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Stable isotope analysis as a critical tool on the advancement of mercury and selenium interaction in biota

New insights on mercury demethylation mechanism^[1]

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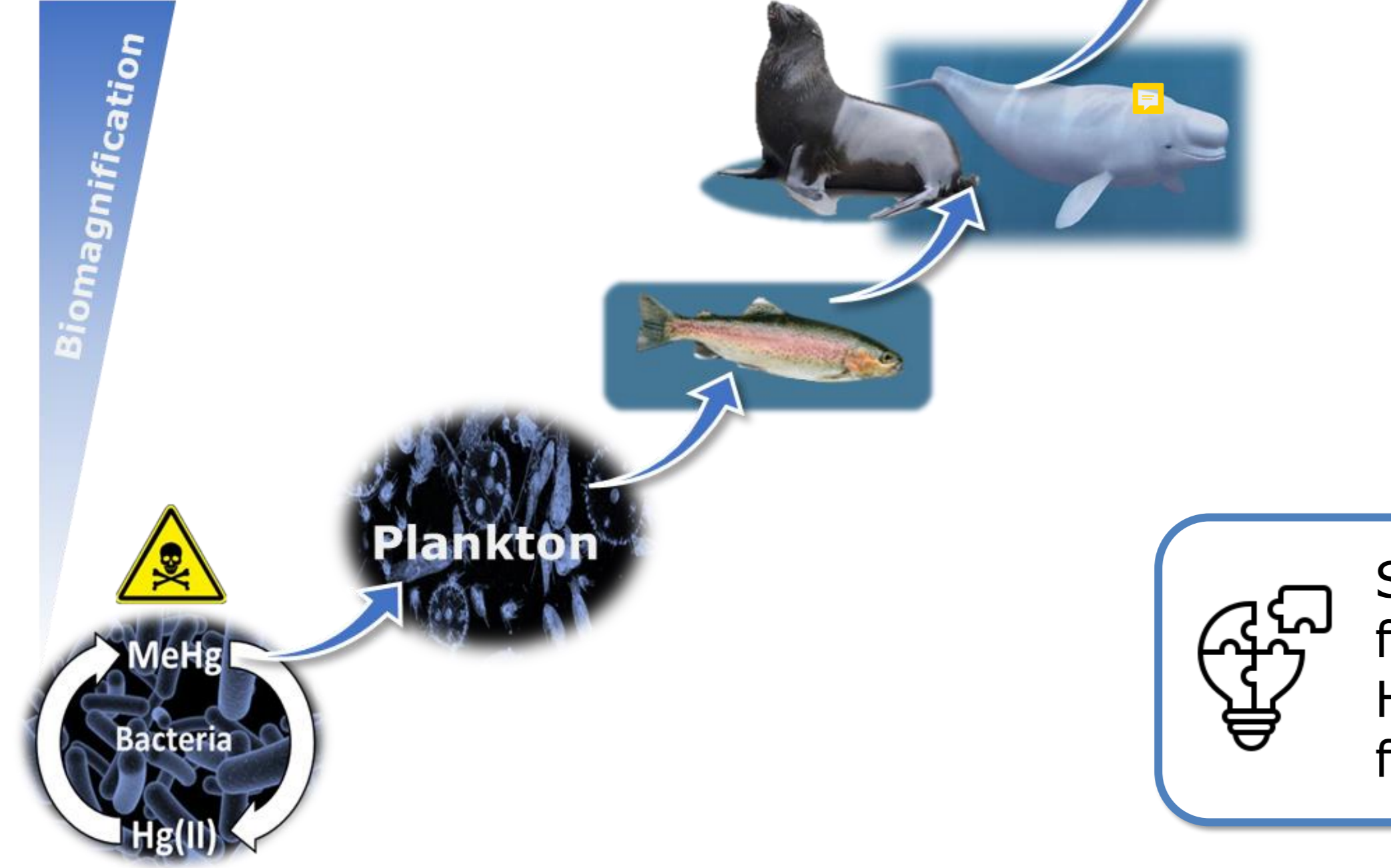
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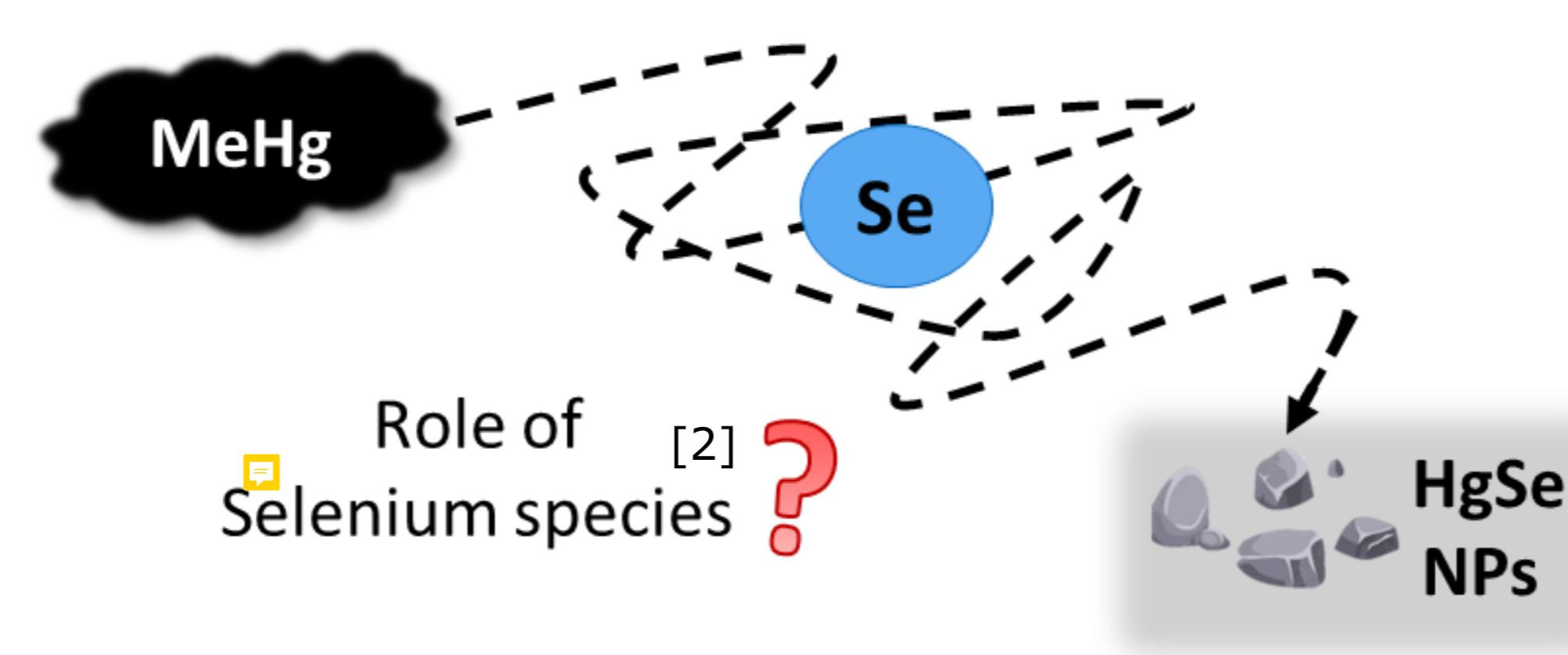
Background

