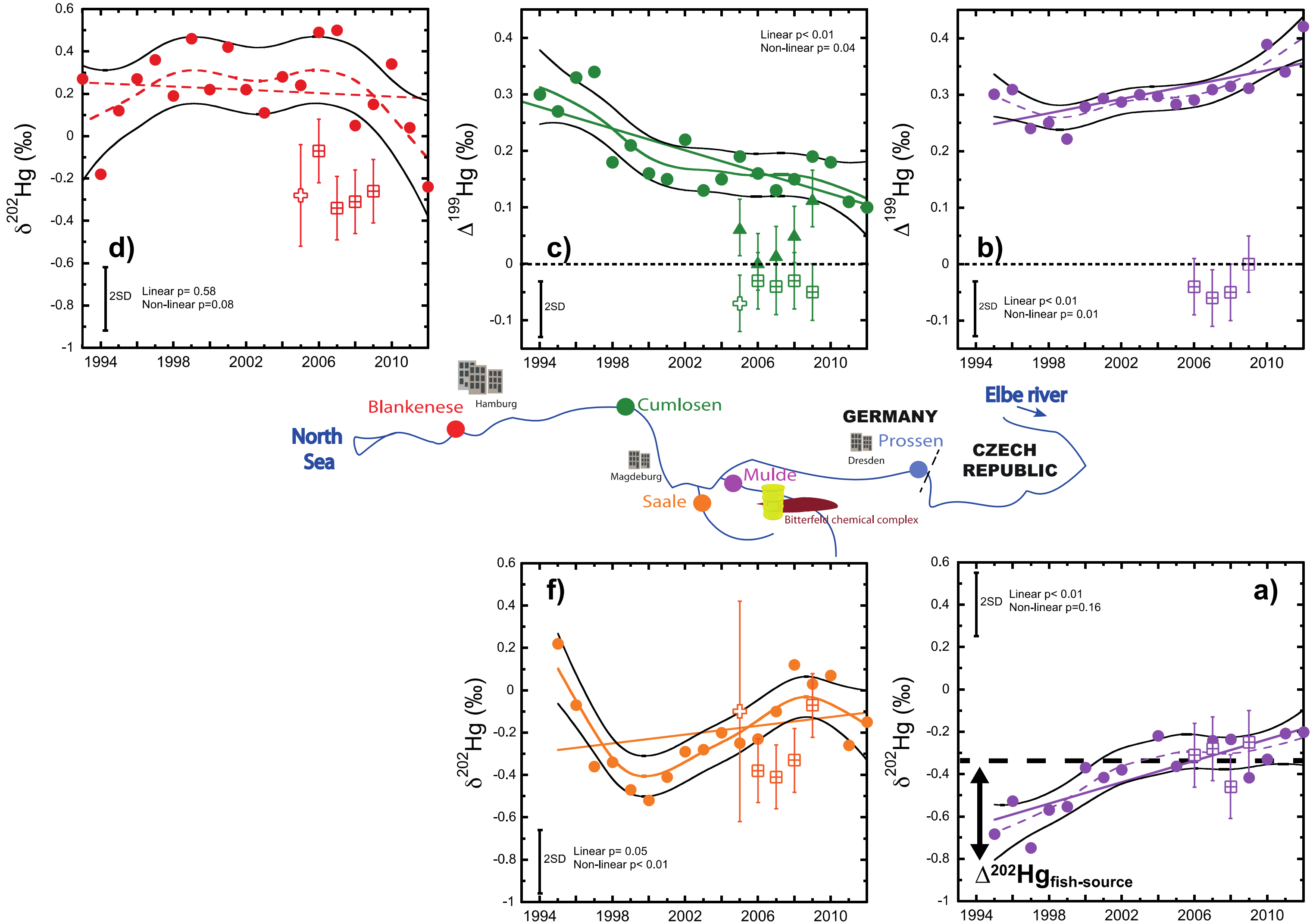
- For the German ESB, ecologically representative environmental and human specimens are collected, analyzed for environmentally relevant substances and stored
- Long-term storage is performed under conditions which exclude any change in composition or chemical properties over a period of several decades
- The ESB archive retains specimens for retrospective analytical characterization concerning unpredictable questions which may arise in future

