[OP 3.8]

Trace Metal Speciation in the Lagoon of Venice: Relation with Dissolved-Particulate Metal Partition

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There is evidence that organic complexation plays an important role in the chemical speciation of metals. However, the effects of complexation on the processes of adsorption/desorption on particulate matter, and hence the effects of speciation on their mobility, are not yet fully understood.
Water samples were collected in the Lagoon of Venice during three campaigns carried out between July 1992 and August 1994, and labile, complexed and particulate metal fractions were differentiated. Anodic Stripping Voltammetry measurements were used to assess the chemical speciation of Cd, Pb and Cu, and AAS was used to determine the trace metal content in particulate matter.
The dissolved fraction represented 90%, 65% and 33% for Cd, Cu and Pb, respectively; however, the partition was strongly dependent on the area examined. The dissolved concentration of the three metals was negatively correlated to the tide level (for the three metals, the value of r was -0.70, -0.66 and -0.81, respectively) and to a lesser extent to the salinity and transmittance.
Cadmium and copper in the dissolved phase were complexed by two classes of ligands, the first class was present at low concentrations (the mean values were 0.2 nmol/l and 13 nmol/l for cadmium and copper, respectively) and they had a high conditional stability constant (the mean value log K' was 11 and 14 for those binding cadmium and copper, respectively), while the second class presented higher concentrations (the mean values were 1.9 nmol/l and 93 nmol/l, respectively) and a lower value of log K' (8.8 and 8.4, respectively); the lead was complexed by a single ligand (mean concentration 1.1 nmol/l and log K=9.9). The labile fraction of dissolved metal concentration was 24%, lower than 1% and 28% for cadmium, copper and lead, respectively. The mean ionic amounts of cadmium and lead were 2 pM; while the mean ionic copper was of few femtomol/l; only in samples collected near the industrial area or the urban area was the concentration as high as 10 pM. Results showed that the variability of the salinity in the central lagoon was low, ranging from 30 to 34.4 psu; therefore, the effect of variations of ionic strength on the exchange dissolved-particulate was very limited. The cadmium and copper in the particulate matter were correlated to the two stronger ligands complexing the two metals (r=0.78 and 0.81, respectively). However, only for cadmium did the first class of ligands show a positive correlation with the partition coefficient, K_d. The particulate lead was correlated to the total dissolved metal concentration.
On the basis of the negative correlation between the dissolved metals and tide level, we can conclude that the dissolved metal concentration in the central lagoon is prevalently controlled by dilution. The organic complexation has an important role in the speciation of the three metals in the lagoon water. The partition of dissolved/particulate cadmium is affected by a complexation by one class of organic ligands.
A comparison of our results with those obtained by other researchers in different areas of the lagoon emphasise that the organic matter may play a different role for metals in the sedimentation and mobilization processes as a function of the examined area and its physical form.

[OP 3.9]

Pathways of TBT Accumulation in the Clam *Ruditapes decussatus*

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Marine organisms can accumulate tributyltin (TBT) directly from water, sediments or from food. However, the accumulation pathways of this pollutant depend on the feeding habits of the organisms and on TBT bioavailability. In deposit feeding bivalves, benthic sediments seem to play an important role as a vector of TBT accumulation. However, this do not seem to be the case in the suspension feeders like the clam *Ruditapes decussatus*.
Laboratory experiments were carried out with adult clams *R. decussatus* exposed to TBT in different phases of the marine environment – water (nominal concentration 100 ng /l), food (*Isochrysis galbana* spiked with a nominal concentration of 100 ng/l ^{14}C-TBT) and sediments (nominal concentration 0.8 µg/g dw as Sn and equivalent to TBT concentrations on the order of 100 ng/l in overlying water) – in order to identify their importance as a vector of TBT uptake. TBT and DBT concentrations accumulated by the clams whole soft tissues were determined, after hexane extraction, by Atomic Absorption Spectrophotometry. ^{14}C-TBT accumulated by the clams were determined by scintillation counter and subsequently expressed as tin on a dry weight basis.
Results indicate that the clam *R. decussatus* accumulates TBT from the different compartments of the environment - water, sediments and the diet. However, for this suspension feeding mollusc, the aqueous phase is the most important vector of TBT uptake.