



## Natural and anthropogenic sources of mercury in the Mediterranean

**D. Žagar** (1), R. Rajar (1), M. Horvat (2), J. Kotnik (2), M. Četina (1)

(1) University of Ljubljana, Faculty of Civil and Geodetic Engineering, Ljubljana, Slovenia (dzagar@fgg.uni-lj.si),

(2) Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia (milena.horvat@ijs.si)

In the frame of the EU project MERCYMS mercury concentrations in the Mediterranean area were measured and modelled. The model PCFLOW3D (Rajar et al., 2000, 2004), upgraded with a mercury biogeochemistry module simulated circulation, transport and mercury transformations and fluxes in the water compartment while RAMS-Hg model (Kallos et al., 2001) was used to determine atmospheric transport and transformations.

Annual Hg mass balances for the entire Mediterranean Sea and for the Gulf of Trieste (Northern Adriatic) were established on the basis of the measurements and the modelling results (Rajar et al. in press). Significantly different sources of Hg are important in both computational domains. The main known sources of Hg for the Mediterranean Sea are atmospheric deposition (+23 t/yr, 57 % of the total Hg input) and inflow with the main rivers (+13 t/yr, 32 % of the total input). The Gulf of Trieste is mostly affected by inflow of Hg with the Soča / Isonzo River (+1.5 t/yr, mostly bound to suspended sediment, more than 99 % of the total input), which drains the impact area of the former Hg mine in Idrija, Slovenia. Although all known natural and anthropogenic sources and sinks were taken into account, both mass balances showed a significant gap between the incoming and outgoing Hg. In both cases, Hg evasion was the main reason of the discrepancy.

In the Gulf of Trieste the annual evasion (approx. 70 kg/yr) exceeds the total quantity of inflowing dissolved Hg and is even higher than the total quantity of dissolved Hg in the Gulf. In order to close the mass balance it was necessary to take into account remobilisation of Hg from sediment, which has already been noticed and described by

Širca et al., 1999.

In the entire Mediterranean Sea annual evasion calculated by different authors, (-50 t/yr, Rajar et al, in press, -100 t/yr, Gårdfeldt et al., 2003, and -110 t/yr, Pirrone et al., 2001) exceeded the input even by itself (other outputs not taken into account). Accounting for the measurements of Hg concentrations in the water column (Cossa et al, 1997, Horvat et al., 2003, and recent measurements during the MERCYMS project) it is not reasonable to believe that the Mediterranean Sea is recovering with such a trend. Measurements also showed an increase of Hg concentrations near the bottom (Horvat et al., 2003), particularly in areas of active volcanism (Southern Tyrrhenian Sea) and enhanced tectonic activity (Central Mediterranean).

As the anthropogenic sources were relatively well studied (Pacyna et al, 2003), and due to the present tectonic activity and the underlying cinnabar belt under the Mediterranean Sea (Gustin, 2003), natural emissions were further studied. Emissions from volcanoes, fumaroles and sulfataras and widespread geological anomalies could represent an important natural source of mercury in the Mediterranean basin (Ferrara et al., 2000). Moreover, Pyle and Mather (2003) critically evaluated atmospheric volcanic emissions and showed that contribution of volcanic Hg is most probably underestimated. Also, recent work of Stoffers et al. (1999) and Astakhov et al. (2004) indicate that submarine tectonic activity with accompanying phenomena could represent an important source of mercury to oceans. Natural emissions from underwater sources were estimated to +16 t/yr and taken into account with the final Hg mass balance of the Mediterranean Sea (Rajar et al, in press). This value represents about one third of the total (so far known) Hg input to the Mediterranean.

A conclusion can be made, that additional release of Hg from the bottom had to be taken into account in both cases. In a coastal area, heavily contaminated due to mining (anthropogenic) activities, it is difficult to distinguish between natural and anthropogenic sources. On the other hand, natural sources are most likely responsible for a significant quantity of mercury pollution in the deep-sea.

**Acknowledgement:** The research was performed in the frame of the EU project MERCYMS (Contr. No. EVK3-CT-2002-00070) with support of the Ministry of Higher Education and Technology of Slovenia (Programmes P1-0143 and P2-180).

### **References:**

Astakhov A.S., Koruykin G.I., Ivanov M.V. (2005). Nature mercury emission from Earth Crust in Arctic and subarctic marine environments. *Geophysical Research Abstracts*, Vol. 7, 00649, 2005.

Cossa, D., Martin, J-M., Takayanagi, K. and Sanjuan J. (1997). The distribution and

cycling of mercury species in the western Mediterranean, Deep-Sea Research II, Vol. 44, No. 34, pp. 721-740, 1997.

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

Gårdfeldt, K., Sommar, J., Ferrara, R., Ceccarini, C., Lanzillotta, E., Munthe, J., Wangberg, I., Lindqvist, O., Pirrone, N., Sprovieri, F., Pesenti, E. and Stromberg, D. (2003). Evasion of mercury from coastal and open waters of the Atlantic Ocean and the Mediterranean Sea, *Atmospheric Environment* 37 Supplement No. 1 (2003) S73–S84.

Gustin, M.S. (2003). Are mercury emissions from geologic sources significant? A status report. *The Science of the Total Environment* 304, 153-167.

Horvat, M., Kotnik, J., Logar, M., Fajon, V., Zvonarić, T., Pirrone, N. (2003). Speciation of mercury in surface and deep-sea waters in the Mediterranean sea. *Atmospheric Environment* 37 Supplement No. 1 (2003) S93–S108.

Kallos, G., Voudouri, A., Pytharoulis, I. and Kakaliagou, O. (2001). Modelling Framework for Atmospheric Mercury over the Mediterranean Region: Model Development and Applications. In ICLSSC, LNSC 2179;. Eds.; S. Margenov, J. Wasniewski and P. Yalamov. Springer-Verlag Berlin Heidelberg, 281–290.

Pacyna J.M., Pacyna, E.G., Steenhuisen, F., Wilson S. (2003). Mapping 1995 global anthropogenic emissions of mercury. *Atmospheric Environment* 37, Supplement 1: S109–S117.

Pirrone, N., Costa, P., Pacyna, J.M, Ferrara, R. (2001). Mercury emission to the atmosphere from natural and anthropogenic sources in the Mediterranean region. *Atmospheric Environment* 35, 2997-3006.

Pyle, D.M. and Mather, A.T. (2003). The importance of volcanic emissions for the global atmospheric mercury cycle. *Atmospheric Environment* 37, pp. 5115-5124.

Rajar, R., Žagar, D., Širca, A. Horvat, M. (2000). Three-dimensional modelling of mercury cycling in the Gulf of Trieste, *The Science of the Total Environment* 260, pp. 109-123.

Rajar, R., Žagar, D., Četina, M., Akagi, H., Yano, S., Tomiyasu, T. Horvat, M. (2004). Application of three-dimensional mercury cycling model to coastal seas, *Ecological Modelling* 171, pp. 139-155.

Rajar R., Četina M., Horvat, M., Žagar, D. (in press). Mass balance of mercury in the

Mediterranean Sea. *Marine Chemistry*. doi: 10.1016/j.marchem.2006.10.001

Širca, A., Horvat, M., Rajar, R., Covelli, S., Žagar, D., Faganeli, J. (1999) Estimation of mercury mass balance in the Gulf of Trieste. *Acta Adriatica.*, vol. 40, No. 2, pp. 75-85.

Stoffers P, Hannington M, Wright I, Shipboard Scientific Party (1999). Elemental mercury at submarine hydrothermal vents in the Bay of Plenty, Taupo volcanic zone, New Zealand. *Geology* 27: 931-934.