E3S Web of Conferences **1**, 17008 (2013)
DOI: 10.1051/e3sconf/20130117008

Dissolved gaseous Hg (DGM) in the Mediterranean surface and deep waters

J. Kotnik[1] and M. Horvat[1]

[1] Jozef Stefan Institute, Department of Environmental Sciences, Jamova 39, Ljubljana, Slovenia, joze.kotnik@ijs.si

Abstract. Dissolved gaseous mercury (DGM) was studied in surface and deep waters of the Mediterranean Sea for last 12 years during several oceanographic cruises on board the Italian research vessel Urania and covered both Western and Eastern Mediterranean Basins as well as Adriatic Sea. DGM was measured together with other mercury species (RHg - reactive Hg, THg - total Hg, MeHg - monomethyl Hg and DMeHg - dimethylmercury), and with some water quality parameters in coastal and open sea deep water profiles, however only DGM will be discussed here. DGM represents a considerable portion of THg (average of about 20 %) in Mediterranean waters. Spatial and seasonal variations of measured DGM concentrations were observed in different indentified water masses as well as iwere observed. DGM was the highest in the northern Adriatic, most polluted part of the Mediterranean Sea as the consequence of Hg mining in Idrija and heavy industry of northern Italy.Generally, average DGM concentration was higher in W and E Mediteranean Deep Waters (WMDW and EMDW) and Leavantine Intermediate Water (LIW) than overlaying Modified Atlantic Water (MAW), however it was the highest in N Adriatic Surface waters and consequently in out flowing Adriatic Deep Waters (ADW). In deep water profiles the portion of DGM typically increased at depths with oxygen minimum and then towards the bottom, especially in areas with strong tectonic activity (Alboran Sea, Strait of Sicily, Tyrrhenian Sea), indicating its bacterial and/or geotectonic origin. A comparison of the results obtained in this study to others performed in the Mediterranean shows no significant differences. Results were also compared to the results obtained in the Pacific and Atlantic Oceans. During last oceanographic cruise in 2011 covering area between Livorno and Lipari Islands a novel method for continuous DGM determination in surface waters (Wangberg and Gardfeldt, 2011) was applied and compared to standard method.

Keywords: dissolved gaseous mercury, surface and deep waters, Mediterranean Sea, Adriatic Sea

Introduction

Closed marine water systems are very sensitive environments to Hg pollution due to limited exchange of water between oceans. Once in the water, mercury can be present in different forms (elemental mercury - Hg^0, Hg(II) complexes and organic Hg forms (mainly methyl mercury (MeHg) and dimethyl mercury (DMeHg)). It may be either dissolved or adsorbed on particles. Dissolved gaseous Hg measured in water is composed of dissolved gaseous elemental Hg (Hg^0) and DMeHg, which is present in very small fraction (< 5 %) and is measurable mostly in deep waters (Horvat et al. 2003, Kotnik et al. 2007). Hg^0 in ocean waters originates from different sources. The most important source is reduction of Hg(II) by aquatic microorganisms (Mason et al., 1995a, b). Second important source of elemental Hg is photo- reduction of Hg(II) (Costa and Liss, 2000). Moreover, it must be taken into account that intense geotectonic activity may be an important source of Hg^0 (Ferrara et al., 2003; Horvat et al., 2003, Kotnik et al. 2007), especially in the Mediterranean basin which is tectonically very active.

The Mediterranean Sea is an enclosed basin connected to the Atlantic Ocean by the narrow Strait of Gibraltar and to the Black Sea by the Strait of Dardanelles, Marmara Sea and Strait of Bosporus. It consists of Western and Eastern sub-basins which are connected by the Strait of Sicily. The Tyrrhenian Sea is the easternmost and deepest part (about 3500 m) of the Western Basin connected to the south in a wide opening between islands of Sardinia and Sicily. The Balearic Sea occupies the central part of the basin and extents northeast to the Ligurnian Sea and to west to the Alboran

Sea and Strait of Gibraltar. Eastern basin consists of four sub-basins: the Ionian, the Adriatic, the Aegean and the Levantine Sea. The Ionian Sea is the deepest (maximum of 5000 m south of Greece) sub basin in the Eastern Mediterranean. It is located between Italy and Greece to the north and Libya and Tunisia to the south. The Aegean Sea joins the Levantine Sea through several passages and straits, located between Turkish and Greek coast and the islands of Crete and Rodos. It has very irregular coastlines and topography with many islands. The Levantine Sea merges with Ionian Sea through Cretan Passage. The Adriatic Sea is connected to the Ionian by the Strait of Otranto. It has depths between about 50 to 1400 m. It is a subject of high inflow of heavily polluted rivers and other direct discharges, especially in its northern and central part as a consequence of heavy industry and in the Gulf of Trieste, it is influenced by natural and anthropogenic load by Hg polluted Soča (Isonzo) River, where in its watershed, world second largest Hg mine in Idrija is located.

