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Dissolved gaseous mercury and mercury flux measurements in Mediterranean coastal waters: A short review

L. Fantozzi[1], R. Ferrara[2] and F. Sprovieri[1]

[1]CNR-Institute of Atmospheric Pollution Research, Rende, ITALY, **l.fantozzi@iia.cnr.it**
[2]CNR-Institute of Biophysics, Pisa, ITALY

Abstract. There is a general agreement in the scientific community that the marine ecosystem can be a sink and/or source of the mercury that is cycling in the global environment, and current estimates of the global mercury budget for the Mediterranean region are affected by high uncertainty, primarily due to the little progress made so far in evaluating the role of chemical, physical and biological processes in the water system and in the lower atmosphere above the sea water (air-water interface). The lack of knowledge of the magnitude of the air-sea exchange mechanisms is, therefore, one of the main factors affecting the overall uncertainty associated with the assessment of net fluxes of Hg between the atmospheric and marine environments in the Mediterranean region. Results obtained during the last 15 years in the Mediterranean basin indicate the quantitative importance of such emission in the biogeochemical cycle of this element, highlighting the need for thorough investigations on the mechanisms of production and volatilization of dissolved gaseous mercury in waters.

Key words: Dissolved gaseous mercury, mercury flux, natural waters, Mediterranean basin

Introduction

Mercury spreads into the environment, particularly air and water systems, through a complex biogeochemical cycle at the base of which there is conversion between the different chemical species of mercury. Several studies performed during the last decade in the framework of both EU research projects (i.e., MAMCS, MOE, MERCYMS) and Italian CNR founded projects (i.e., MEDOCEANOR) have highlighted the key role played by air–water exchange processes of gaseous mercury in the global cycle of this contaminants (Sprovieri et al., 2003, 2010; Andersson et al., 2007). However, the relative contribution of these complex mechanisms has not yet been determined, and is one of the main factors affecting the overall uncertainty associated with the assessment of net fluxes of mercury between the atmospheric and marine environments. The flux of mercury from water surface depends on the formation in the water column of volatile dissolved forms of mercury (90% elemental mercury), named Dissolved Gaseous Mercury (DGM), which passes from the water into the atmosphere due to their low water solubility (60μg/L at 25 °C) and high volatility (Henry coefficient < 0.3). The transfer of volatile forms of mercury through the air-water interface is governed by the concentration difference between the air and the water surface and by the transfer velocity of mercury (Liss, 1983). From a global perspective, the emission of mercury from surface water to the atmosphere is as much as 50% of total annual emissions of this metal into the atmosphere (Pirrone and Mason, 2009). Moreover it must be highlighted that in this way is also removed part of Hg(II) to the processes of methylation and subsequent bioaccumulation along the food chain (Horvat et al., 2003). Consequently, the formation of DGM and its volatilization in aquatic systems hold a noteworthy ecological importance in the context of the biogeochemical cycle of mercury. This paper provides a short overview of DGM and mercury flux measurements in Mediterranean coastal waters. Major findings of key studies carried out during ten years of ship-borne activities have been highlighted.

Methods

DGM concentration and flux measurements have been collected at several sites throughout the Mediterranean basin in the last 15 years. Mercury fluxes were measured using a floating flux chamber connected to an atomic absorption analyzer, described elsewhere (Lanzillotta et

al., 2003). Detailed descriptions of the devices used for the determination of DGM concentrations are reported in Ferrara et al. (2003), Gardfeldt et al. (2002) and Horvat et al. (2003).

Results and Discussion

Table 1 summarizes the knowledge acquired as the result of investigations on the concentration of dissolved gaseous mercury in Mediterranean coastal waters and its flux to the atmosphere.

The results obtained during the measurement campaign carried out in 1998 by Ferrara et al. (2000) produce a wide annual average of 23 x 10^3 ng m^{-2} of mercury emission from the sea surface. If this value is considered representative for the entire Mediterranean, a value of annual emission of mercury close to 60 tons is obtained, suggesting that mercury emission from water surfaces represent the major natural source of mercury for the atmosphere in the Mediterranean area. The magnitude of the phenomenon was confirmed by Gardfeldt et al. (2003), who calculated, using DGM data and empirical gas-exchange model, a value of about 66 tons of mercury released to the atmosphere from the Mediterranean Sea during the summer.

The evasional flux of mercury generally shows a daily trend that mimics that of solar radiation intensity, reaching the maximum emission rates when the Photosintetically Active Radiation (PAR) reaches the maximum value, as observed by several authors (Ferrara et al., 2000; Ferrara et al., 2001; Ferrara et al., 2003; Gardfeldt et al., 2001; Gardfeldt et al., 2003; Lanzillotta and Ferrara, 2001; Andersson et al., 2007; Fantozzi et al., 2007). The efficiency of the process of mercury evasion depends not only on the intensity of the solar radiation, but also on the air and water temperatures. Loux (2000) states that the daily cycles of atmospheric temperature could have a significant role in the daily rates of mercury evasion.