Mercury (Hg) is a globally distributed pollutant

Its more neurotoxic chemical form methylmercury (MeHg) bioaccumulates and biomagnifies through the aquatic food chain



Hg fate and its detoxification mechanism in biota remains unclear



Simultaneous information about the (pollution) sources and the fate on living organisms of Hg can be obtained by investigating Hg isotopes mass dependent (MDF) and mass independent fractionation (MIF)

Isotopic characterization

$\delta^{202}\text{Hg}$ (MDF) - insights into Hg internal transformations

$\Delta^{199}\text{Hg}$ (MIF) - insights into Hg food sources

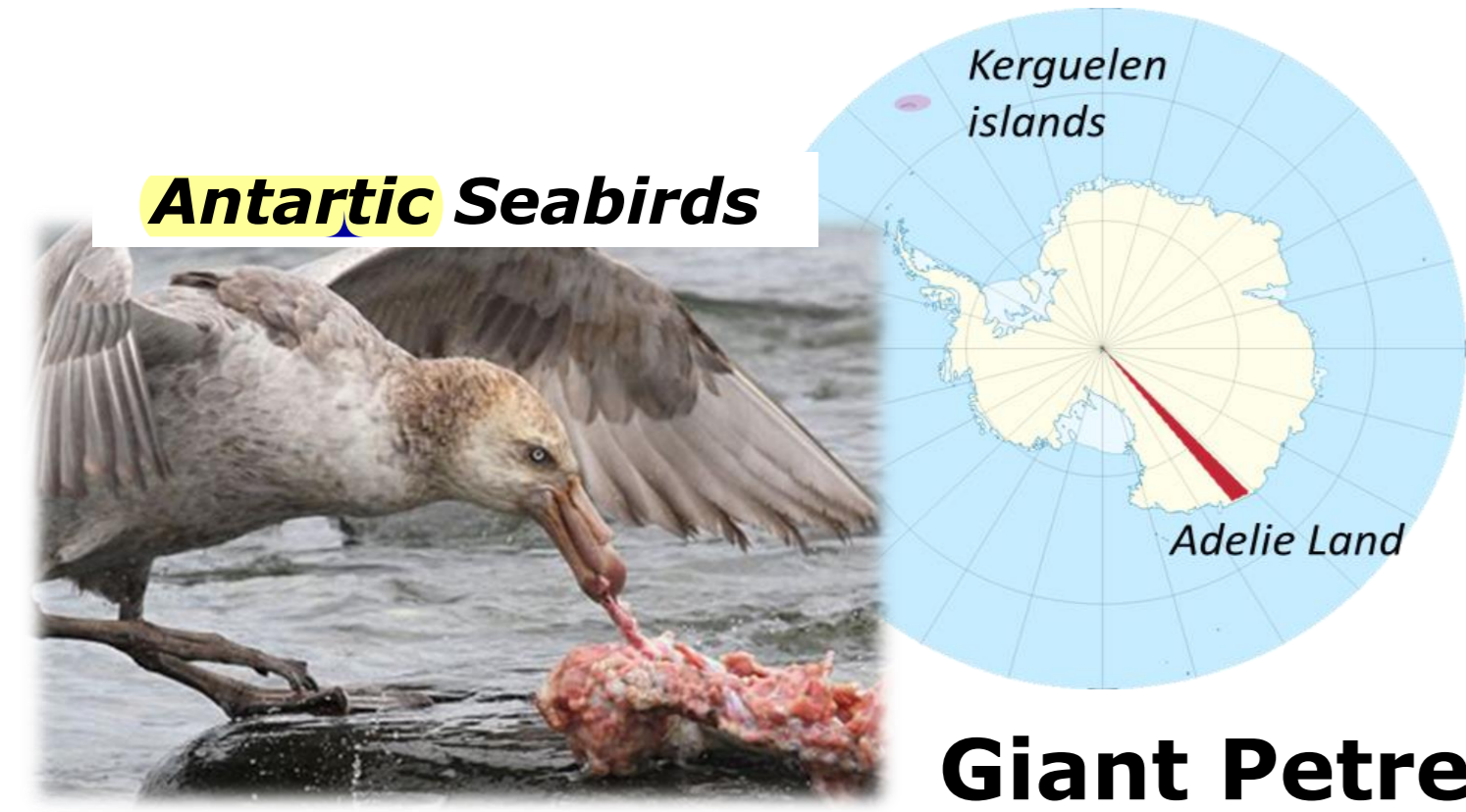
Total Hg in tissue

HgSe NPs in the tissue



Ultimate product of MeHg detoxification bioaccumulated in these seabird tissues

Methodology



- **Top scavengers** of the Southern Ocean
- **High Hg and Se bioaccumulation** in tissues (up to 445 mg(Se) g⁻¹ and **1 mg(Hg) g⁻¹**)
- Samples from 5 key tissues of **11 dead individuals (liver, kidneys, muscle, and brain) - 41 tissues**

Sample digestion

Predigested tissue with 5mL of HNO₃ conc.

Microwave Ultrawave (Milestone, srl)

