Methyl mercury in sediments and its cycling in the Lagoon of Venice: a synthesis of multi-compartment study.

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Introduction: Among contaminants identified in the sediments of the Lagoon of Venice, mercury (Hg) presents potentially a high risk for the ecosystem. The mean Hg concentration in sediments is equal to the Probable Effect Level (PEL) and exceeds PEL in the central–northern and northern parts of the lagoon. However, bioavailability of Hg and its bioaccumulation in organisms depend strongly on Hg speciation in the sediments, with methyl mercury (MMHg) being the form that biomagnifies in the food chain. Our recent study of total mercury (THg) and MMHg in various compartments of the Lagoon of Venice adds a new insight into mercury dynamics. Here, we summarise and integrate the results from various compartments of lagoon (i.e. water, sediment, porewater, benthic invertebrates).

Methods: Sediment cores and water samples were collected in September 2008 and 2009 in two subtidal sites in the northern part of the Lagoon characterized by contrasting hydrodynamic features. One site (VE1) was located in the proximity of Torcello Island, close to salt marshes, in a confined and accumulating area, while the other site (VE2) was situated close to the Canale di Burano, representing open lagoon area characterized by free water circulation and weakly accumulating or erosive conditions. THg and MMHg concentrations were measured in sediment profiles (in solids and in porewater), integrated porewater profiles (obtained by peepers), overlying water and suspended matter. Furthermore, the THg and MMHg in porewater (obtained with micro-needle sampler at 2, 4 and 6 cm depth) and overlying water were also measured at VE1 during two tidal cycles with one-hour resolution. Finally, *Chironomus salinarius* larvae were caged for four days and sampled daily to follow bioaccumulation of THg and MMHg in the larvae.

Results: Mean THg and MMHg concentrations at site VE1 (621.9 ± 40.4 ng g^{-1} and 1.11 ± 0.18 ng g^{-1}, respectively) doubled those from the site VE2, and were well correlated with fine silt content at both sites. Time integrated profile of MMHg in porewater (obtained with peepers) showed distinct peaks at depths corresponding to the activity of both iron and sulphur reducing bacteria. A high inter- and intra-site variability of MMHg concentrations was observed in porewater extracted from sediment cores. Time series of THg and MMHg concentrations in porewater (at 2 cm depth) showed distinct peaks at late stage of flood tide but not at ebb tide. In the overlying water, peaks of suspended matter and particulate THg and MMHg concentrations were also observed at flood, but not at ebb tide. All these features were consistent at the two monitored tidal cycles.
Chironomus salinarius larvae caged for 4 days showed no or only weak Hg (mostly MMHg) cytosolic bioaccumulation rate over the initial concentration. Interestingly, the larvae caged without access to the lagoon sediments accumulated more Hg (probably from suspended particles deposited in cages during exposure) than the larvae having access to sediments.

Discussion: Production and fate of MMHg in sediments of the Lagoon of Venice is difficult to evaluate because large- and small- scale spatial variability of MMHg concentrations in sediments, which depends on sediment grain size, organic matter content, THg concentration and redox conditions. This variability can possibly be better constrained by further systematic studies, provided the tide dependent variability is carefully considered. THg and MMHg bound to settling particles appear to be the more available source of this metal to Chironomids than the sediments. Because of the recurrent Hg cycling between pore- and overlying water and due to improvement in the tropic state of the lagoon (i.e. lower dilution by plankton biomass, lower Chironomid biomass) the seston-based food chain might be equally or more important than the benthic food chain for Hg accumulation by fish.

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