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To Methylate or not to Methylate? Study of Mercury Speciation along the Venetian Littoral System (Q-ALiVe project)

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Abstract **-** The biogeochemical cycle of mercury (Hg) is affected not only by the physical, chemical and hydrological characteristics of the environment, but also by changes in productivity and biodiversity. In waters the complexes of Hg are related to the salinity and to the load of dissolved organic carbon (DOC) in the dissolved and in the particulate phases. Surface and bottom seawater were sampled along the Venetian coast at ten sites with different characteristics. Samples were analyzed employing hyphenated techniques and LOD (limit of detection) and LOQ (limit of quantification) were quantified. Although for some samples both the species were under the LOQ, the presence of methyl mercury (CH_3Hg^+) and ionic mercury (Hg^{2+}) at the same time in surface and in bottom waters were observed. Variability in CH_3Hg^+ concentrations may be due to changes in the phytoplankton communities, which in turn may be affected by nutrient loads from the catchment area and port mouths of the Venice Lagoon. Thus, monitoring these nutrient loads may be essential for the health of the Venetian littoral system, since they may affect blooms, methylation and hyper-bioaccumulation along the trophic web, with effects on the environment and on human health.

Keywords**:** Mercury Methylation, Venice Lagoon, Mercury Speciation, seawater

1. Introduction

The biogeochemical cycle of mercury (Hg) is affected not only by the physical, chemical and hydrological characteristics of the environment, but also by changes in productivity and biodiversity. In waters the complexes of Hg are related to the salinity and to the load of dissolved organic carbon (DOC) in the dissolved and in the particulate phases. In seawater and in shallow brackish systems three different species of Hg, Hg^0, Hg^{2+} and methylated species (di-methyl mercury and mono-methyl mercury), which are the most toxic, may be present. Hg methylation has been observed in several bacteria, which are present in the water column and in the sediments. Inside the Hg biogeochemical cycle these species may change into one another through abiotic and biotic processes (fig.1). Unfortunately, the net amount of methyl mercury may be enriched and worsened by the human impact, especially in environments such as the wetlands or coastal areas where the human activities are intense. Thus, investigating the distribution of the mercury species in these environments is very important, since the inter-conversion mechanisms may directly influence environmental and human health by the diffusion of toxic species along the trophic web.

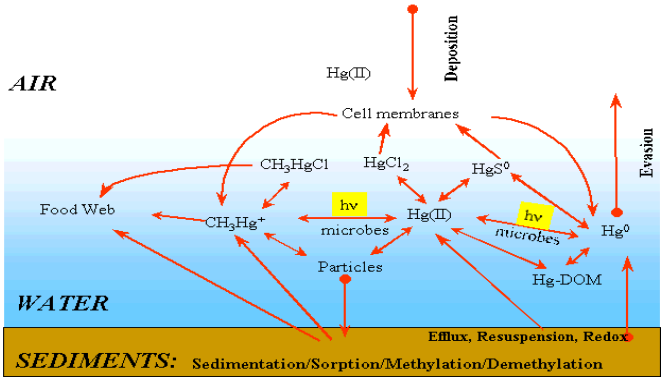


Fig. 1. Mercury biogeochemical cycle (as shown by Krabbenhoft et al., 2000).

2. Materials, Methods and Results

Surface and bottom seawater were sampled along the Venetian coast at sites with different characteristics; some sites were at the port mouths of the Venice Lagoon (Chioggia and Lido), while the others were situated at the mouths of the Brenta river and Adige river respectively. Once sampled the surface seawater and the bottom seawater were filtered (membrane filters (mixed cellulose esters) 0.2 µ cut off, filtration apparatus made of glass, previously cleaned in order to minimize any contamination) and then stored at -20°C in amber glass bottles, till the analysis. The amber glass bottles were previously cleaned to minimize any contamination.

Samples were analyzed according to the method by Cairns et al. (2008), which employs hyphenated techniques and no derivatization steps are required. LOD (limit of detection) and LOQ (limit of quantification) were respectively quantified as 3σ and 10σ, where σ is the standard deviation of the blanks. In this study the LOD for Hg^{2+} is 0.016 ng/l and the LOQ is 0.052 ng/l, while the LOD for CH_3Hg^+ is 0.033 ng/l and the LOQ is 0.11 ng/l. A quadrupole ICP-MS Agilent model 7500 was used for ICP-MS measurements. The operating conditions for ICP-MS detector coupled on-line with the exit of the HPLC column are summarized in fig. 2.

Analysis
•Ion pairing Agent: 0.5% L-Cysteine + 0.005% 2-Mercaptoethanol
•Flow rate 0.2 ml/min
•Quartz spray chamber
•Poly-Pro St nebulizer
•HPLC Injection Valve (Peek)
•Pre-concentration C18 column
•Separation C18 column
•Quartz Torch
•Ni Sampler Cone
•Ni Skimmer Cone
•Injection vol.: 5 ml

Fig. 2. ICP-MS and HPLC operating conditions.

The trends of CH_3Hg^+ and Hg^{2+} concentrations are reported in figg. 3-8. In all the samples analyzed the concentration of CH_3Hg^+ and Hg^{2+} were always above the LOD, although in some samples the concentrations of the two species were under the LOQ. Taking into account all the sampling campaigns, in all the sites sampled and in both the surface and the bottom waters the presence of CH_3Hg^+ and Hg^{2+} were concurrently observed. Furthermore, the concentrations of CH_3Hg^+ in the bottom waters were an order of magnitude higher than those in the surface waters.