HgSe NPs extraction

Tissue soft digestion with 50% formic acid (v/v) at 85 °C for 2 hours

Centrifugation and filtration with 50 kDa cut-off filters

Analysis

Digested tissue

HgSe NPs extract



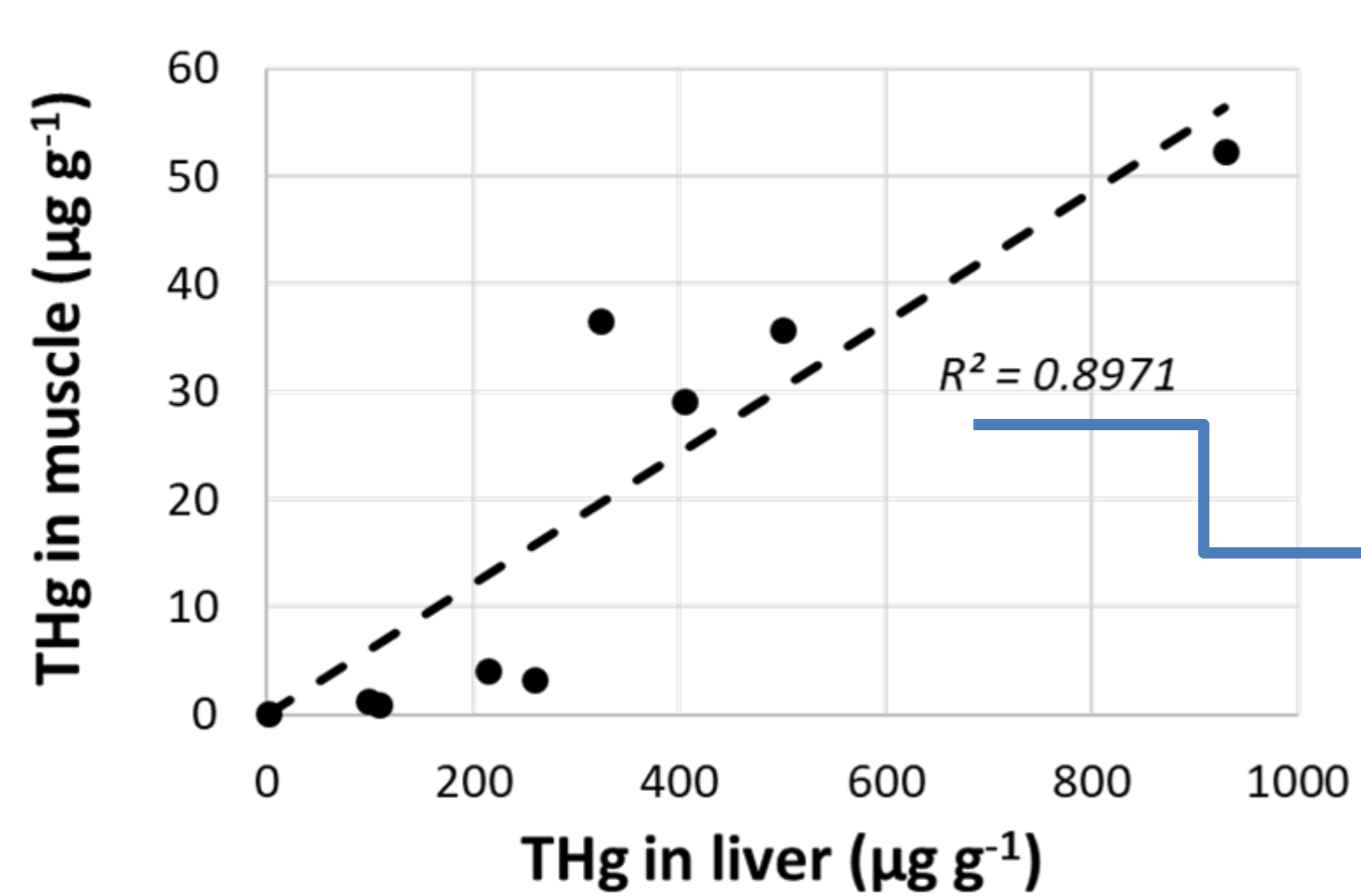
