Available online at www.sciencedirect.com
ScienceDirect
Marine Chemistry 107 (2007) 104–116
MARINE CHEMISTRY
www.elsevier.com/locate/marchem

Reprint of "Seasonal and daily variation of mercury evasion at coastal and off shore sites from the Mediterranean Sea"☆

Maria E. Andersson [a,*], Katarina Gårdfeldt [a], Ingvar Wängberg [b], Francesca Sprovieri [c], Nicola Pirrone [c], Oliver Lindqvist [a]

[a] *Department of Chemistry, Göteborg University, Göteborg, Sweden*
[b] *IVL Swedish Environmental Research Institute, Göteborg, Sweden*
[c] *Institute for Atmospheric Pollution of the National Research Council (CNR IIA), Rende, Italy*

Received 30 June 2006; received in revised form 16 November 2006; accepted 16 November 2006
Available online 26 July 2007

Abstract

Dissolved gaseous mercury (DGM) was measured continuously using two newly developed techniques and a manual technique. The continuous techniques were based on the equilibrium between the aqueous and gaseous phase (DGM = Hg_{extr} / H', Hg_{extr} is the measured mercury concentration in the gas phase, H' is the Henry's Law coefficient at the desired temperature). In order to calculate the annual mercury evasion from the Mediterranean Sea, diurnal and seasonal measurements of DGM, total gaseous mercury in air (TGM), water temperature and wind speed were performed. During August 2003, March–April 2004 and October–November 2004 measurements of these parameters were conducted on board the RV Urania. The continuous measurements of DGM showed a diurnal variation in concentration, at both coastal and off shore sites, with higher concentrations during daytime than nighttime. The concentration difference could be as large as 130 fM between day and night. The degree of saturation was calculated directly from the measurements, S = Hg_{extr} / TGM and was found to vary between the different seasons. The highest average degree of saturation (850%) and the largest variation in saturation (600–1150%) was observed during the summer. The spring showed the lowest variation (260–360%) and the lowest average degree of saturation (320%). The autumn also showed a large variation in saturation (500–1070%) but a lower average (740%) compared to the summer cruise. This might be explained by the temperature difference between the different seasons, since that parameter varied the most. The flux from the sea surface was calculated using the gas exchange model developed by Nightingale et al. [Nightingale, P.D., Malin, G., Law, C.S., Watson, A.J., Liss, P.S., Liddicoat, M.I., Boutin, J., Upstill-Goddard, R. C., 2000. In situ evaluation of air–sea gas exchange parameterization using novel conservative and volatile tracers. Global Biogeochemical Cycles, 14(1):373–387]. The evasion varied between the different seasons with the highest evasion during the autumn, 24.6 pmol m^{-2} h^{-1}. The summer value was estimated to 22.3 pmol m^{-2} h^{-1} and the spring to 7.6 pmol m^{-2} h^{-1}. Using this data the yearly evasion from the Mediterranean Sea surface was estimated to 77 tons.

Keywords: Mercury; Evasion; Mediterranean Sea; Biogeochemistry; *In situ* measurements; Gas exchange

☆ The publisher regrets that this article was previously published in an issue of Marine Chemistry, for citation purposes please use the original publication details; Andersson, M.E., Gårdfeldt, K., Wängberg, 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 104 (2007) 214–226.
DOI of original article: 10.1016/j.marchem.2006.11.003.

* Corresponding author. Tel.: +46 31 772 2888.
E-mail address: maria80@chem.gu.se (M.E. Andersson).

0304-4203/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.marchem.2007.06.020

1. Introduction

Mercury is a natural component of the Earth's crust and is naturally emitted to the atmosphere. However, anthropogenic mercury has been released since preindustrial time with an increase in emissions coinciding with the industrial revolution. Today mercury is considered a chronic pollutant problem in our environment. The element can be released from both anthropogenic and natural sources, e.g. fossil fuel combustion, chlor-alkali and paper pulp production, mining, volcanoes and re-emission from soil and water surfaces. The Earth's surface consists of more than 25 mercury containing minerals (Schroeder and Munthe, 1998). In the Mediterranean area there are several deposits, e.g. Almadén (Spain), Idrjia (Slovenia) and Monte Amiata (Italy), from where mercury has been released by both natural and anthropogenic activities.

