# Mercury speciation in surface and deep-sea waters of the Mediterranean Sea

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**Abstract:** A study of the speciation and distribution of Hg in the surface and deep-sea water profiles of the Mediterranean Sea is presented.

**Key words:** deep-sea, water, mercury, speciation.

## INTRODUCTION

This study was made within the on-going EU-project MERCYMS (An integrated approach to assess mercury cycling in the Mediterranean Basin), whose overall objective is to investigate major patterns affecting the cycle of mercury within and between the atmospheric and marine ecosystem of the Mediterranean basin. In order to achieve the proposed objectives several coastal and offshore intensive measurement campaigns are planned. Open sea measurement campaigns were carried out aboard the CNR-Research Vessel Urania where atmospheric Hg measurements were coupled with surface and deep seawater measurements. In water samples analysis of different Hg species (i.e., reactive Hg (RHg), particulate and dissolved total Hg (Hg-T) and methylmercury (MeHg), dissolved gaseous mercury (DGM) and dimethylmercury (DMeHg)) was performed. In this research we focus on the distribution of Hg species at the surface and in the water profiles in relation to the physical processes and biogeochemical mediation in the Mediterranean region. These processes are not only important for the formation and distribution of Hg species, but also for their fate and transport in this dynamic marine environment.

## METHODS

Samples were taken during an oceanographic sampling campaign aboard the research vessel Urania between August 6 and 28, 2003 and between March 17 to April 5, 2004 in the eastern and western basins of the Mediterranean. Sampling locations are presented in Figure 1. Ultra clean protocols were employed for sampling. A detailed description of the analytical methods to determine different Hg species in water samples is given elsewhere (HORVAT ET AL., 2003).

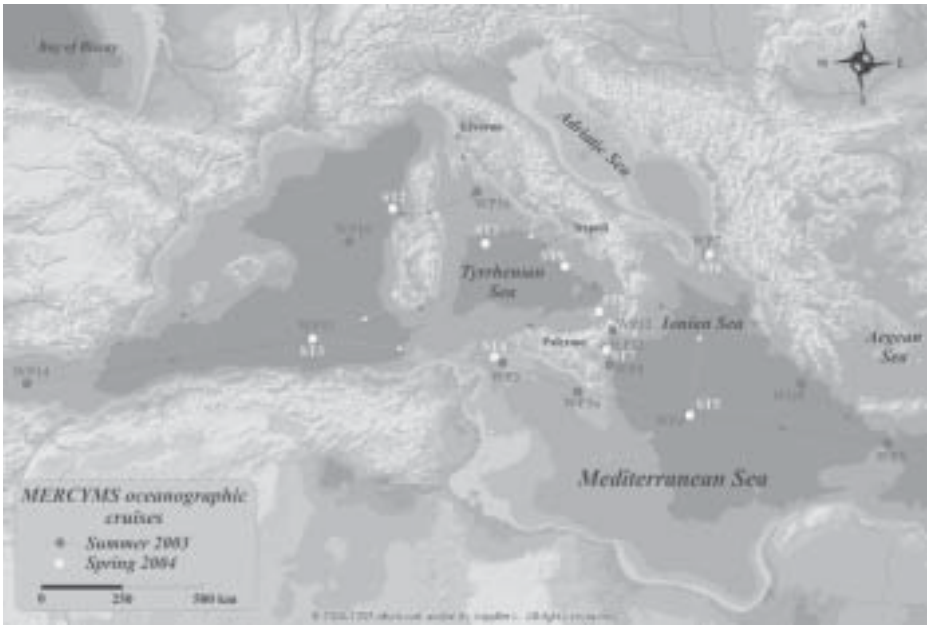


**Figure 1.** Sampling locations during the MERCYMS oceanographic cruises in summer 2003 (WP*) and spring 2004 (ST*).

## RESULTS AND DISCUSSION

Results showed that Hg and MeHg concentrations in open seawaters are relatively low compared to coastal waters (FAGANELI ET AL., 2001; HORVAT ET AL., 1999; HORVAT ET AL., 2003). On average 70 % of mercury was present in the dissolved form. Hg-T concentrations ranged from 0.2 to 6.4 pM. The Hg-T profiles were rather uniform, although a tendency toward a sub-thermocline maximum is visible. Higher concentrations of Hg-T were also observed near the bottom of the water column. Dissolved MeHg concentrations were found to be between 0.08 and 0.68 pM.

The concentrations of dimethymercury (DMeHg) in the surface as well as in the water column in eastern parts were under the detection limit (< 0.1fM). These results indicate that there is only methymercury (MeHg) present in the dissolved phase and also bound to the particulate and colloidal fraction. The percentage of Hg as MeHg represents about 20%. Hg-T and MeHg concentrations in the surface waters in the Mediterranean Sea were comparable to those obtained in a previous oceanographic cruise in the year 2000 as a part of the MED-OCEANOR project (HORVAT ET AL., 2003).

RGM concentrations, mostly inorganic Hg(II), ranged from 0.05 and 1.52 pM, with an average value of 0.28 pM. RGM/Hg-T ratios varied from <5 % at the surface to 69 % at intermediate depths. Thus most Hg was strongly bound to organic compounds. These results are in good agreement with the data obtained by COSSA ET AL. (1997). DGM concentrations were the lowest at the surface,

ranging between 0.04 and 0.25 pM, and the highest near the bottom of the water column. The highest concentrations were mostly observed at the bottom near tectonically active regions typical of the Mediterranean basin, indicating an important source of DGM in the water column. The concentrations of DGM were significantly higher during the winter sampling campaign with an average of 0.31 pM compared to the summer DGM concentrations with a mean value of 0.17 pM. This difference can reflect seasonal variations, and therefore the results have to be compared with other measured parameters.

Surface concentrations of Hg in the eastern and western part are comparable, except for DGM. Higher DGM concentrations were observed in the eastern part as compared to the western part of the Mediterranean.

The results of this study clearly show that Hg species distribution in the water column is affected by several dynamic processes within the water column such as photochemical transformation processes at the surface, phytoplankton biomass stratification in the photic zone, development of an oxygen depletion zone at intermediate depths and diffusion from deeper layers due to biological or/and tectonic activity. Any process that modifies and changes the distribution of Hg species in the deep-sea waters will have an important influence on the global cycling of Hg at the earth's surface.

## CONCLUSIONS

The data obtained in this study should help to improve our understanding of different natural processes involved in the cycling of mercury in the Mediterranean region. Additionally, they provide a basis for improvement of methodological schemes for Hg speciation and analysis in marine waters.

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