



## **Impact of Reduction and Evasion Processes on Hg Mass Balance in different Scales**

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Mercury studies in the Mediterranean region have shown a significant difference in biogeochemical transformation processes of mercury between the relatively less polluted deep-sea environment and the coastal region, where concentrations of all mercury species can be higher for an order of magnitude or even more. The case study gives a comparison of reduction / evasion computation in the Mediterranean Sea in its entirety, conducted in the frame of the EU project MERCYMS, and the Gulf of Trieste, Northern Adriatic, where the River Soca brings about 1500 kg/ yr of mercury from a former mercury mine region in Idrija, Slovenia. Annual mercury mass balances for both domains were calculated. Širca et al. (1999) estimated a provisional mass balance for the Gulf of Trieste. The quantity of mercury evasion from the Gulf was roughly estimated to a few kg/yr, while the computations for the Mediterranean showed that evasion (about 50 t/yr) was the most significant sink of mercury for the water compartment.

Seasonal simulations of circulation and biogeochemical transformation processes of a typical year for both domains were performed by the 3D baroclinic hydrodynamic and transport / dispersion model PCFLOW3D (Rajar et al., 2000, 2004), which has been upgraded with a biogeochemical module. As the mercury transformation processes are highly complex, the whole mercury cycling should be modelled at the same time. The PCFLOW3D model can deal with the basic processes and fluxes: methylation, demethylation, reduction, oxidation, exchange with the bottom and exchange with the

atmosphere. In order to improve the modelling results the water model was coupled by the atmospheric model RAMS / SKIRON, which provided meteorological data and the concentrations of Hg in the atmosphere. Transformation coefficients for the Mediterranean and for the Gulf of Trieste were determined from measurements and the literature (Rolfhuss and Fitzgerald, 2004), respectively. Simulated concentrations of elemental mercury were compared to measurements and an acceptable agreement was achieved, at least near the surface.

The evasion was calculated as suggested by Gårdfeldt et al. (2003) and compared to the modelling results, which were in both cases lower for a factor of two (Mediterranean 50 t/yr model and 100 t/yr calculation and the Gulf of Trieste 75 kg/yr model and 130 kg/yr calculation). Increase of reduction coefficients did not show any significant improvement, as the surface layer became depleted of elemental mercury (and other dissolved mercury species that could enter the reactions). Although the amount of evasion represents a very different part of the total dissolved mercury, both domains are highly affected by the evasion. In the Mediterranean, the annual evasion represents roughly 5 % of the total dissolved mercury; still, the output of mercury is higher than the input for at least 25 t/yr. This leads to an opinion that not all sources of mercury were taken into account correctly. On the other hand, the total quantity of dissolved mercury species in the Gulf of Trieste is only about 25 kg and the inputs (the Soča River, deposition) contribute about 50 kg/yr. As some Hg is also flushed to the Northern Adriatic, release from the bottom had to be taken into account. Resuspension, diffusive and benthic fluxes were estimated to some 400 kg/yr (Širca et al., 1999); however, only a part of this quantity is released in dissolved form. About 60 kg/yr of dissolved Hg from the bottom release had to be taken into account to close the mass balance of the Gulf of Trieste.

From both case studies it can be seen that, despite the difference in processes between the deep-sea and the coastal region, the evasion represents a very important factor in the mass balance of both computational domains. As reduction of divalent Hg is an important source of elemental Hg, these two processes need to be studied together.

**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:

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.

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.

Rolfhus, K. R., Fitzgerald, W.F. (2004). Mechanisms and temporal variability of dissolved gaseous mercury production in coastal seawater. *Marine Chemistry* 90, 125-136.

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