# **Slovenia**

### Meetings

Participation at the Workshop "The ocean chemistry of bioactive trace elements and paleoclimate proxies" May 29 to June 1, 2012, Geel, Belgium (L. Benedik – acting as an invited speaker, M. Vahčič as a participant).

#### Cruises

Participation of J. Kotnik, M. Vahčič and A. Bratkič on the FENICE 2012 cruise in W Mediterranean led by F. Sprovieri (CNR-IIA, Italy) from August 11 to August 29 2012. The cruise was organized within the EU project GMOS (Global Mercury Observation Systems). The activities were related to the cycling of Hg species in marine environment including deep water profiles of dissolved gaseous Hg (DGM), total (THg), monomethyl Hg (MeHg) and dimethyl Hg (DMeHg) in open ocean waters. All these analysis are still in progress.

#### New results

Results obtained during the James Cook cruise represent a part of PhD study of A. Bratkič entitled: "Mercury biotransformations in marine environments" defended in July 2013. All Hg speciation analyses were performed at the Department of Environmental Sciences at Jožef Stefan Institute under the supervision of M. Horvat.

The primary goal of the South Atlantic Ocean expedition was to perform Hg speciation analysis in ocean water at very high vertical and spatial frequency, which would indicate whether Hg transformation in the deep sea is a more active process than is currently reported. Secondary goals were to apply new strategies for sample storage and transport; and to obtain all the necessary supporting data on nutrients and physico-chemical parameters which could help with the interpretation of the data.

Oceanographic sampling for Hg speciation was demanding from the logistical point of view and particular attention was given to the issues of storage and transport of samples. During the time of storage and transport, samples never thawed, which contributed to the results being accurate and representative of the actual environmental conditions. The combination of freezers and dry ice proved to be sufficient for the safe transport of samples to the laboratory, where they could be stored in freezers with an uninterruptible power supply. Particularly useful was simple, but efficient double packing in zip-lock plastic bags. Besides preventing contamination of the bottles, they also prevented some physical damage to them.

The South Atlantic Ocean cruise from South Africa to Uruguay along the 40°S parallel resulted in a remarkably high spatial (both vertical and horizontal) frequency of Hg speciation measurements. Up to 24 depths per station were measured, which was indeed an above average number of sampling depths in this region, and in the ocean in general.

Total Hg (THg) profiles indicated a possible increase in deep waters as a result of the geothermal activity of the Mid-Atlantic Ridge. THg values were lower in the uppermost water layers, suggesting degassing of Hg<sup>0</sup> to the atmosphere. This is globally important because the large ocean surface represents a great potential flux of Hg<sup>0</sup> to the atmosphere. Even small changes in conditions that would affect dissolved gaseous mercury (DGM) formation in the ocean would also result in regionally significant Hg evasion or retention.

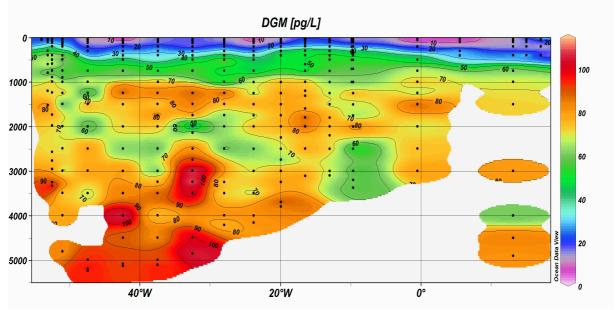
THg values in seawater were higher off the coast of South America, probably due to the influence of large cities and transport by the Rio de la Plata. The Argentine Basin also showed an increase.

Interestingly, water masses could be distinguished by DGM content, but not by THg. Upper Circumpolar Deep Water (UCDW) mass in the South Atlantic had higher DGM concentrations than North Atlantic Deep Water (NADW). Higher values in the Argentine

Basin were unexpected, but might easily be explained by higher DGM solubility under high pressure, or might result from a Hg increase in newly formed Antarctic Bottom Water (AABW). Moreover, surface DGM distribution closely resembled that of Chl *a* (and hence photosynthetic organisms), but not of the bacterial community. This suggested that DGM might be formed principally by photosynthetic microbes and algae without the *mer* operon, and not by *mer* containing heterotrophic microbes. In addition, *merA* was not detected, but that was likely a consequence of unsuitable oligonucleotides which did not cover the marine *merA* diversity.

Methyl mercury (MeHg) concentrations were often below the limit of detection. Nevertheless, MeHg is formed in the South Atlantic Ocean water column as there were no increases of this species above the sediment or in the surface waters, where aerial deposition might be a source. The general decrease formed at the surface might be indicative of photodemethylation. In two instances MeHg coincided with the Chl *a* peak, which might be indicative that its formation is connected with primary production. Bacterial and archaeal 16S rRNA sequences were detected at all depths at one deep ocean station; therefore it is likely that heterotrophic activity contributes to the observed MeHg levels.

Dimethy methyl mercury (DMeHg) was measured only at one station. As expected, it was higher below 1000 m and very low above that depth, especially in the surface waters. It reached its highest concentration in UCDW, similarly to DGM, probably due to lower oxygen concentrations and hence lower oxidation potential.