The hydrology of the Mediterranean Sea is characterized by four main water masses: Modified Atlantic Water (MAW), Levantine Intermediate Water (LIW), West Mediterranean Deep Water (WMDW) and East Mediterranean Deep Water (EMDW). The surface waters (MAW) flowing into the Mediterranean through the Strait of Gibraltar are subject of evaporation and mixing with the underlying waters causing an increase of salinity towards east (Zavatarelli and Mellor, 1995). The origin of LIW is the result of winter convection processes in the Eastern Mediterranean.

Deep water formation areas of W and E Mediterranean are geographically separated at the Strait of Sicily, preventing exchange between deep water masses. The source of the E Mediterranean deep waters (EMDW) is the Adriatic Sea, where evaporation and winter cooling processes cause their sinking along the continental slope over the Strait of Otranto and spreading to the whole E Mediterranean basin. The source of W Mediterranean deep water is located in the Gulf of Lions, where in winter intensive convective movements occur under the influence of cold and dry winds causing the sinking and mixing of cold and salty surface waters (Zavatarelli and Mellor, 1995).

Mediterranean basin is also characterized by strong tectonic activity as a consequence of subduction of African plate under the Eurasian plate. According to Lopez Casado et al. (2001) strong seismic activity of W Alboran Sea corresponds to sinking of Iberian and African plates. The central Mediterranean is composed of a myriad of continental microplates and irregular oceanic basins, which form the youngest part of the whole basin. It is possible to distinguish three main domains characterized by different structures. The Tyrrhenian basin corresponds to the back-arc basins of the Apenninic subduction. The basins in the vicinity of the Italian coast are actively extending (Salerno and Paola Basins). Second structure is Apennines, a Neogene thrust system. Third tectonic structure in Central Mediterranean is the Adriatic region consisting of two Adriatic blocks. The northern is characterized by thin continental lithosphere and high subsidence rate. The Eastern Mediterranean region comprises two distinct tectonic domains that were juxtaposed by subduction and plate collision.

Materials and Methods

Sampling and Analysis

The oceanographic cruises onboard Italian research vessel Urania were part of several EU and national research projects (MEDOCEANEOR, MERCYMS, GMOS, etc.), covering regions from Alboran Sea on the west and western part of Levantine Sea on the east as well as Adriatic Sea with the Gulf of Trieste as Mediterranean most northern part. The data and samples were collected in summer 2000 (Horvat et al. 2003), summer 2003, early spring 2004 (Kotnik et al. 2007), fall 2004, summer 2005, summer 2009 and fall 2011.

Special attention was also given to quality control steps by comparing data on board the ship by different laboratories (IJS Slovenia, IVL Sweden, UGOT Sweden, CNR-IIA Italy, IFREMER France) using different analytical procedures on samples collected on board and intercomparison of some selected samples. All analytical methods used were validated and intercompared (Ogrinc et al. 2004).

Samples were collected immediately after boarding from Niskin bottles into 0.5 L glass bubbler by 20 cm acid cleaned silicon tube to prevent rapid mixing of sample and losses of volatile Hg species. DGM was determined on board the vessel. The sample was purged for 10 min and collected on a gold trap which was then transferred to a double amalgamation CV AFS analyzer system. Hg on the sampling gold trap was then released by thermal desorption and detected by a CV AFS analyzer (Tekran 2500). The system was calibrated by gas phase Hg (Hg^0) kept at defined temperature (Tekran, model 2505 mercury vapour calibration unit). The detection limit was 5 pg/L based on three standard deviations of the blank. The repeatability of the method was 4 %. The method is described in detail by Horvat et al. (2003) and Gardfeldt et al. (2003). It should be noted that DGM concentrations reported correspond to all volatile Hg species present in sea water – elemental Hg (Hg^0) and dimethyl Hg ($(CH_3)_2Hg$).

In fall 2011 DGM was measured also by continuous method developed by Wangberg and Gardfeldt (2011) and Andersson et al. (2008). Hg free ambient air was equilibrated with the seawater in a Plexiglas purging bottle with opposite air and water flow. The flow of Hg free ambient air was introduced through a glass frit positioned at the bottom of the bottle. Released DGM was then detected by Lumex RA 915+ AAS detector with Zeeman correction.