CV-AFS
Total concentration



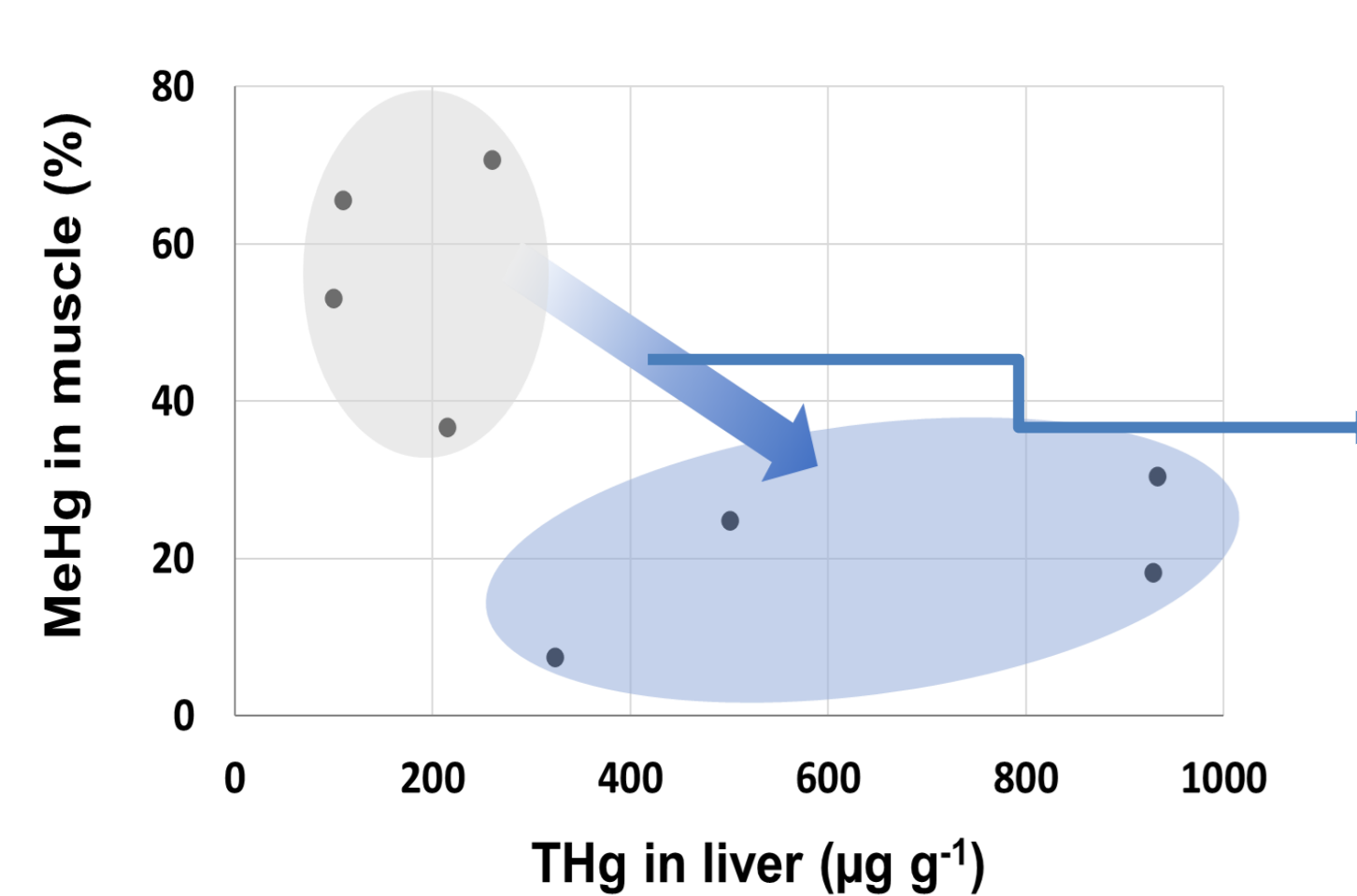
MC-ICP-MS
Isotope ratio

Results

Hg and MeHg concentration

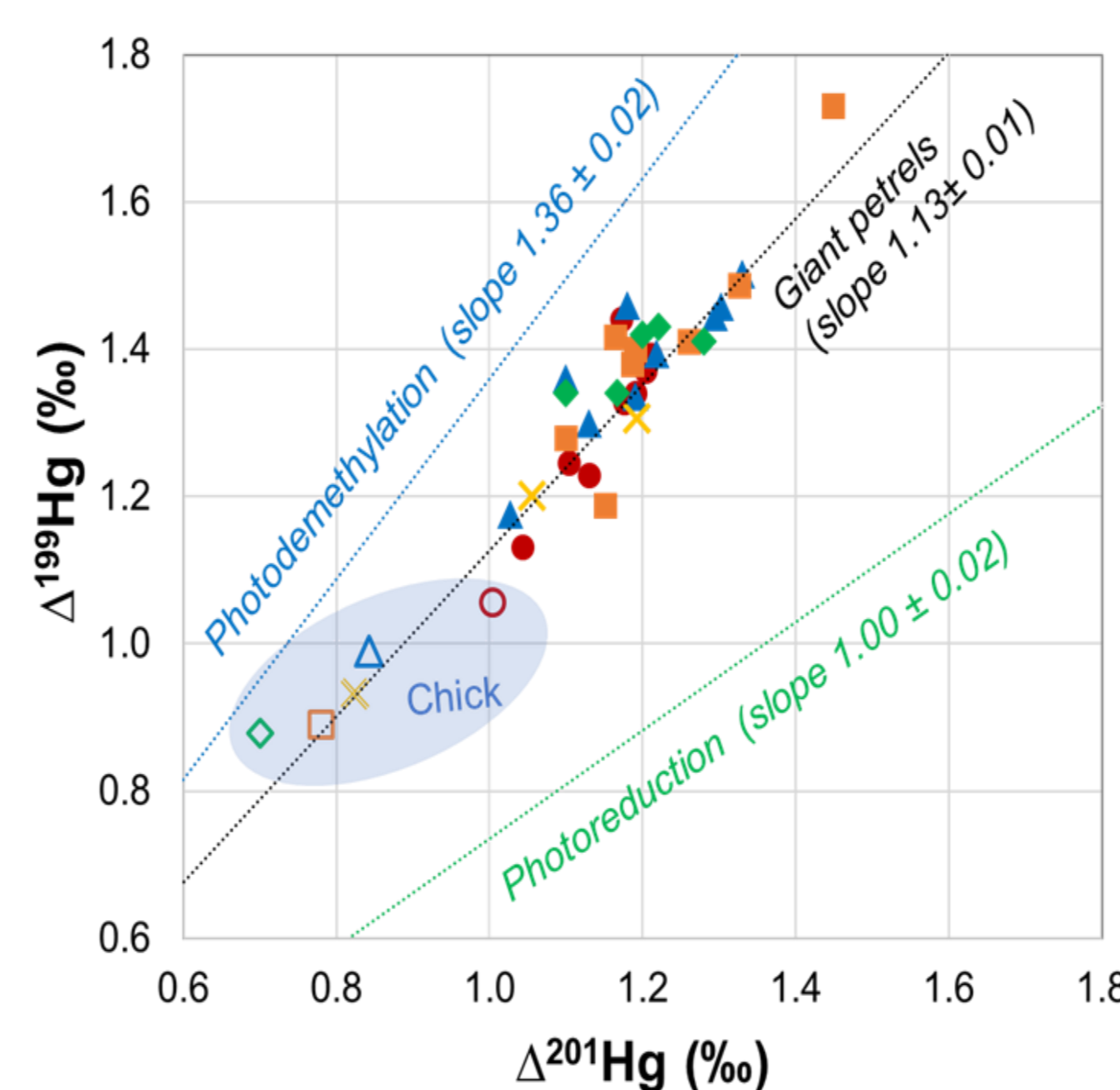


- Total Hg content are among the highest ever reported in seabirds, up to 933 µg g⁻¹ in the liver
- Hg being mainly retained in the liver but its excess being directly transferred towards the muscles as suggested by previous studies [Manceau, 2021]



