The Effect of Sampling and Sample Pretreatment on MeHg Concentration in Coastal Marine Sediments

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Abstract: The effect of sampling on monomethylmercury (MeHg) concentration in coastal marine sediments was investigated. It was shown that samples taken under nitrogen atmosphere provided significantly higher results compared to those processed under open atmospheric conditions. This study confirms that the sampling is the most important factor influencing the accuracy and uncertainty of MeHg in sediments.

Keywords: MeHg, coastal sediments, accuracy, sampling

Introduction

Two mercury contaminated coastal sites were investigated in the current study. The Minamata Bay in Japan was chosen as a case study due to its well-known history of mercury pollution. It was severely contaminated with mercury and MeHg from the Chisso acetaldehyde and vinyl chloride plant in Minamata City until 1968 (Kᴜᴅᴏ ᴀɴᴅ Tᴜʀɴᴇʀ, 1999; Tᴏᴍɪʏᴀꜱᴜ ᴇᴛ ᴀʟ., 2000). After extensive clean-up actions, Minamata Bay was again open for fishing in August 1998. The second study area was the Gulf of Trieste located in the North eastern part of the Adriatic Sea (Mediterranean Sea) where the origin of mercury is due to riverine transport of mercury enriched particles from the former mercury mine in Idrija, Slovenia

(Hᴏʀᴠᴀᴛ ᴇᴛ ᴀʟ., 1999, 2002). In order to control the environmental behavior of Hg in the both study areas continuous environmental monitoring is necessary. This should include determination of Hg-T and MeHg in marine organisms for the purpose of health monitoring, while spatial changes and trends of Hg pollution require accurate measurements of mercury and its species in air and in sediments and water samples. This would allow an assessment of the current status and model the future trends of Hg pollution in this coastal environment. Reliable results for Hg-T and MeHg are, therefore, essential for further biogeochemical studies, the assessment of Hg-T and MeHg fluxes from sediment into the water column and the mass balance of Hg ts exchange with the outher seas (Rᴀᴊᴀʀ ᴇᴛ ᴀʟ., 2004).

The focus of this study is the accuracy of the results for MeHg obtained in sediments. Comparison of the results obtained by the use of different analytical techniques has been demonstrated previously (LOGAR ET AL., 2002), however the main problem associated with the accuracy of the data is related to the representativenes of the sample and the effect of sampling. Sediment is considered as the primary source of MeHg in the aquatic environments. The process of MeHg formation is still not well understood and a number of studies have shown that this process depends on various environmental conditions such as pH, temperature, presence of sulfato-reduction bacteria, redox conditions etc. Although, this is well documented in the literature a number of research groups still determine MeHg in sediments sampled under uncontrolled sampling conditions, which may result in decomposition of MeHg during sampling. As a result, concentrations of MeHg in the sediments may significantly be changed and poorly represent MeHg status in the sediments.

EXPERIMENTAL

In this study we compared the results obtained for MeHg in two contaminated coastal areas: (1) Minamata Bay, Japan was chosen as a case study due to its well known history of mercury pollution due to industrial pollution and (2) the Gulf of Trieste in the Northern Adriatic due to past mercury mining in Idrija. Sampling in Minamata was conducted in 2000 and the sampling in the Gulf of Trieste was conducted in 2003. Core samples of the bottom sediments were taken at several locations in each study area. After the cores were removed from the sea, the samples were cut in 1 to 2 cm slices under nitrogen atmosphere on-board ship in order to keep the redox conditions unchanged. The slices were stored in plastic containers and kept under nitrogen until further processing in the laboratory, where slices were divided into two portions. One was kept under the nitrogen throughout the sample homogenization, weighing and first extraction step in which MeHg was extracted from the sediment into the organic solvent. The second aliquot was transferred into another glass container, and the samples were further processed under the normal laboratory conditions, exposed to normal laboratory atmospheric conditions.

During sample preparation in Japan in 2000, pore water was also removed from the sediment core slices by centrifugation in nitrogen atmosphere, and the solid phase was then also analyzed for MeHg under the normal laboratory conditions.

The samples were analyzed using the different analytical methods verified for their comparability in another study (LOGAR ET AL., 2002). Analytical methods for determination MeHg in sediments analyzed by the NIMD consisted of acid leaching and extraction of MeHg dithizonates into toluene followed by a clean-up step, back extraction into toluene, separation by packed column gas chromatography and detection of MeHgCl by an electron capture detector (GC ECD) (AKAGI ET AL., 1991). The method used at IJS was based on acid leaching and solvent extraction into CH_2Cl_2, followed by back extrac-

tion into water phase, ethylation, room temperature pre-collection on Tenax, gas chromatography, pyrolyses and CV AFS detection. Comparability of the results obtained by two different methods was demonstrated by intercomparison exercises and by the analysis of CRMs (HORVAT ET AL., 1993; LOGAR ET AL., 2002).