Results, Discussion and Conclusions

Relatively high concentrations and portions of DGM indicate high reactivity of Hg in open marine waters. DGM was present in surface waters mainly as Hg^0 as no DMHg was detected at the surface, while towards the bottom a noticeable, but relatively small portion of DMeHg is present in most of the Mediterranean. In Middle and Southern Adriatic DMeHg was present in much higher fraction and was detected in surface waters, but in very low concentrations.

Vertical profiles show that DGM generally increases with depth, suggesting the presence of a source of volatile Hg in deeper waters. This is also confirmed by the fact that average DGM concentration was the highest in deep water masses (WMDW and EMDW). One possible source of DGM in deeper and bottom waters could be intensive tectonic activity of the seafloor, which may be the main source of DGM in deep waters as is indicated by higher concentrations and portions of DGM near the bottom at locations with strong tectonic activity (Alboran Sea, Strait of Sicily, Tyrrhenian Sea, Strait of Otranto). It is well known that emissions from tectonic activity and geological anomalies could represent an important source of mercury (Ferrara et al., 2000; Gustin, 2003). Rajar et al. (2007) calculated total natural underwater emission of Hg in the Mediterranean Sea to be 11 to 20 tons y^{-1} with mean estimate of 15 tons per year. In order to test this hypothesis measurements of radon were carried out (Vaupotič et al., 2007), confirming the source of this gas at tectonically more active areas. Second possible source can be bacterial activity that may produce DGM (Ramamorthy et al., 1983; Ferrara et al,. 2003). From certain profiles it is possible to observe that increase of DGM corresponds to a decrease in dissolved oxygen levels, suggesting that bacteria produce DGM in the oxygen minimum zone confirming findings of Kim and Fitzgerald (1988) for Tropical Pacific Ocean and Ferrara et al. (2003) for W Mediterranean, who found significant negative correlation between DGM and oxygen levels in deeper ocean waters.

The observed decrease towards the surface is a result of the balance between production and loss processes. Photo production and bacterial activity is probably the main source of volatile Hg in surface waters as it was shown in several laboratory and field studies (Costa and Liss, 2000; Gardfeldt et al., 2001a, b; Lanzillotta and Ferrara, 2001; Lanzillotta et al., 2002). Loss of DGM could be due to its emissions to atmosphere (Ferrara et al., 2000; Gardfeldt et al., 2003; Ferrara et al., 2003). Another important loss of DGM in surface waters can be due to oxidation of DGM due to strong UV irradiation and the presence of chlorine and/or bromine (Horvat et al., 2003) and photolytically produced hydroxyl radicals (Gardfeldt et al., 2001b; Mason ed al., 2001).

It has been suggested, that Hg^0 production is an important mechanism for reducing availability of Hg(II) as a substrate for the methylation of Hg (Mason et al., 2001; Fitzgerald et al., 1994).

The spatial distribution of DGM in Adriatic is connected to water circulation in the basin, however there could be several other biological and/or geological factors affecting the DGM distribution. The concentrations of DGM measured in open Adriatic waters were within the range reported for the Mediterranean Sea (Cossa et al. 1997, Horvat et al. 2003, Ferrara et al., 2003, Kotnik et al., 2007, Anderson et al., 2007), however the concentrations at N Adriatic locations were significantly higher.

Deep water profiles in S Adriatic are mostly connected to oxygen concentration. Typically DGM is low at the surface, and in oxygen minimum zone it increase to its maximum levels. At most locations DGM sharply increase again in bottom water layer. Such distribution reflect the importance of evasion and photochemical oxidation due to strong UV radiation and presence of chlorine and bromine (Horvat et al. 2003) and hydroxyl radicals (Garfeldt et al. 2001, Mason et al. 2001) at the surface. In deeper water layers DGM distribution indicate the importance of reduction and/or oxidation processes due to microorganisms activity, and towards the bottom microorganisms production and diffusion from sediment and/or tectonic activity, especially at locations in S Ariatic Pit, which is tectonically very active.

Acknowledgement

The authors wish to acknowledge the financial support of different EU projects (6^{th} and 7^{th} FP) and several national projects financed by Italian and Slovenian governments.

References

Andersson ME, Gardfeldt K, Wangberg I, Sprovieri F, Pirrone N, Lindqvist O, 2007. Seasonal and daily variation of mercury evasion at coastal and off shore sites from the Mediterranean Sea. Marine Chemistry, 104, 3-4, 214-226.

Costa, M. and Liss, P. 2000. Photoreduction and evaluation of mercury from sea water. Science of the Total Environment, 261: 125-135.

Ferrara, R., Mazzolai, B., Lanzillotta, E., Nucaro, E. and Pirrone N. 2000. Volcanoes as emission sources of atmospheric mercury in the Mediterranean basin. The Science of The Total Environment, 259: 115-121.

