MERCURY ISOTOPIC ANALYSIS VIA COLD VAPOR GENERATION - MULTI-COLLECTOR-ICP-MASS SPECTROMETRY AS A KEY TOOL FOR EVALUATING POLLUTION IN MARINE ECOSYSTEMS

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Introduction

Mercury (Hg) pollution is of worldwide scientific interest due to the high toxicity of this heavy metal, with methylmercury (MeHg) being of the highest environmental concern. Hg bioaccumulates throughout the aquatic food web, and fish and/or shellfish consumption is considered as the primary source of human MeHg exposure. In addition to quantification and speciation, Hg isotopic analysis has demonstrated to be a powerful tool for achieving a more profound insight into its biogeochemistry and for identifying sources, pathways and sinks. Hg shows two different natural isotope fractionation effects, i.e. mass-dependent and mass-independent (MDF and MIF) fractionation (Blum et al., 2014), the effects of which are expressed via the δ^{202}Hg and $\Delta^{199,201}$Hg values, respectively. However, Hg isotopic analysis is not free from challenges, and a number of pitfalls needs to be overcome. First, the natural variation in the isotopic composition of Hg is really small, requiring the use of high-precision multi-collector inductively coupled plasma – mass spectrometry (MC-ICP-MS). Secondly, instrumental mass discrimination, i.e. the result of differences in the efficiencies of ion extraction, transmission and detection as a function of nuclide mass, needs to be adequately corrected for. Finally, the low Hg concentration in the samples of interest necessitate the use of a high-efficiency sample introduction system, and cold vapor generation (CVG) of Hg (0) has been selected as the most appropriate in this context (Rua-Ibarz et al., 2016).

Hg isotopic analysis via CVG-MC-ICP-MS has been used for the study of different marine ecosystems affected by Hg pollution. As an example, the environmental impact of the U-864 German submarine, sunk during WWII in the proximity of Fedje island (Norway) and carrying 67 tons of metallic Hg intended for war use in Japan, has been assessed by combining Hg quantification, MeHg speciation and Hg isotopic analysis.

Methods

The method developed for the evaluation of Hg pollution in aquatic ecosystems combines Hg quantification (via sector field ICP-MS – SF-ICP-MS), speciation analysis (via isotope dilution gas chromatography ICP-MS – GC-ICP-IDMS (Valdersnes et al., 2012)) and Hg isotopic analysis (via CVG-MC-ICP-MS (Rua-Ibarz et al., 2016)). The CVG-MC-ICP-MS approach relied on a commercially available cold vapor generation unit (HGX-200, Teledyne Cetac Technologies) for Hg introduction, coupled to a MC-ICP-MS unit (ThermoScientific Neptune). Prior to the environmental analyses, the performance of CVG-MC-ICP-MS for Hg isotopic analysis was compared to that of pneumatic nebulization MC-ICP-MS (PN-MC-ICP-MS).

Results

CVG provided an approximately 20-fold enhancement in Hg signal intensity in comparison to PN. In addition, the matrix composition does not affect the isotope ratio results with CVG, thus avoiding the chromatographic Hg isolation required for PN. Accurate and precise Hg isotopic analysis was achieved with a long-term precision of <0.006 % RSD (N = 250, 18 months). The results were validated with various reference materials of environmental relevance.

The method was then applied for evaluating the environmental impact of the metallic Hg leaking from the U-864 wreck. Hg isotope ratios were measured for metallic Hg salvaged from the submarine wreck, sediments and *Cancer pagurus* tissues. Overall, the data obtained in this work provide an expected, but now undeniable link between the Hg pollution in the sediments and the metallic Hg leaking from the U-864 wreck. The Hg isotope ratio results for crab claw meat and brown meat differ from one another and provide insight into the introduction of the submarine Hg into the local marine food chain.

Conclusion

CVG-MC-ICP-MS allows precise and accurate Hg isotopic analysis at low Hg concentration levels. The combination of Hg quantification, MeHg speciation and Hg isotopic analysis was demonstrated a powerful tool to study the degree of Hg pollution in a marine ecosystem and Hg introduction into the marine food web.

References

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