TP041: BIOMONITORING ALONG THE FRENCH COASTLINE: COULD MERCURY ISOTOPIC COMPOSITION INDICATE A TEMPORAL CHANGE IN Hg REACHING THE COASTAL ZONE?

Briant Nicolas [a], Chouvelon Tiphaine [a], Brach-Papa Christophe [a], Chiffoleau Jean François [a], Savoye Nicolas[‡], Sonke Jeroen[∫], Knoery Joël [a]

[a] Laboratoire de Biogéochimie des Contaminants Métalliques, *IFREMER, Centre Atlantique, F-44311, Nantes Cedex 3, France*
[‡] *Université Bordeaux, EPOC, UMR 5805, F-33400 Talence, France*
[∫] *Observatoire Midi-Pyrénées, laboratoire Géosciences Environnement Toulouse, CNRS/IRD/université Paul-Sabatier, 14, avenue Edouard-Belin, F-31400 Toulouse, France*

Introduction

The global biogeochemical cycle of **Mercury (Hg)** is dominated by atmospheric fluxes that are disrupted by human activities (Amos et al., 2015). Marine organisms bioaccumulate and bioamplify this element throughout their food webs. Indeed, Hg is the only metal for which the bioaccumulation and biomagnification of its organic forms in particular (e.g., methyl mercury, MeHg) in food chains or food webs are well known (Fitzgerald et al., 2007). Since the 1970's, the **ROCCH**, a French Mussel Watch -- like program, monitors contaminants on France's metropolitan coastline using bivalves as quantitative indicators of coastal chemical contamination. One of the purposes of this monitoring network is to track contamination sources.

Recently, the advent of MC-ICP-MS analyses provides easier access to information embedded at the isotopic level of trace elements. The stable isotopic geochemistry of mercury is indeed a very promising way to trace its processes and transfers from one biogeochemical reservoir to another (Sonke and Blum, 2013).

Aims of this study

⇒ To draft the map, for the first time on large spatial and temporal scales, of the Hg stable isotopic composition and variability, as a preamble to tracing its origin at the coastline of a temperate country.

Materials & Methods

Mercury isotopic ratios

7 stable isotopes : ^{198} to ^{204}Hg

Mass Independent Fractionation (MIF):

$$\delta^{xxx}Hg = \left(\frac{\left(\frac{^{xxx}Hg}{^{198}Hg}\right)_{sample}}{\left(\frac{^{xxx}Hg}{^{198}Hg}\right)_{SRM\ 3133}} - 1 \right) \times 1000‰$$

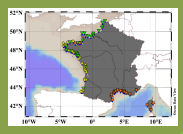
Reference solution

$$\Delta^{199}Hg = \delta^{199}Hg - (\delta^{202}Hg \times 0.252)$$
$$\Delta^{201}Hg = \delta^{201}Hg - (\delta^{202}Hg \times 0.752)$$

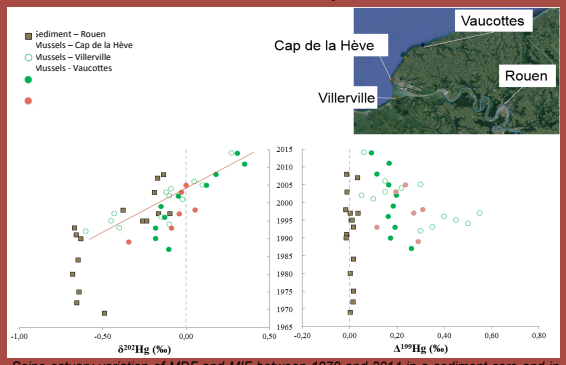
Methods

Samples : freeze-dried bivalves from the environmental sample bank **ROCCH**: Mussels (*M. edulis* and *M. galloprovincialis*) and oysters (*C. gigas*) that were collected in February and March 2014

Hg isotope analyses : MC-ICP-MS Neptune (GET Toulouse). Standard deviation for δ^{202}Hg : natural samples ±0.1‰ (2σ), UM Almaden standard 0.58±0.16‰ (2σ)