**Figure 1.** DGM concentrations for the whole water column from JC068 South Atlantic cruise (40°S parallel). Black dots represent sampling depths. Distinct layering of DGM can be observed. Deep waters in the Argentine Basin were characterized by the highest DGM values measured during the cruise.

In order to understand Hg biogeotransformations in the South Atlantic Ocean better, more sampling campaigns with such resolution are needed. The deep ocean is very important where Hg cycling is probably more intensive than is generally accepted.

### Other activities

S. Tamše obtained GEOTRACES fellowship to perform his research on stable isotope composition of N and O in nitrates in marine samples. The research was conducted at the

Laboratoire de Glaciologie et Géophysique de l'Environnement (CNRS/UJF), Grenoble, France during September 3 to October 26 2012.

#### **Publications**

Original scientific article

- KORON, Neža, BRATKIČ, Arne, RIBEIRO GUEVARA, Sergio, VAHČIČ, Mitja, HORVAT, Milena. Mercury methylation and reduction potentials in marine water. Appl. radiat. isotopes. [Print ed.], 2012, vol. 70, issue 1, str. 46-50, doi: 10.1016/j.apradiso.2011.07.015.
- ACQUAVITA, Alessandro, COVELLI, Stefano, EMILI, Andrea, BERTO, Daniela, FAGANELI, Jadran, GIANI, Michele, HORVAT, Milena, KORON, Neža, RAMPAZZO, Federico. Mercury in the sediments of the Marano and Grado Lagoon (northern Adriatic Sea): sources, distribution and speciation. Estuar., coast. shelf sci., 2012, vol. 113, str. 20-31, doi: 10.1016/j.ecss.2012.02.012.
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- DE VITTOR, Cinzia, FAGANELI, Jadran, EMILI, Andrea, COVELLI, Stefano, PREDONZANI, Sergio, ACQUAVITA, Alessandro. Benthic fluxes of oxygen, carbon and nutrients in the Marano and Grado Lagoon (northern Adriatic Sea, Italy). Estuar., coast. shelf sci., 2012, vol. 113, str. 57-70, doi: 10.1016/j.ecss.2012.03.031.
- KORON, Neža, FAGANELI, Jadran. Benthic fluxes of mercury during redox changes in pristine coastal marine sediments from the Gulf of Trieste (northern Adriatic Sea). Journal of soils and sediments, 2012, vol. 12, 10, 1604-1614, graf. prikazi. http://dx.doi.org/10.1007/s11368-012-0602-1.
- BRATKIČ, Arne, OGRINC, Nives, KOTNIK, Jože, FAGANELI, Jadran, ŽAGAR, Dušan, YANO, Shinichiro, TADA, Akihide, HORVAT, Milena. Mercury speciation driven by seasonal changes in a contaminated estuarine environment. Environ. res. (N.Y.), [in press] 2013, 8 str., doi: 10.1016/j.envres.2013.01.004.
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# Book chapter

 OGRINC, Nives, COVELLI, Stefano, OGORELEC, Bojan, FAGANELI, Jadran, BUDJA, Mihael. Reconstruction of the Holocene palaeoenvironment of the Gulf of Trieste by using geochemical methods. V: ANDRIČ, Maja (ur.). Dolgoročne spremembe okolja 1, (Opera Instituti Archaeologici Sloveniae, 25). Ljubljana: Inštitut za arheologijo ZRC SAZU, 2012, 81-88.

## Scientific conference contribution

- HORVAT, Milena, PIRRONE, Nicola, SPROVIERI, Francesca, CINNIRELLA, Sergio, KOTNIK, Jože, OGRINC, Nives, ŽAGAR, Dušan, CINNIRELLA, Sergio. Mercury in the Mediterranean status and mass balance. V: 6th SETAC World Congress/SETAC Europe [and] 22nd Annual Meeting, 20-24 May 2012, Berlin, Germany. Abstract book. Brussels: SETAC, 2012, 126.
- HORVAT, Milena, VAHČIČ, Mitja. Comparability, traceability and uncertainty of the results for mercury analysis and speciation in the marine environment. V: 6th SETAC World Congress/SETAC Europe [and] 22nd Annual Meeting, 20-24 May 2012, Berlin, Germany. Abstract book. Brussels: SETAC, 2012, 401.
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#### Technical Report

- KOCMAN, David, HORVAT, Milena, WILSON, Simon, OUTRIDGE, Peter, TELMER, Kevin. Global releases of mercury to aquatic environments. V: BIEBER, Elke. /Technical background report for the global mercury assessment 2013/. Oslo: UNEP = United Nations Environment Programme, 2013, 69-81.
- OUTRIDGE, Peter, MASON, Robert P., KOCMAN, David, HORVAT, Milena, MUNTHE, John. Aquatic pathways, transport and fate. V: BIEBER, Elke. /Technical background report for the global mercury assessment 2013/. Oslo: UNEP = United Nations Environment Programme, 2013, 82-94.

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