In shallow coastal waters the DGM photoproduction is favored because light penetrates the water column and the warm water temperatures can significantly increase both the abiotic reactions of DGM production that these biotic (Lanzillotta and Ferrara, 2001). The presence of dissolved organic matter can significantly affect the rate of DGM formation. Humic substances can act as photosensitizers in the reactions of mercury photoreduction (Spokes and Liss, 1995; Lanzillotta et al., 2004). In the Mediterranean region the magnitude of these processes are particularly relevant because of the favorable climatic conditions and the extensive presence of cinnabar deposits through the entire region. The synergy of these factors leads, as shown in Table 1, to high evasional fluxes from the water surface during most of the year. In particular, the highest values are found in the contaminated area of Rosignano Solvay for the presence of a chlor-alkali plant. High values of DGM concentration have been also measured in the northern Adriatic Sea in 2004 (70-206 pg L^{-1}, see Table 1). This area is both influenced by anthropogenic and natural mercury emissions, e.g. the rivers exiting into this area have elevated mercury concentrations since they pass through the mercury mining district of Slovenia (Andersson et al., 2007).

The DGM measured on a wide geographical scale for the first time in the Mediterranean during the international cruise MED-OCEANOR on board the National Research Council of Italy from 14 July to 9 August 2000, showed differences in the concentrations of the Western basin than the Eastern. The Eastern Mediterranean basin was characterized by an average concentration of DGM in surface water (42.2 pg L^{-1}) higher than that measured in the Western basin (17.6 pg L^{-1}) (Gardfeldt et al., 2003). The reasons for these differences lie in the different biogeochemical, hydrodynamic and geotectonic characteristics of the two basins (Ferrara et al., 2003).

Conclusion

In summary the behavior of DGM and mercury flux in coastal seawaters is characterized by both daily and seasonal trends. Notwithstanding, the processes involved in Hg transport from emission source is strongly influenced by the emission types and characteristics, the prevailing meteorological conditions and the factors influencing the photochemical and biochemical processes of Hg° formation, like the presence of dissolved organic matter. The Mediterranean basin is characterized by large cinnabar deposits, intense solar radiation over many months of the year and intense geotectonic activity, that may constitute an additional source of elemental mercury. Emission data are never complete or entirely accurate mainly because of the difficulties encountered in direct measurement of mercury flux. Current estimates of the spatial resolved evasional flux of gaseous mercury from water surfaces were derived primarily from theoretical assumptions and calculations, by applying gas exchange models. Therefore there is a need to improve emission estimates and inventories on local and regional scales both for natural and anthropogenic sources and it is essential the knowledge of the DGM concentration in the water because, using gas exchange models, it is possible to estimate the emission of mercury from water surfaces (Wanninkof, 1992; Nightingale et al., 2000; Johnson, 2010).

References

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

Fantozzi L, Ferrara R, Frontini FP, Dini F. Factors influencing the daily behaviour of dissolved gaseous mercury concentration in the Mediterranean Sea. Mar Chem 2007; 107:4-12.

Table 1. Results for DGM concentration, water and air temperature and Hg flux from different coastal sites of the Mediterranean Sea in the last 15 years.

Location	Year	DGM* ($pg\ L^{-1}$)	Hg flux* ($ng\ m^{-2}\ h^{-1}$)	PAR** (Wm^{-2})	Air temp** (°C)	Water temp** (°C)	Reference
Northern Tyrrhenian Sea (unpolluted area)	1998	-	1.2-5.7	215-460	20-30	14-27	Ferrara et al., 2000
	1999	15-35	1.5-7.0	400	-	12-25	Ferrara et al., 2001
	2001	10-39	-	82-350	22-30	14-22	Lanzillotta et al., 2002
	Winter 2001	6-39	0.2-2.0	30-200	7-19	8-10	Ferrara, unpublished data
	2002	-	5.65±0.53 - 21.71±2.17	360-430	27-37	22-26	Lanzillotta et al., 2003
	2004	45.0	-	430	-	-	Fantozzi et al., 2007
Northern Tyrrhenian Sea (polluted area, Rosignano Solvay)	1998	-	6.8	400	34	-	Ferrara et al., 2000
	1999	30-130	2.5-14.0	465	-	12-26	Ferrara et al., 2001
	2001	73-140	10.3-24.2	250-325	14-17	15-17	Ferrara, unpublished data
	2004	50-92	1.0-9.0	380	-	27	Fantozzi et al., 2007
Central Tyrrhenian Sea (unpolluted coastal water)	2000	8-47	-	350	-	-	Lanzillotta and Ferrara, 2001
Mediterranean Sea-Eastern Basin	2000	35-43	-	-	-	27	Horvat et al., 2003; Gardfeldt et al., 2003
	2004	70-206	-	-	-	-	Andersson et al., 2007
Mediterranean Sea-Western Basin	2000	15-18	2.8 -3.8	-	-	26	Horvat et al., 2003; Gardfeldt et al., 2003
Strait of Messina	2000	60	-	-	-	26	Gardfeldt et al., 2003;
	2003	44	-	-	-	-	Andersson et al., 2007
Ionian Sea	2003	36-50	-	-	-	-	Andersson et al., 2007
	2004	16-28	-	-	-	-	Andersson et al., 2007

