Formation, uptake and bioaccumulation of methylmercury in coastal seas – a Baltic Sea case study

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Akademisk avhandling

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Abstract
Methylmercury (MeHg) is a potent neurotoxin which can bioaccumulate to harmful levels in aquatic food webs. Methylmercury formation is a predominantly biotic process which involves phylogenetically diverse microorganisms (e.g. iron- or sulfate-reducing bacteria). The formation of MeHg is related to the presence of organic matter (OM) which contains substrates essential for methylating microbes and reduced sulfur ligands (thiols, RSH) that form strong bonds with inorganic mercury (HgII) and affect its bioavailability. In aquatic systems, MeHg is bio-concentrated from the water column to the base of the food web and this step is crucial for MeHg levels found at higher trophic levels. Trophic transfer processes of MeHg in the food web are also of great importance. Discharge of OM in coastal areas affects light conditions needed for phytoplankton growth, and promotes heterotrophy, i.e. bacteria production. This may lead to a shift from the phytoplankton-based to the longer bacteria-based (microbial loop) food web and influence the amount of bioaccumulated MeHg in higher trophic levels. Methylmercury levels in predatory biota is thus affected by the bioavailability of HgII for methylation (studied in Paper I & II), MeHg speciation in the water column, crucial for MeHg incorporation at the base of the food web (Paper III), and the structure of the pelagic food web (Paper IV).

In this thesis, it is shown that OM can act as a predictor of dissolved MeHg levels in estuarine and coastal systems. It impacts MeHg levels both by affecting HgII bioavailability (through Hg complexation with humic matter) and the activity of methylating microbes (providing metabolic electron donors) (Paper I). Moreover, elevated concentrations of particulate and dissolved HgII and MeHg, are associated with the presence of pelagic redoxclines in coastal seas. The redoxcline affects HgII speciation in the water column and its bioavailability for methylation (Paper II). It is further shown that the molecular structure of ligands in MeHg complexes affects the kinetics of MeHg uptake in phytoplankton. Rate constants for association of MeHg to the cell surface of a green algae were higher in treatments containing smaller thiol ligands of simpler structure than in treatments with larger thiols and more “branched” structure (Paper III). Finally, it is demonstrated that MeHg bioaccumulation in zooplankton can increase in systems with highly heterotrophic food webs and enhanced loadings of terrestrial OM. Such conditions are expected to occur in northern latitude coastal systems following climate changes (Paper IV).

Keywords
Mercury, methylmercury, bioaccumulation, mesososm, isotope tracers, methylation, demethylation, stability constant, kinetic model, coastal sea, ICPMS, LC-MS/MS