- High variability of MeHg content among individuals
- The proportion of MeHg in the muscle decrease with age
- Brain exhibited the highest percentage of MeHg (34–74%)

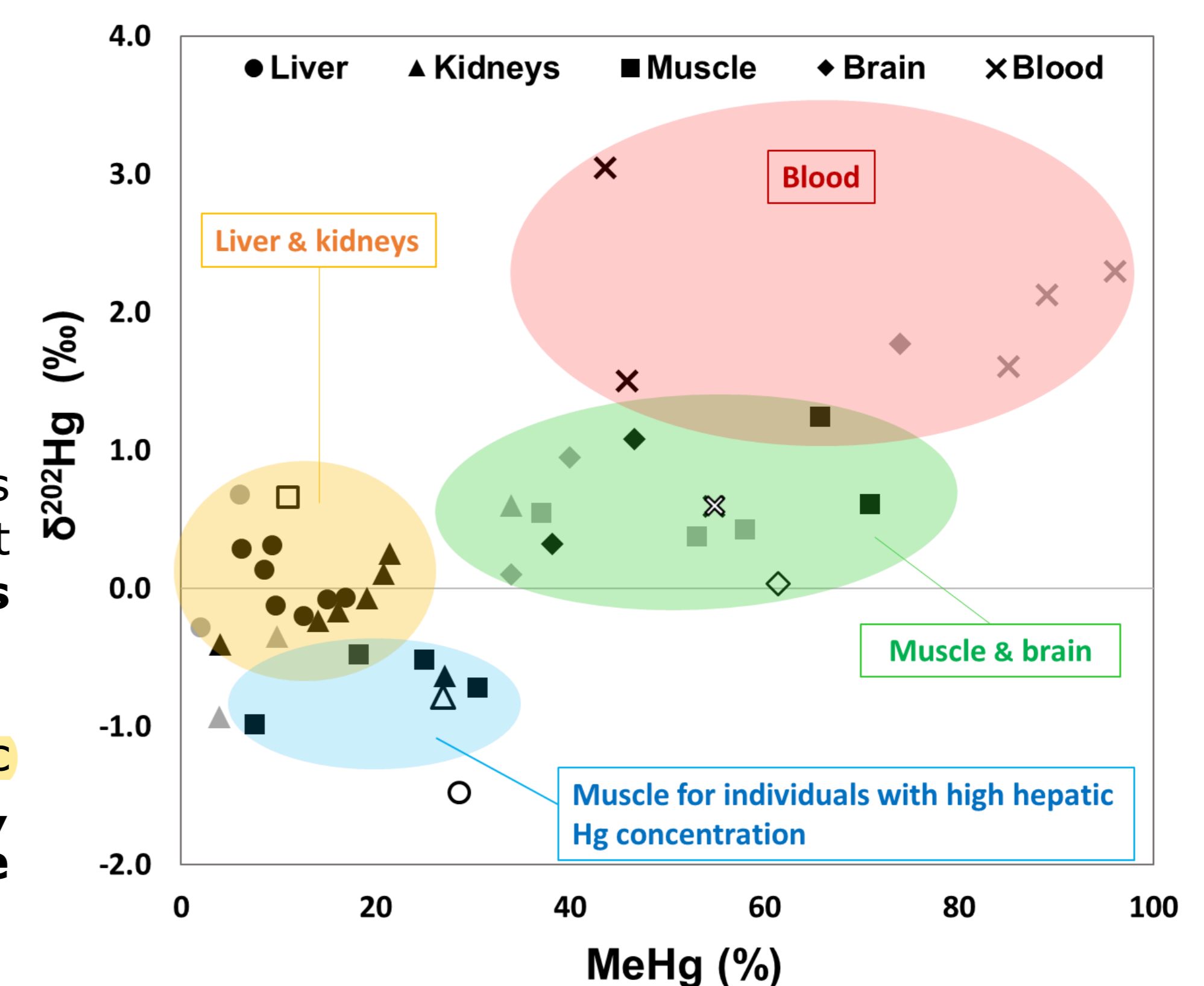
Isotopic characterization



- **Brain**, it is generally enriched in heavier isotopes compared to liver and kidneys, suggesting that **residual MeHg from the blood streams subsequently accumulate in this organ**
- **Muscle MDF** is inversely proportional to **hepatic THg content**. Hence, for **older individuals, demethylation occurs effectively in this tissue**