*Area-averaged values

**Maximum values measured in different seasons at the sampling area

Ferrara R, Mazzolai B, Lanzillotta E, Nucaro E, Pirrone N. Temporal trends in gaseous mercury evasion from the Mediterranean Sea Waters. Science of the Total Environment 2000; 259:183-190.

Ferrara R, Lanzillotta E, Ceccarini C. Dissolved gaseous mercury concentration and mercury evasional flux from seawater in front of a chlor-alkali plant. Environmental Technology 2001; 22:971-978.

Ferrara R, Ceccarini C, Lanzillotta E, Gardfeldt K, Sommar J, Horvat M, Logar M, Fajon V, Kotnik J. Profiles of dissolved gaseous mercury concentration in the Mediterranean seawater. Atmospheric Environment 2003; 37:85-92.

Gårdfeldt K, Horvat M, Sommar J, Kotnik J, Fajon V, Wängberg I, Lindqvist O. Comparison of procedures for measurements of dissolved gaseous mercury in seawater performed on a Mediterranean cruise. Analytical and Bioanalytical chemistry 2002; 374:1002-1008.

Gårdfeldt K, Sommar J, Ferrara R, Ceccarini C, Lanzillotta E, Munthe J, Wängberg I, Lindqvist O, Pirrone N, Sprovieri F, Pesenti E, Strömberg D. Evasion of mercury from coastal and open waters of the Atlantic Ocean and Mediterranean Sea. Atmospheric Environment 2003; 37:S73–S84.

Horvat M, Kotnik J, Fajon V, Logar M, Zvonaric T, Pirrone, N. Speciation of Mercury in Surface and Deep-Sea waters in the Mediterranean Sea. Atmospheric Environment 2003; 37/S1:93-108.

Johnson MT. A numerical scheme to calculate temperature and salinity dependent air-water transfer velocities for any gas. Ocean Science 2010; 6:913-932.

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

Lanzillotta E, Ceccarini C, Ferrara R. Photo-induced formation of dissolved gaseous mercury in coastal and offshore seawater of the Mediterranean basin. Sci Total Environ 2002; 300:179-187.

Lanzillotta E, Ceccarini C, Ferrara R. Improving mercury flux chamber measurements over water surface. Environmental Technology 2003; 24:913-919.

Lanzillotta E, Ceccarini C, Ferrara R, Dini F, Frontini FP, Banchetti R. Importance of the biogenic

organic matter in photo-formation of dissolved gaseous mercury in a culture of the marine diatom *Chaetoceros sp*. Sci. of Tot. Env.2004; 318(1-3):211-221.

Liss PS. Gas transfer: experiments and geochemical implications. In: Air-sea exchange of gaseous and particles, Liss PS and Slinn WGN (eds.), NATO ASI Series, D. Reidel Publishing Company, Dordrecht, Boston, Lancaster; 1983. p. 241-259.

Loux NT. Diel temperature effects on the exchange of elemental mercury between the atmosphere and underlying waters. Environmental Toxicology and Chemistry 2000; 19:1191-1198.

Nightingale P, Malin G, Law C, Watson A, Liss P, Liddicoat M, Boutin J, Upstill-Goddard R. In situ evaluation of air-sea exchange parameterizations using novel conservative and volatile tracers. Global Biogeochemical Cycles 2000; 14:373-387.

Pirrone N, Mason R. Mercury Fate and Transport in the Global Atmosphere: Emission, Measurements and Models, United Nation Environment Programme (UNEP), A report of the UNEP-Global Partnership on Atmospheric Mercury Transport and Fate Research, Geneva, Springer, USA; 2009. p. 637.

Sprovieri F, Pirrone N, Gardfeldt 694 K, Sommar J. Atmospheric Mercury Speciation in the Marine Boundary Layer along 6000 km Cruise path over the Mediterranean Sea. Atmos Environ 2003; 37(S1): 63-71.

Sprovieri, F., Hedgecock, I. M., and Pirrone, N.: An investigation of the origins of reactive gaseous mercury in the Mediterranean marine boundary layer, Atmos. Chem. Phys., 10, 3985–3997, doi:10.5194/acp-10-3985-2010, 2010.

Wanninkof R. Relationship between wind speed and gas exchange over the ocean. Journal of Geophysical Research 1992; 97:7373–7382.