

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 sont 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 <sup>65</sup>Zn and <sup>210</sup>Pb-<sup>210</sup>Bi 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 μ membrane filter. The experiments were performed in 100% and in 30% and 10 % sea water to stimulate 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  $^{65}\text{Zn}$  and  $^{210}\text{Pb}$  give two zones, a cationic one and a second one which does not move in the electric field.  $^{210}\text{Bi}$  gives only tailing into the anionic direction. In 0,55 M NaCl, the behaviour of the radionuclides is slightly different, both  $^{65}\text{Zn}$  and  $^{210}\text{Pb}$  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 some tendency to metal chelation at the more elevated humic acid concentrations. The chelating effect of humic acid becomes stronger in diluted sea water and in NaCl solutions. However, the concentration of humic acid needed to chelate the investigated radionuclides is above the natural concentration level of dissolved acid in the open ocean, while in lower salinity estuarine waters humic acid chelates of the studied trace metals might contribute somewhat 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.  
Interactions 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, London 1979

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Paper presented by L. Musani (Yugoslavia)

### Discussion

#### R. FUKAI: Comment

Your experiments show that as far as the marine environment is concerned humic acid is a moderate chelator. I think the situation is quite different in fresh water systems or in soil, in which humic acid complexation is much stronger.

G. CAUWET: 1. Humic matter in sea water is mainly in the form of fulvic acid, more soluble and more active than humic acid.

2. By what means did you obtain crystallized humic acids?

3. Did you measure the ash content?

4. The purification of humic acids is a problem not concerning material but the ash content, constituted of silica-alumina and trace metals. (Comment)

5. Commercial humic acids are of very bad quality; they are composed of humic acids, fulvic acids, humin and many impurities; they cannot be suitable for such experiments.

L. MUSANI: 1. Nevertheless the concentration of dissolved fulvic acid plus dissolved humic acids in the open sea is still too low to act as a significant chelator for Pb, Cd and Zn.

2. 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. No

5. Commercial 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 by humic acid, the Chelex-100 was used.

B. RASPOR: Comment

It seems that people are rather disappointed with the fact that humic acids are not such a strong chelating agent as it was expected. Due to the exclusive chelation of dissolved humic material with Ce and Mg cations in sea water, there should not be a significant difference in complexing ability between terrestrial and marine sediment humic substances. As the experimental results with NTA showed, a large amount ( $\approx 3 \times 10^{-4} \text{M}$ ) of NTA is necessary to chelate only 20% of total Cd concentration ( $3 \times 10^{-9} \text{M}$ ) and as it is known, NTA is a rather strong chelator having a significantly higher stability constant with trace metals than humic acid.

V. ZUTIC: 1. Have you found significant differences between interactions of metal ions with commercial humic materials you used previously, and marine sediments you are studying now?  
2. You have measured freshly mixed systems: what was the effect of aging?

L. MUSANI: 1. We have found some differences in the behaviour of humic acid from marine sediment origin and the commercial one, but they are not significant. It seems that humic acid of marine sediment origin binds the investigated metals at lower concentrations more than the commercial one. It should be mentioned that experiments with humic acid of marine sediment origin have been performed in more detail. Moreover, systems with diluted sea water were prepared in order to simulate the estuarine conditions.  
2. Effect of aging does not seem to play an important role

in the binding of metals by humic acid, although in the case of commercial humic acid in NaCl solution some de-complexing of Pb-humates occurs in older systems at the concentration of 20 mg humic acid/l. At higher humic acid concentration no effect of aging was found any longer.

