

Interaction of Some Toxic Metals and Humic Acid of Marine Sediment  
Origin in Sea Water

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Summary: Interactions of Zn-65 and Pb-210 - Bi-210 with humic acid of marine sediment origin in sea water were investigated by high voltage paper electrophoresis. Experiments were performed in 100%, 30% and 10% sea water as well as in 0.55 M NaCl solution. The results are of importance for organic speciation of toxic metals in sea water and estuarine waters.

Résumé: L'interaction du Zn-65 et du Pb-210 - Bi-210 avec l'acide humique de l'origine de sédiment marin a été étudiée par l'électrophorèse à haute tension sur papier. Les expériences ont été effectuées dans l'eau de mer de 100%, 30% et de 10% et dans la solution de 0.55 M NaCl. Les résultats ont de l'importance pour la formation des espèces organiques avec les métaux toxiques dans l'eau de mer et dans les eaux estuariennes.

Toxic metals, radionuclides and various organic products are the main pollutants of natural waters. Toxicity and fate of metals in natural waters and their participation in the biogeochemical cycle depend strongly on the physico-chemical forms of metals entering natural waters. Determinations and characterizations of the species of metals actually present in aquatic systems are thus of special importance.

The present speciation study deals with the interaction of some toxic metals and humic acid of marine sediment origin in sea water. The easily detectable radioisotopes of the investigated toxic metals have been utilized.

The interaction of Zn-65 and Pb-210 - Bi-210 with humic acid (isolated from marine sediments) was investigated by high voltage paper electrophoresis in sea water and 0.55 M NaCl solutions. The sea water originated from the Ligurian Sea and was filtrated through 0.45  $\mu$  membrane filter. The experiments were performed in 100% and in 30% and 10% sea water to simulate also estuarine situations. For comparison was also measured in 0.55 M NaCl solutions. The humic acid was isolated from the marine sediments by extraction with 0.2 M NaOH - 0.2 M Na<sub>2</sub>CO<sub>3</sub>, purified by repeated precipitation, dialysis and finally by Chelex-100 to remove the bound metals. The concentration of humic acid in the systems was varied from 3 to 300 mg/l; pH was adjusted to 8.0. The behaviour of investigated radioisotopes of the studied toxic metals was followed by measuring their electropho-

retic mobility as function of the concentration of humic acid in the various systems and on aging of these systems from 0 to 7 days.

Without addition of humic acid to sea water Zn-65 and Pb-210 give two zones, a cationic one and a second one which does not move in the electric field. Bi-210 gives only tailing into the anionic direction. In 0.55 M NaCl the behaviour of the radionuclides is slightly different, both Zn-65 and Pb-210 give only a cationic zone. By addition of humic acid to sea water (100%) the radionuclides partly changed their electrophoretic mobility to anionic values and the zone at the starting point becomes more pronounced than in the absence of humic acid indicating gradually increasing metal chelation with the elevation of the humic acid concentration. The chelating effect of humic acid becomes stronger in diluted sea water and in NaCl solutions according to a different pattern for Zn-65 and Pb-210. Nevertheless, the concentration of humic acid needed to chelate the investigated radionuclides is above the natural concentration level of dissolved humic acid in the open ocean, while in lower salinity estuarine waters humic acid chelates of the studied trace metals might contribute to the distribution of the respective metals over the various dissolved chemical species. In general the results with this humic acid type of marine origin confirm our earlier findings<sup>1)</sup> with terrestrial humic acid yielding negligible chelation of Pb(II) in sea water, although the studied marine humic acid has a higher chelation efficiency.

#### References

- (1) Musani, Lj., Valenta, P., Nürnberg, H.W., Konrad, Z., Branica, M. Interaction of Pb-210 with some natural organic materials in sea water, Proc.Int.Expert Discuss. Lead-Occurrence, Fate and Pollution in the Marine Environment, Rovinj 1977, Pergamon Press, Oxford 1979

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## DISCUSSION

## Questions and comments:

1. Humic matter in sea water is mainly in the form of fulvic acid, more soluble and more active than humic acids.  
(G. CAUWET, France)
  - Nevertheless the concentration of dissolved fulvic acid plus dissolved humic acids in the open sea remains too low to act as significant chelator for Pb, Cd, and Zn.
2. By what means did you obtain cristallized humic acids?  
(G. CAUWET, France)
  - In the final step of purification of humic acid separated from marine sediments it was precipitated with HCl, washed out with distilled water and dried in acidic form at 40°C.
3. Did you measure the ash content? (G. CAUWET, France)
  - No.
4. The purification of humic acids as a problem not concerning the organic material but for the ash content, constituted of silica, alumina and trace metals. (G. CAUWET, France)
5. Commercial humic acid are of very bad quality, they are composed of humic acids, fulvic acids, humin and many impurities; it can not be suitable for such experiments.  
(G. CAUWET, France)
  - Commercially available humic acid was purified before using it in the experiments. Purification was done by repeated precipitation with HCl, in that way impurities and fulvic acid were removed. In order to remove the metals bound to humic acid, the Chelex-100 was used.

