

Mercury speciation in deep-sea waters of the Mediterranean Sea

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This communication presents results of the investigation of the distribution and speciation of mercury (Hg) in deep-sea waters of the Mediterranean Sea during oceanographic cruise on board the Italian research vessel URANIA as a part of GMOS project. The study includes deep water profiles of dissolved gaseous Hg (DGM), reactive Hg (RHg), total (THg), monomethyl Hg (MeHg) and dimethyl Hg (DMeHg) in open ocean waters. A special attention is paid on the distribution of DGM, which plays the major role in the exchange of Hg between water and atmosphere. Average concentrations of measured Hg species were characterized by seasonal and spatial variations. Overall average THg concentrations ranged between 0.41 to 2.65 pM (1.32 ± 0.48 pM) and were comparable to those obtained in previous studies for the Mediterranean Sea [1,2]. Generally, average THg concentration was higher in W and E Mediterranean Deep Waters (WMDW and EMDW) and Levantine Intermediate Water (LIW) than overlying Modified Atlantic Water (MAW). High concentrations and portions of DGM and MeHg indicate high reactivity of Hg in open ocean waters. DGM was present in surface waters mainly as Hg⁰ as no DMHg was detected at the surface, while towards the bottom a noticeable, but relatively small portion of DMeHg is present. DGM represents a considerable proportion of total Hg (average 20%, 0.23 ± 0.11 pM). The portion of DGM typically increased towards the bottom, especially in areas with strong tectonic activity (Alboran Sea, Strait of Sicily, Tyrrhenian Sea), indicating its bacterial and/or geotectonic origin. This is also confirmed by the fact that average DGM concentration was the highest in deep water masses (WMDW and EMDW). The percentage of MeHg (0.22 ± 0.12 pM) was on average approximately the same as for DGM. The observed increase of MeHg towards the bottom could be the consequence of photochemical degradation and/or microbial actions in surface and microbiologically mediated methylation in deeper waters [3,4].

Results will be also compared to the results obtained in the last GEOTRACES Atlantic Ocean cruise.

[1] Horvat *et al.* (2003) *Atmosph. Environ* **37/S1**, 93-108. [2] Kotnik *et al.* (2007) *Mar. Chem.* **107**, 13-30. [3] Monperrus *et al.* (2007) *Mar. Chem.* **107**, 49-63. [4] Heimbürger *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 5549-5559.

Hydrochemistry of shallow groundwater in areas affected by livestock burial

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As a result of an outbreak of foot and mouth disease (FMD) between late 2010 and early 2011 in South Korea, a large number of livestock carcasses (> 3.4 million) were buried in ~4,400 pits (usually 5 m deep) throughout the country. As a result, there is concern about the potential impacts of leachates from livestock burial sites on shallow groundwater. In addition, there are debates about the origin of groundwater contamination around livestock burial sites, as groundwater in agricultural areas is also usually contaminated by nitrogen-bearing compounds and chlorine from preexisting non-point and point sources. Therefore, we conducted hydrochemical surveys of groundwater in a few areas potentially affected by livestock burial, with the main purpose of assessing the potential impacts on groundwater quality. An additional objective was to identify geochemical indicators which can be used for differentiating contamination from agricultural areas and livestock burial sites. We collected hydrochemical (i.e., major cations and anions and trace metals) and isotopic data for nitrate ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) for groundwater from domestic and agricultural wells (< 300 m away from burial sites) as well as leachate samples from burial sites. The obtained data were interpreted using factor analysis to reveal the relationships between variables and to cluster the samples based on hydrochemical processes.

The results show that only a few monitoring wells at distances of < 5 m from the burial sites were impacted by leachate from burial sites yielding groundwater that was strongly anoxic and high in ammonium and other solutes such as HCO₃, Ca, Cl, Mg, Na, K, SO₄, Br, Fe, Mn and B. The leachates and groundwaters affected by burial sites were hydrochemically a Ca-HCO₃ type, while unaffected groundwater was mostly Ca-Cl(NO₃) type due to pervasive impacts from agrochemicals. The isotopic composition of traces of nitrate in leachate and groundwater affected by burial sites were variable and inconsistent with values known for diverse nitrate sources such as fertilizers, manure and sewage, possibly due to nitrification under isotopic disequilibrium or due to other nitrogen transformation processes. We propose the use of following geochemical parameters for differentiating groundwater contamination from leachate of livestock burial sites and from agricultural areas: 1) redox-sensitive parameters such as ammonium, Fe and DO (especially, the occurrence of ammonium ion) and 2) hydrochemical water types in conjunction with (Na+K)/ Σ cations versus (SO₄+Cl) relationship.