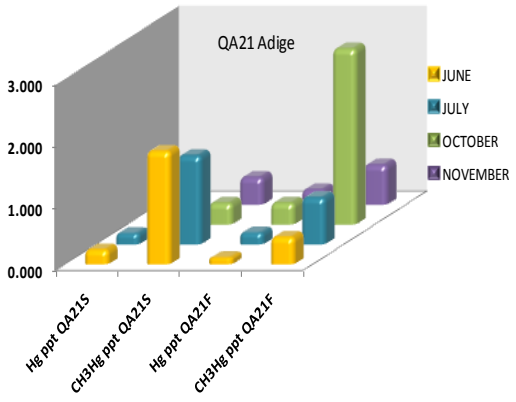


Fig.3.

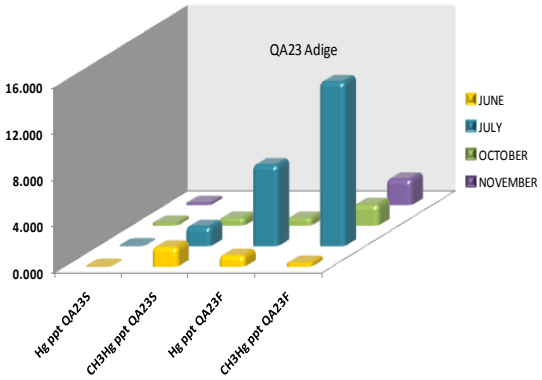
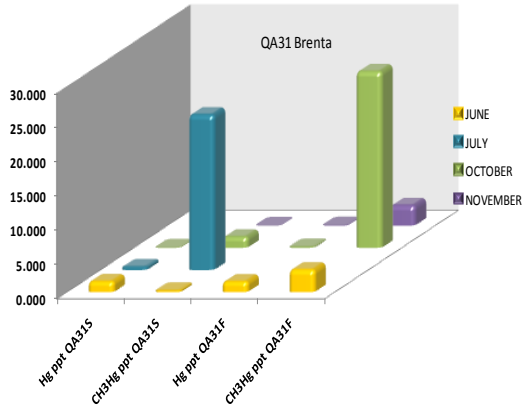


Fig. 4.



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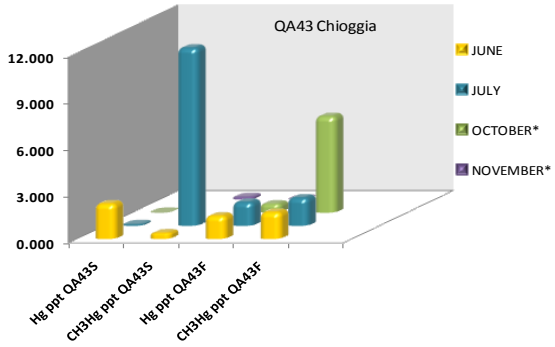

Fig. 6.

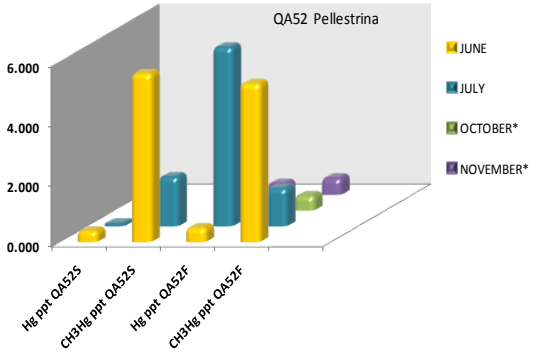

Fig. 7.

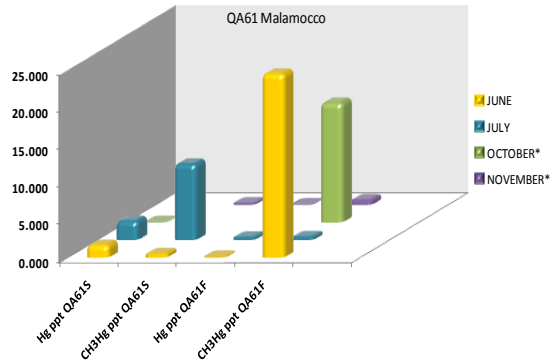

Fig. 8.

Fig. 3-8. Concentrations of CH_3Hg^+ and Hg^{2+} (ng/l) in all the sites studied along the Venetian littoral zone

3. Conclusion

Besides the contribution of sedimentary methylation, that may also be due to the bottom bacterial community, variability in CH_3Hg^+ concentrations may be due to seasonal changes in the phytoplankton communities. In other coastal areas of the Mediterranean Sea maximum concentrations of CH_3Hg^+ were observed in late summer –early fall, which did not correspond to maximum productivity, but they could occur at the same time with abundances of nano- and pico-phytoplankton (Heimburger et al. 2010). Some phyla of nano- and pico-phytoplancton may efficiently uptake mercury and they may then promote its methylation. In the water column mercury methylation may be promoted by bacteria in the sediments and in the bottom waters and by nano- and pico-phytoplanckton in the surface waters. Furthermore, the nano- and pico-phytoplanktonic communities in turn may be affected by nutrient loads from the catchment area and port mouths of the Venice Lagoon. Thus, monitoring these nutrient loads may be essential for the health of the Venetian littoral system, since they may affect blooms, methylation and Hg hyper-bioaccumulation along the trophic web, with effects on the environment and on human health

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Web sites:

Web-1: http://sofia.usgs.gov/geer/2000/posters/merc_cycle/ consulted 27 Feb. 2013.