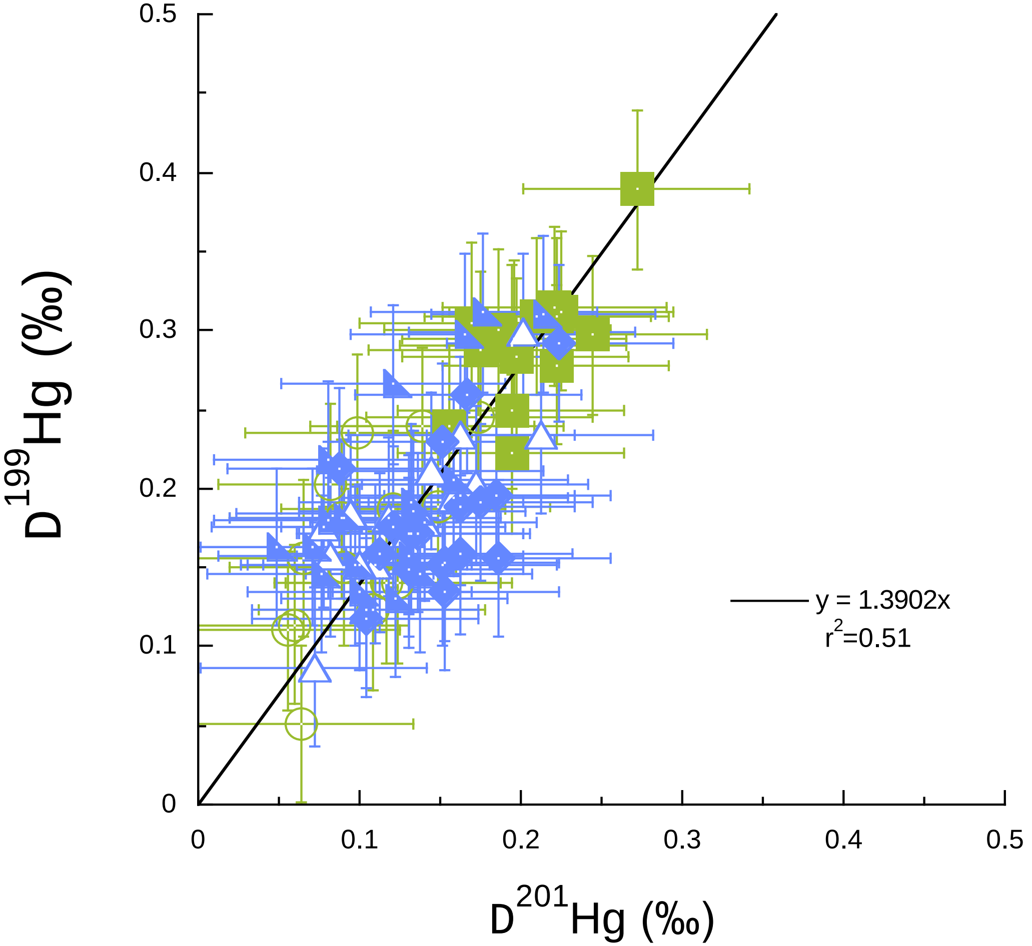

Umwelt Bundesamt

Fraunhofer IME

# Sediments as a source



# Elbe and Elbe tributaries, MIF

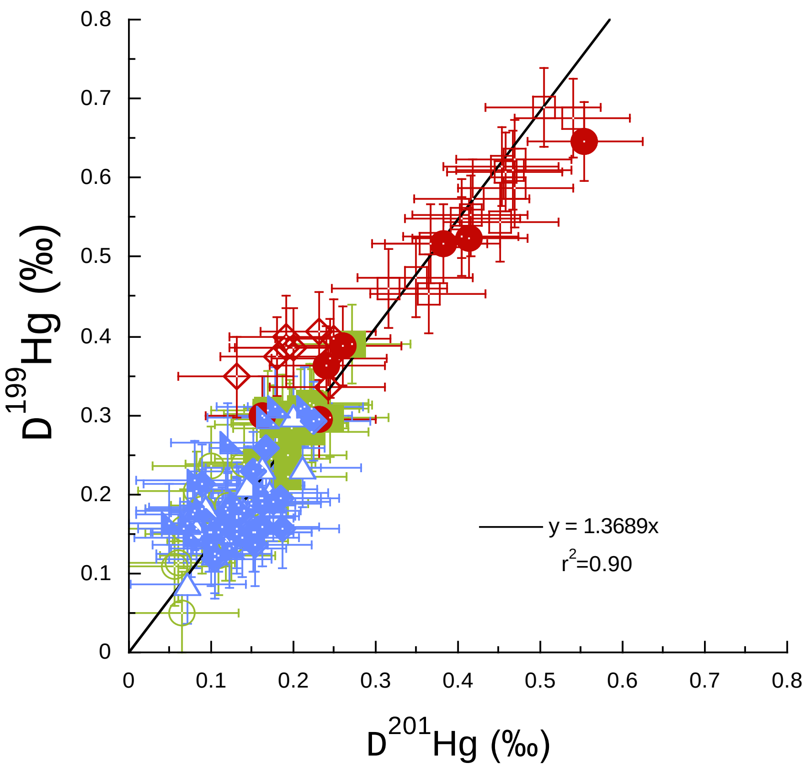


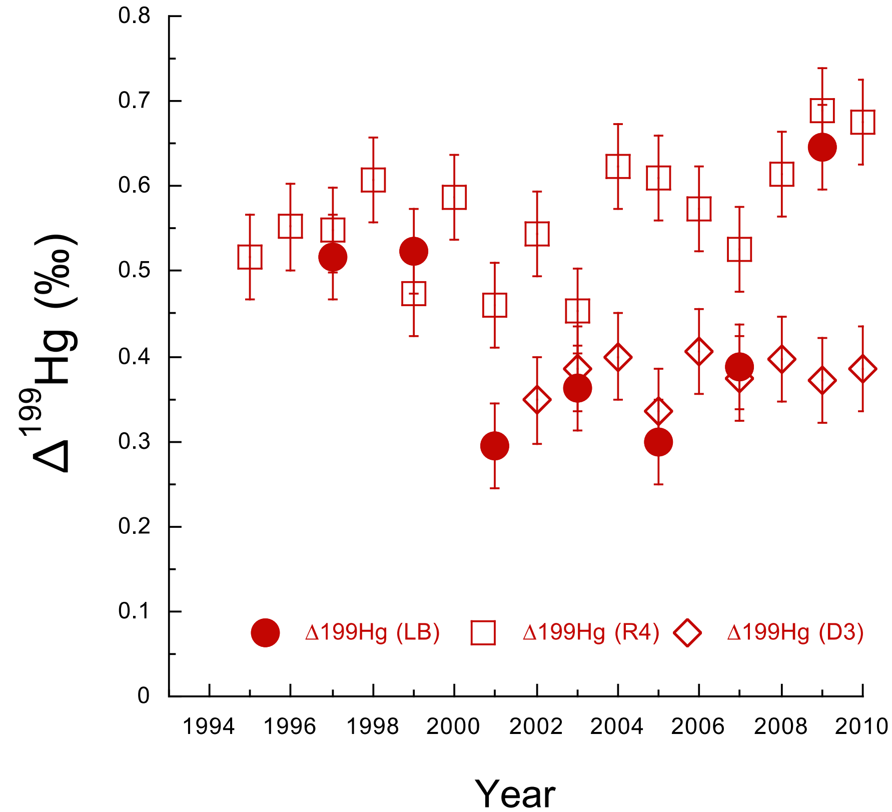

- $\Delta^{199}$Hg and $\Delta^{201}$Hg values close to 0. Slope of 1.39 but $r^2$=0.51 (forced through 0)

incorporation of MeHg photo-demethylated into the water column (small extent).

