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Optimization, Application and Challenges of Diffusive Gradient in Thin Film for Ultratrace Methylmercury measurements in the Open and Coastal Ocean

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Mercury concentrations in ocean surface waters have tripled since pre-industrial times. However, the mercury cycle in the ocean, governed by biotic and abiotic processes, is still poorly understood. In suboxic environments, microorganisms methylate inorganic mercury (HgII) into monomethylmercury (MMHg) and dimethylmercury (DMHg). DMHg, degraded by sunlight, also contributes to MMHg formation at the surface of the oceans.

MMHg accumulates in the food chain, involving neurological risk for humans. The Minamata disaster in the 1960s led to the establishment of the Minamata Convention. One of its key objectives is to assess MMHg levels in the environment. Our knowledge of the mechanisms governing MMHg levels in aquatic organisms, is still lacking, mainly because data is lacking.

Due to the low concentrations of MMHg in seawater and the high risk of contamination during sampling, current analyses are restricted to expert laboratories. In situ diffusive Gradient in Thin-Film (DGT) passive samplers address these challenges by preconcentrating MMHg by diffusion in a binding gel. This gel accumulates both MMHg and HgII, using a 3-mercaptopropyl-functionalized silica (3MFS) resin embedded in either an agarose or polyacrylamide polymer.

To selectively analyze MMHg in the binding gel, we tested different elution methods using acidic thiourea solutions. The results showed that polyacrylamide-3MFS binding gels exhibited higher elution efficiency (94 ± 3% vs. 41 ± 6%), improved precision, and better handling compared to agarose-3MFS gels. We applied this methodology to DGT samplers deployed on moorings in a) the Western Tropical South Pacific Ocean (WTSP), via an automated system enabling monthly sampling over a year, and in b) shallow Peruvian coastal waters, where DGTs were deployed at different depths.

DGT-MMHg concentrations were in good agreement with discrete water samples analyzed via GEOTRACES reference methods during oceanographic cruises in the same regions. In the WTSP, DGT times series data illustrated the occurrence of seasonal MMHg trends, while in the Peruvian coast, DGT profiles showed the benthopelagic gradient. Compared to traditional oceanographic campaigns, DGTs offer several advantages: in situ preconcentration, low background contamination, limited logistical requirements, lower costs and time-integrated concentrations. They represent a valuable and promising tool to study the marine Hg cycle.