RESULTS

The results obtained for sediments in Minamata area are presented in Figure 1. Two stations in Minamata area were investigate: (1) the central station of the Minamata Bay (left figure), and (2) the Fukuro Bay affected by the local wood industry (right figure). Evidently, the concentration of MeHg in sediments treated under nitrogen atmosphere are much higher than those treated under open laboratory conditions. Moreover, the results obtained for MeHg after the removal of pore water are even higher, but the differences are not so high. Comparison of the results obtained in Fukuro Bay sediments

are similar to those obtained in Minamata Bay, except for MeHg in sediments after the removal of pore water. The results obtained in solid phase after the removal of pore water and the whole sediment prepared under open laboratory conditions are similar, and much lower from the results obtained under the nitrogen atmosphere. Evidently, the sampling and sample pretreatment may significantly influence the results for MeHg in sediments. These are also dependant on the type of sediments. MeHg concentrations in Minmata area were generally higher at the subsurface layer, which generally provides favorable conditions for MeHg formation.

The results obtained in sediments of the Gulf of Trieste shown in Figure 2 also confirmed that the results obtained under nitrogen conditions are higher than those obtained under the open laboratory conditions, however the differences are much smaller as compared to Minamata Bay. This again confirms the above observations that the differences are very much dependent on the type of the sediments.
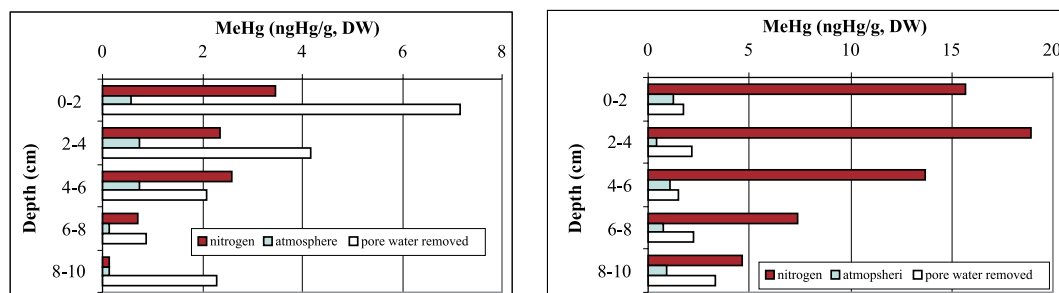

Figure 1. Concentrations of MeHg in sediments obtained during different sample preparation procedures in Minamata (left) and Fukuro Bay (right), November 2000. Left: Minamata Bay, where the total Hg concentration varies between 2 to 6 mg/kg, DW; right: Fukuro Bay , total Hg concentration varies between 7 to 8 mg/lg, DW.
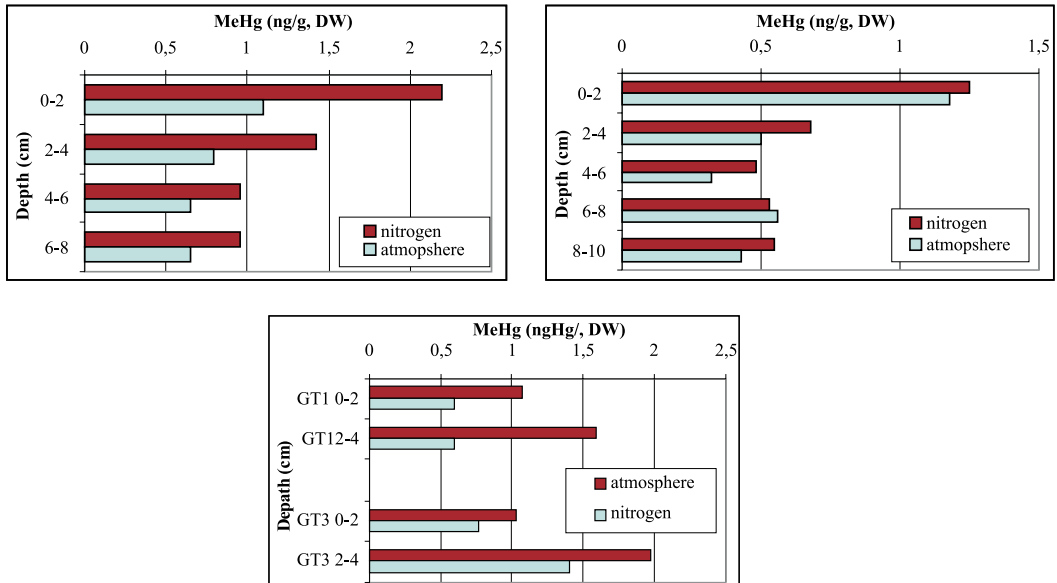
Figure 2. Concentrations of MeHg in sediments obtained using different sample preparation procedures in the Gulf of Trieste, September 2003. Left: Station GT3 with total Hg concentration between 2 to 4 mg/kg and right at the station GT1 where total Hg concentration is below 1 mg/kg. The figure below shows the results obtained in duplicate cores.

CONCLUSIONS

The results of this study suggest, that the results of MeHg in sediments are very dependent on the sampling protocol. The results reported for MeHg in the literature obtained under uncontrolled sampling conditions should, therefore, be treated with great caution. It seems that the sampling protocol may be the most significant source of uncertainty for MeHg in sediments.

Acknowledgements

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