# MIF issues

- Others systems improve the $r^2$ slope value

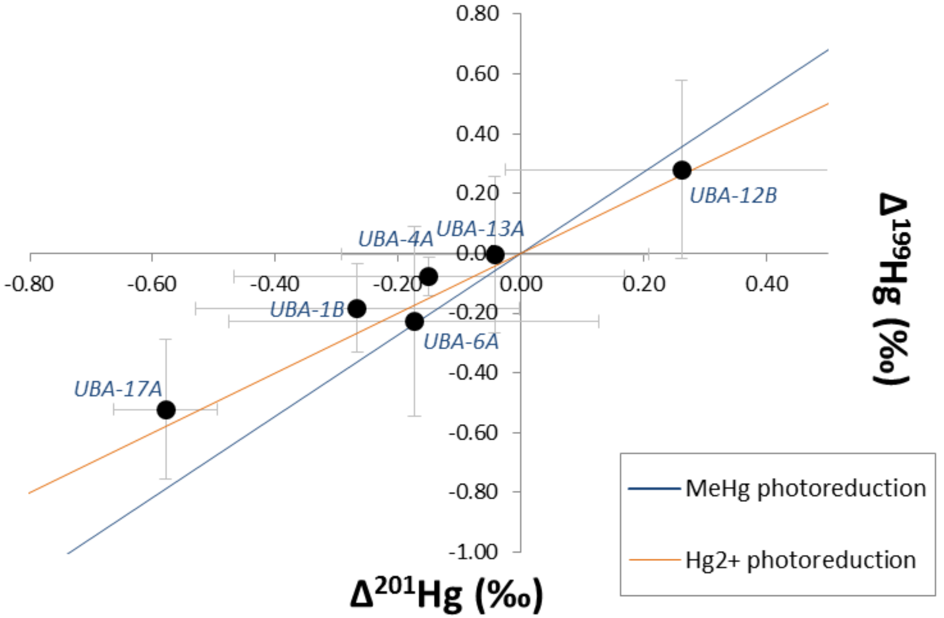



- R4: odd isotope enrichment (up to + 0.7‰), larger than all other. Restricted range of isotope fractionation (≈0.25‰), no clear temporal trend
- D3 : no trend
- LB : Largest range (0.3‰) and contrasted trend

| Sample | Date of sampling | [Hg] (ng/L) | Volume (ml)* | δ202Hg (‰) | Δ200Hg (‰) | Δ199Hg (‰) |
|---|---|---|---|---|---|---|
| UBA 1B | 05/01/2016 | 3.8 | 912 | -0.68 | 0.10 | -0.18 |
| UBA 4A | 26/01/2016 | 3.5 | 851 | -0.72 | -0.05 | -0.08 |
| UBA 6A | 09/02/2016 | 5.2 | 805 | -0.61 | 0.04 | -0.23 |
| UBA 12B | 22/03/2016 | 3.7 | 498 | -0.35 | 0.12 | 0.28 |
| UBA 13A | 29/03/2016 | 4.7 | 633 | -0.28 | 0.22 | 0.00 |
| UBA 17A | 26/04/2016 | 5.5 | 512 | -0.47 | 0.17 | -0.52 |

** collected on 1 week duration for each*




Significant ≠ MIF : different origin of Hg ?