Ferrara, R., Ceccarini, C., Lanzillotta, E., Gardfeldt, K., Sommar, J., Horvat, M., Logar, M., Fajon, V., Kotnik, J. 2003. Profiles of dissolved gaseous mercury concentration in the Mediterranean seawater. Atmospheric Environment, 37 (1): S85-S92.

Gårdfeldt, K., Feng, X., Sommar, J., and Lindqvist, O. 2001a. Total gaseous mercury exchange between air and water at river and sea surfaces in Swedish

coastal regions. Atmospheric Environment, 35 (17): 3027-3038.

Gårdfeldt, K., Sommar, J., Strömberg D. and Feng X. 2001b. Oxidation of atomic mercury by hydroxyl radicals and photoinduced decomposition of methylmercury in the aqueous phase. Atmospheric Environment, 35 (17): 3039-3047.

Gårdfeldt, K., Sommar, J., Ferrara, R., Ceccarini, C., Lanzillotta, E., Munthe J., Wängberg, I., Lindqvist, O., Pirrone, N., Sprovieri F., 2003.Evasion of mercury from coastal and open waters of the Atlantic Ocean and the Mediterranean Sea . Atmospheric Environment, 37 (1):73-84.

Horvat M., Kotnik J., Logar M., Fajon V., Zvonarić T. and Pirrone N., 2003, Speciation of mercury in surface and deep-sea waters in the Mediterranean sea, Atmos. Environ. 37, pp. S93–S108.

Kim, J.P. and Fitzgerald, W.F. 1988. Gaseous mercury profiles in the Tropical Pacific Oceans. Geophysical Research Letters, 15: 40-43.

Kotnik, J., Horvat, M., Tessier, E., Ogrinc, N., Monperrus, M., Amouroux, D., Fajon, V., Gibičar, D., Žižek, S., Sprovieri, F. 2007. Mercury speciation in surface and deep waters of the Mediterranean Sea. Mar. Chem., 2007, 107, 1, 13-30.

Lanzillotta, E. and Ferrara, R. 2001. Daily trend of dissolved gaseous mercury concentration in coastal seawater of the Mediterranean basin. Chemosphere, 45 (6-7): 935-940.

Lanzillotta, E., Ceccarini, C. and Ferrara, R. 2002. Photo-induced formation of dissolved gaseous mercury in coastal and offshore seawater of the Mediterranean basin. The Science of The Total Environment, 300, (1-3): 179-187

Lopez Casado, C. 2001. The structure of the Alboran Sea: an interpretation from seismological and geological data. Tectonophysic, 338: 79-95.

Mason, R.P., Lawson, N.M. and Sheu. G.-R. 2001. Mercury in the Atlantic Ocean: factors controlling air–sea exchange of mercury and its distribution in the upper waters. Deep Sea Research Part II: Topical Studies in Oceanography, (48): 2829-2853.

Mason, R.P., Rolfhus, K.R. and Fitzgerald, W.F. 1995a. Methylated and elemental mercury cycling in the surface and deep ocean waters of the North Atlantic. Water, Air and Soil Pollution, 80: 665-677.

Mason, R.P., Morel, F.M.M. and Hemond, H.F. 1995b. The roleof microorganisms in elemental mercury formation in natural waters. Water, Air and Soil Pollution, 80: 775-787.

Ogrinc, N., Logar, M., Gibicar, D., Horvat, M., fajon, V., Kotnik, J., Monperrus, M., tessier, E., Amouroux, D., Donard, O., Cossa, D., Gardfeldt, K., Andersson, M. 2004. Determination of Total mercury and monomethylmercury in water samples, estuarine sediments and biological samples. RMZ – Materials and Geoenvironment, 51 (2): 2001-2004.

Rajar, R., Žagar, D., Horvat, M., Četina, M. 2007. Mass balance of mercury in the Mediterranean Sea. Marine Chemistry, 2007, 107, 1.

Vaupotič, J., Gregorič, A., Kotnik, J., Horvat, M., Pirrone, N. Dissolved radon and gaseous mercury in the Mediterranean seawater. J. environ. radioact., 2008, issue 7, vol. 99, str. 1068-1074

Wangberg, I, and Gardfeldt, K., 2011. Measurement technique allowing continuous automatic determination of DGM in oceanic surface waters. International Workshop on Mercury in the marine environment: a global metrology challenge Piran, Slovenia 9-12 May 20011

Zavatarelli, M. and Mellor, G.L. 1995. A numerical study of the Mediterranean Sea Circulation. Journal of Physical Oceanography, 25: 1384-1414.