It has been found that a majority of the aquatic environments are supersaturated with respect to dissolved gaseous mercury (DGM) (Schroeder and Munthe, 1998). Parts of this DGM may be emitted to the atmosphere and Mason et al. (1994a) estimated the emission of mercury (mostly elemental mercury) from the water surfaces to account for 30% (2000 tons per year) of the total emission of mercury to the atmosphere. The total global emission from the sea surface has been re-evaluated (Mason and Sheu, 2002) to 2600 tons per year, however the error in this estimation could, according to the authors, be as high as a factor of 5. The oceans receive 90% of its mercury through wet and dry deposition, where a significant fraction of the mercury is in the oxidised form (Mason et al., 1994a). Oxidised mercury may be transformed into DGM by several processes in the aqueous phase; both biotic and abiotic processes have been proposed (Allard and Arsenie, 1991; Xiao et al., 1994, 1995; Mason et al., 1995; Costa and Liss, 1999; Amyot et al., 1997, 2004). Even though the atmospheric contribution of oxidised mercury may be considered large, there are other sources available for oxidised mercury e.g. up welling and river input (Mason et al., 1994a,b). Many scientists have shown the influence of solar radiation on the formation of DGM from oxidised mercury and a daily trend in DGM concentration has been recorded at various coastal sites (Amyot et al., 1994, 1997; Lanzilotta and Ferrara, 2001; Gårdfeldt et al., 2001). On the other hand the occurrence of daily trends in DGM concentration in off shore waters has been an open question, relevant to the estimation of mercury fluxes from water surfaces.

There are two general methods when estimating mercury fluxes, the flux chamber techniques (Xiao et al., 1991; Kim and Lindberg 1995; Capri and Lindberg, 1998; Poissant and Casimir, 1998; Ferrara and Mazzolai, 1998; Gårdfeldt et al., 2001, 2003; Ferarra et al., 2000, 2001; Amyot et al., 2004) and different gas exchange models (Lindberg et al., 1995a; Kim et al., 1995; Gårdfeldt et al., 2001; Rolfhus and Fitzgerald, 2001; Poissant et al., 2000; Wängberg et al., 2001a,b; Baeyens et al. 1991; Baeyens and Leermakers, 1998; Cossa et al., 1997), both with advantages and disadvantages. The chamber technique is often used because of it simplicity and good detection limits, but it disrupts the local environment by covering the study area, and affects the meteorological parameters and the concentration gradient of mercury. The calculation methods on the other hand include separate measurements of gaseous mercury in air and water, wind speed and water temperature. These measurements do not disrupt the environment and meteorological parameters are included. A limitation with these methods is the need for multiple samples in order to get a proper estimate. When comparing the methods it has been shown that the flux chamber technique consistently measures lower values than the calculations (Lindberg et al., 1995a,b; Gustin et al., 1999).

The major objective with this study was to investigate the concentrations of DGM at various locations in the Mediterranean Sea during different seasons, in order to calculate the annual mercury evasion. A further aim was to compare the contribution of evasion of elemental mercury from the Mediterranean Sea surface on a global scale. This was accomplished by using two new techniques for continuously measuring DGM and a manual technique. Total gaseous mercury (TGM), water temperature and wind speed were also measured continuously. By using these parameters, the evasion of mercury from the sea surface was estimated using the gas exchange model developed by Nightingale et al. (2000). Measurements were conducted during three seasons, August 2003, March–April 2004 and October–November 2004.

2. Experimental

During three Mediterranean cruises, DGM, TGM, wind speed and water temperature were measured. The first two cruises were performed in August 2003 and March–April 2004 and covered parts of the Eastern and Western Mediterranean basin, Figs. 1 and 2. The last cruise was performed in October–November 2004 and covered the Adriatic Sea, Fig. 3.

The measurements were conducted on the Italian Research Vessel Urania, a 62 m long and 11 m wide ship equipped with meteorological and oceanographic instrumentations including winches and a CTD system with a cable length of 5000 m.