Total Hg in tissue

- **High $\delta^{202}\text{Hg}_{\text{bulk}}$ variability** among the tissues while **quite homogenous $\Delta^{199}\text{Hg}_{\text{bulk}}$ values** were found
- The highest $\delta^{202}\text{Hg}$ values correspond to **blood samples**, suggesting a **transport of residual MeHg (enriched in heavier isotopes) in the blood stream**



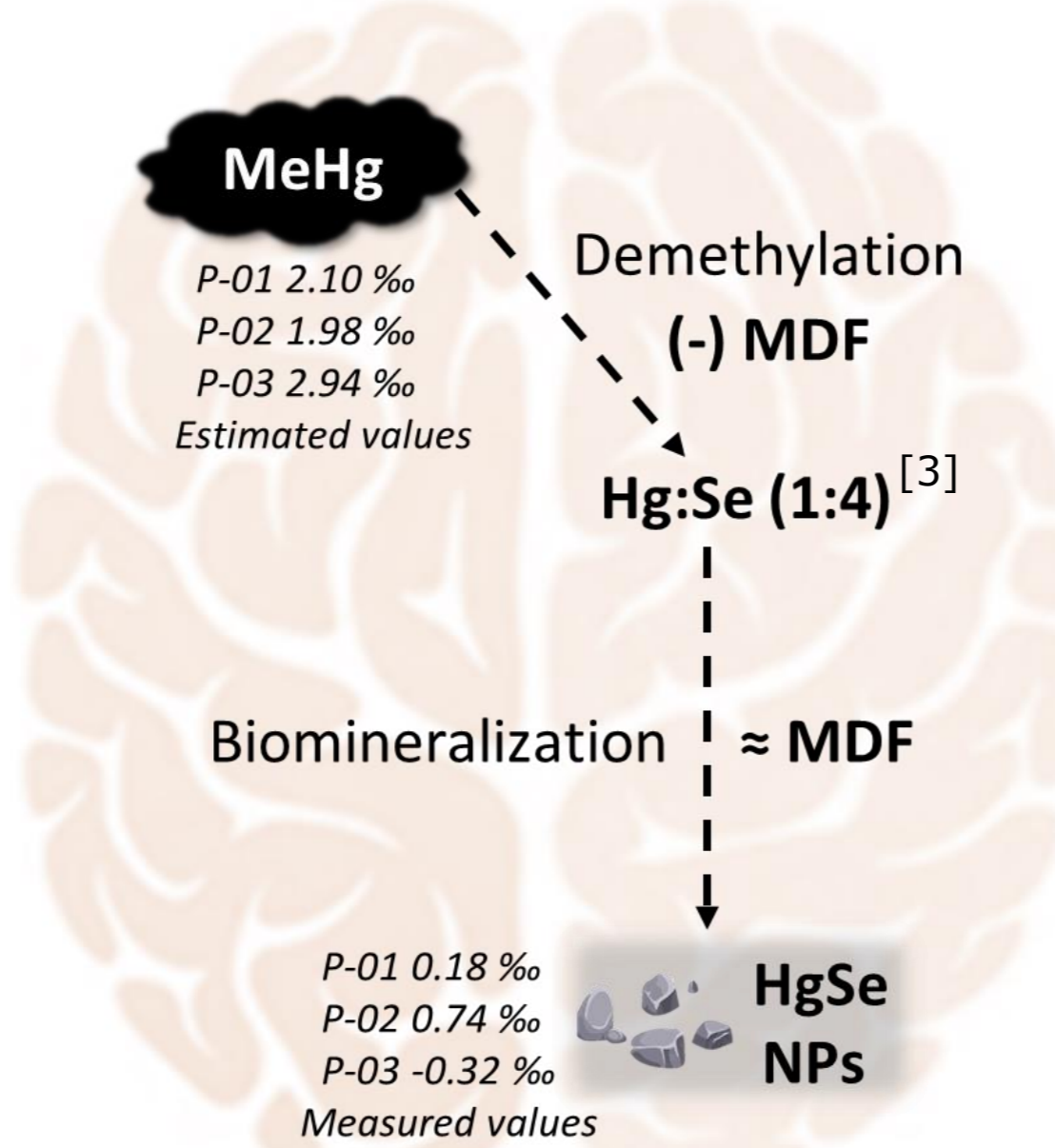
- **HgSe NPs in liver (P-11) and kidneys (P-10) are enriched in heavier isotopes** in comparison to the bulk, which are unexpected results considering HgSe NPs the final product of MeHg breakdown

- **Muscle and brain's HgSe NPs (P-10) are enriched in lighter isotopes** compared with the bulk, in agreement with the higher fraction of Hg present as MeHg in those tissues