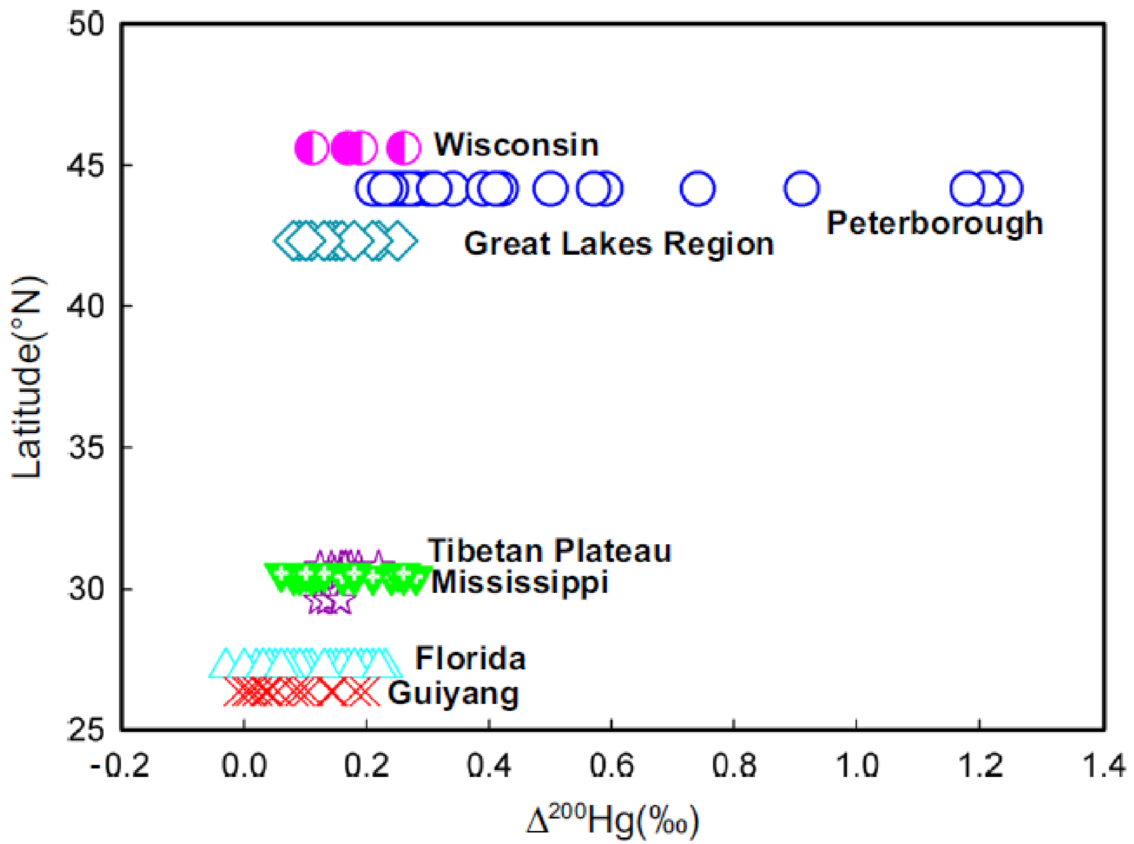



**Fig. 4** Even-MIF in precipitation samples collected from the North America and China (modified from Wang et al. 2015) [24, 36–39, 41, 42]. The Wisconsin rain samples collected in summer are similar to those samples in Peterborough of the same season. The fact that $\Delta^{200}$Hg displays a general increase with latitude implies an upper atmosphere provenance of even-MIF