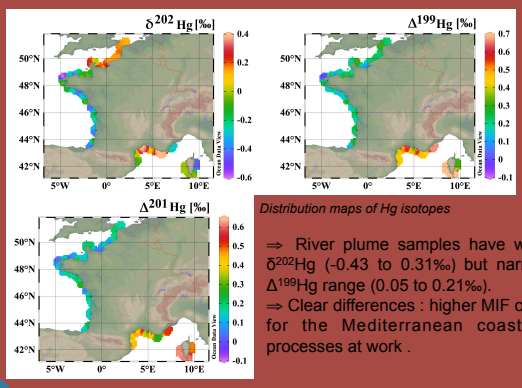
Quality check #1 : bivalve and sediment Hg isotope trends match in the Seine Estuary



Seine estuary variation of MDF and MIF between 1970 and 2014 in a sediment core and in bivalves.

Pre-2014 bivalves and dated sediment core from Seine sediments exhibit similar variations of δ^{202}Hg during 1987-2014.

Results : large scale spatial distribution



Distribution maps of Hg isotopes

⇒ River plume samples have wide range of δ^{202}Hg (-0.43 to 0.31‰) but narrow range of Δ^{199}Hg range (0.05 to 0.21‰).
⇒ Clear differences : higher MIF of Hg isotopes for the Mediterranean coast: additional processes at work .

Quality check #2 : Hg MIF in some Mediterranean bivalve samples is consistent with an open-sea mercury source

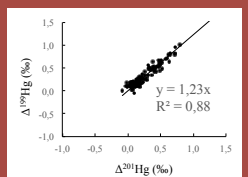
Sample sites and main NW Mediterranean currents (green pin for 0.14 < MIF < 0.70‰, orange pin for MIF > 0.74 ‰).

Orange symbols for bivalve samples with MIF consistent with that of rainfall (~ surface ocean Hg supply).

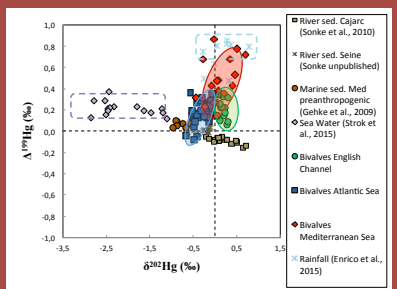
Sites most open to the ocean reflect this supply, consistent with Cossa et al. (2017), but less so in the Gulf of Lyons.

Results : Hg processes and sources

Observed MIF slope (**~1.23**) is between MeHg photoreduction slope (**1.36**) and Hg photoreduction slope (**1.00**) and similar to fish tissue samples (**1.28,** Berquist and Blum, 2007).
⇒ MIF results are consistent with literature data.



Bivalve soft parts : MIF and associated slope (n=132)



δ^{202}Hg versus Δ^{199}Hg in various samples

Hg isotopes allow to differentiate coastal systems like the English Channel, Atlantic Ocean or Mediterranean Sea, but no particular « type » of ecosystems: estuary, back barrier lagoon, open sea...

Conclusions

- First study of Hg isotopes in bivalves at the national scale
- Results show a spatial trend for MIF isotopes and a real difference between the Mediterranean Sea and the Atlantic Ocean or English Channel.
- Hg isotopes don't allow to determine specific ecosystems signatures but allow to track Hg sources in some local systems

Additional, ongoing work will provide more insight to better understand coastal Hg sources and temporal trends

Bibliography:
Amos et al., 2015 - Observational and Modeling Constraints on Global Anthropogenic Enrichment of Mercury, *Environ. Sci. Technol.* 2015, 49, p4036-4047
Bergquist and Blum, 2007 – Mass-dependent and independent fractionation of Hg isotopes by photoreduction in aquatic systems. *Nature*, 2007, 388, p353-359
Fitzgerald et al., 2007 - Marine Biogeochemical Cycling of Mercury, *Chem. Rev.* 2007, 107, p641-662
Sonke and Blum, 2013 - Advances in mercury stable isotope biogeochemistry. *Chemical Geology, 2013*, 336, p1-4
Laurier, Cossa et al.,2007 - The impact of groundwater discharges on mercury partitioning, speciation and bioavailability to mussels in a coastal zone. *Marine Chemistry*, *106*(1), 352-364.

Acknowledgements:
We gratefully acknowledge funding of this study obtained from Ifremer, Région Pays de la Loire (Pollusols), and EC2CO.