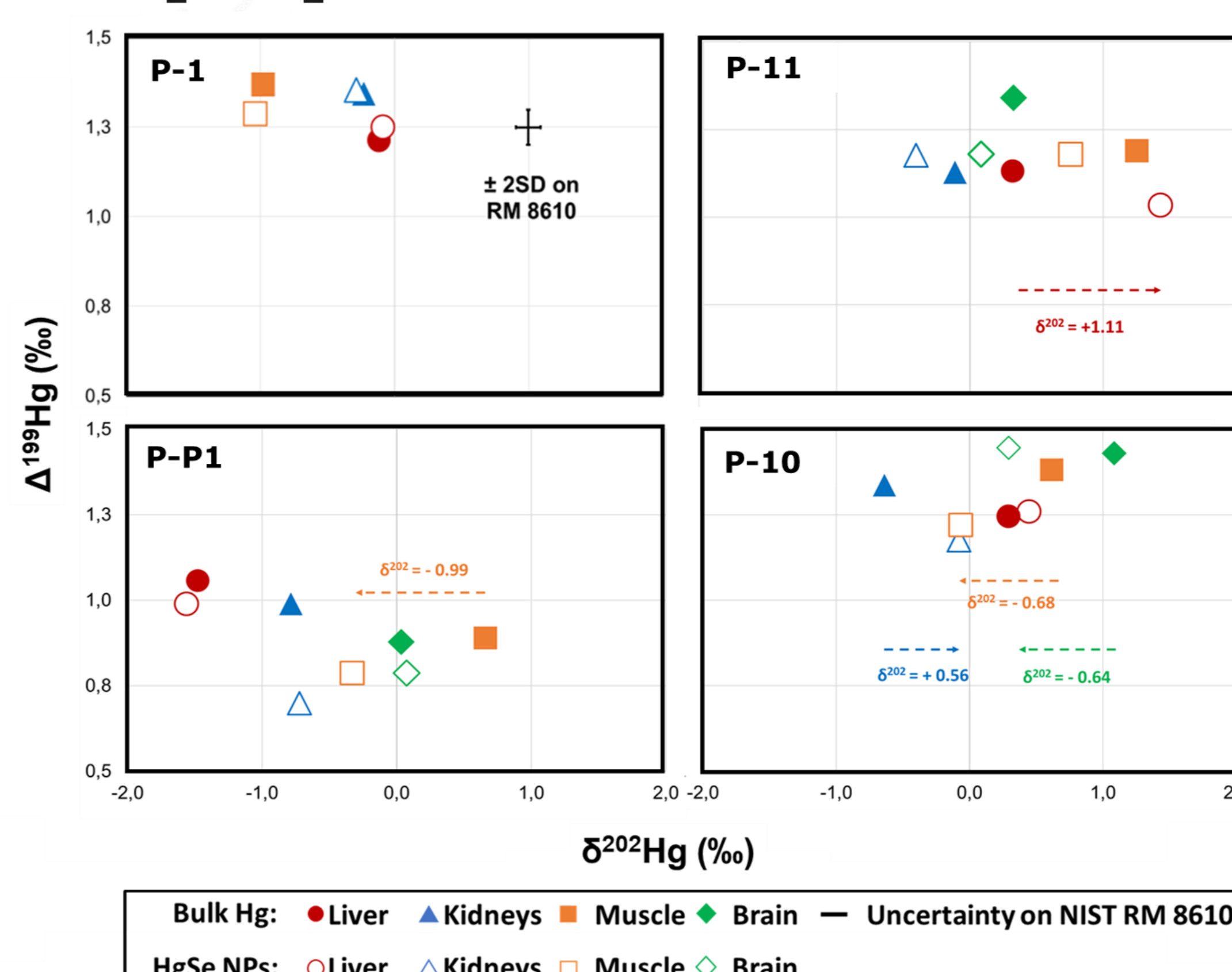
- A **match for both MDF and MIF**, was observed in liver, kidneys, and muscle **between $\delta^{202}\text{Hg}_{\text{bulk}}$ and $\delta^{202}\text{Hg}_{\text{HgSe}}$** of individuals exhibiting the highest THg hepatic concentrations (P-1), suggesting that **no isotopic fractionation is induced during the biomineralization step from the precursor (demethylated) species**.

Conclusions

1. First time HgSe NPs species-specific (Hg) isotopic characterization ($\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$) in seabirds and the largest characterization of this compound in biota
2. No isotopic fractionation appears to be induced during the HgSe NPs biomineralization step from the precursor-demethylated species
3. A shift of 2–3 ‰ $\delta^{202}\text{Hg}$ could be associated to the cleavage of the C-Hg bond. **Because the difference btw Hg isotopic composition of MeHg (estimated) and demethylated species.**



Species-specific Hg isotopic signature



References

- [1] S. Queipo-Abad et. al., *Journal of Hazardous Materials*, 2022, 127922, 1-8.
- [2] K. El Hanafi et. al., *Environmental Science & Technology*, 2022, 5, 3288-3298.
- [3] A. Manceau et. al., *Environmental Science & Technology*, 2021, 55, 1515-1526.