Cai et al. Review on even MIF : Science Bull. 2016

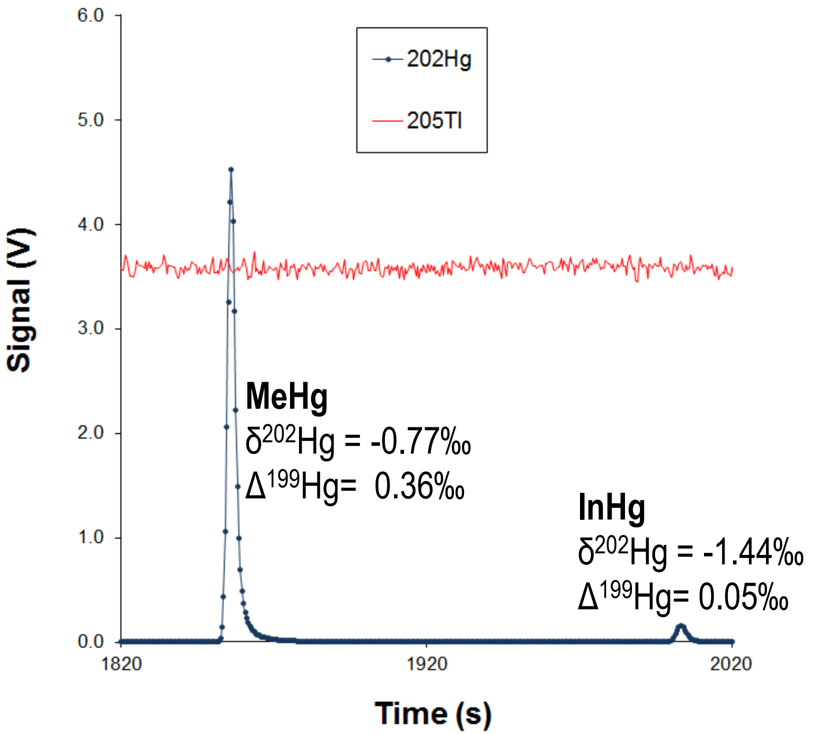
# GC vs CVG / MC-ICP-MS

**Example** : Bremen muscle sample

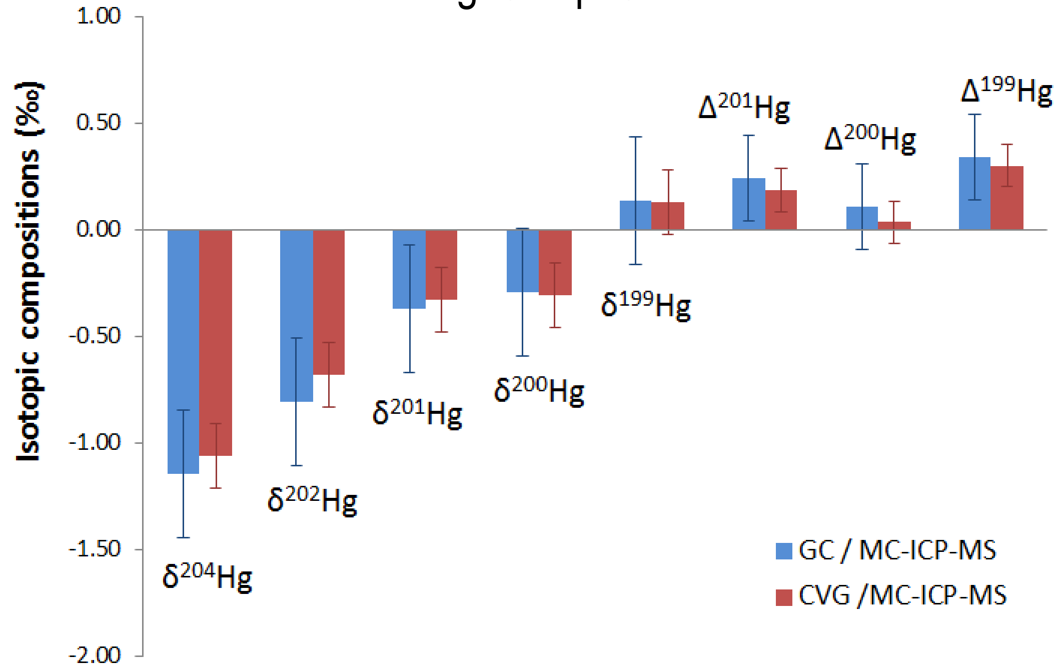
Speciation : [MeHg] = 94 % of total Hg

[InHg] = 6% of total Hg

**Species specific** Hg isotopes by GC / MC-ICP-MS :




**Total** Hg Isotopes :



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