

## INTERACTION OF SOME METAL IONS WITH FULVIC ACID ISOLATED FROM MARINE ENVIRONMENT\*

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### ABSTRACT

Fulvic acid is soluble in alkali, acid, water and also in sea water. Solubilization and/or complexation of Zn, Mn, Co, Fe, Zr, Th and Pu by a fulvic acid extracted from a marine sediment is studied in ammoniacal medium. Most of the elements (except Zn) were found to be associated with the fulvic acid in non-cationic complex forms. The elements were also observed to be associated in different states of combination with fulvic acid.

### INTRODUCTION

MOST of the global organic matter is present in the ocean in dissolved form and in the sediments as humus material (Pillai *et al.*, 1970) which consists of humic acid (acid precipitable and alkali soluble), fulvic acid (soluble both in acid and alkali) and humin (insoluble). It is recognised now that the distribution of trace elements in the marine environment is significantly affected by dissolved and precipitated organic constituents. While dissolved organic constituents can form complexes with certain trace elements and keep them in solution, the precipitated organic materials will carry away the elements with them (Koshy *et al.*, 1969a,b). Geochemical behaviour of trace elements can be fully understood only after the influence of these organic constituents on the physico-chemical state of the elements is ascertained.

Duursma (1965), Hood (1963), Koshy *et al.* (1969c), Desai and Ganguly (1970), and Pillai and Ganguly (1970) have indicated the presence of a wide spectrum of organic constituents in dissolved form in sea water. These include carbohydrates, amino acids, peptides, humic substances, nucleic acids, etc. Sorption of trace elements on marine sediments was significantly affected by the organic matter present in the sediment as described by Ganapathy *et al.* (1968) and Pillai *et al.* (1970). Koshy *et al.* (1969a, 1969c), Desai and Ganguly (1970), and Desai *et al.* (1970) also demonstrated that the humus material, a major fraction of organic matter from marine sediments, sorbed many trace elements, formed complexes with many metallic ions and that the trace elements existed as humus-metal complexes. Authors also observed that 75 to 100  $\mu\text{g}$  of marine humic acid is soluble in one millilitre of sea water. It is thus important to know the interaction of trace elements with humus material-humic and fulvic acids. The interaction of humic acid with trace elements is reported elsewhere (Koshy *et al.*, 1969b; Koshy and Ganguly, 1969c; Desai and Ganguly, 1970; and Desai *et al.*, 1970) and in this paper the interactions of some metal ions with fulvic acid obtained from a marine sediment are described. It is to be borne in mind that fulvic acid assumes importance since it is soluble in acid, alkali, water and also in sea water.

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*Preparation and properties :*

Humus material was extracted from a marine sediment (collected 21 miles off shore at 50 m depth) as described elsewhere (Koshy and Ganguly 1969c ; Desai and Ganguly 1970). Humic and fulvic acids were separated and purified by dialysis and prolonged electro dialysis as detailed in our previous publications (Koshy and Ganguly 1969c ; Desai and Ganguly 1970).

Preliminary experiments on fulvic acid showed that fulvic acid is negatively charged and that it remains in solution in sea water. Trace amounts of metal hydroxides such as of Zn, Mn, Mg, Cu, Co, rare earths, Fe and Al are solubilized by fulvic acid. In the qualitative experiments with about 2 mg each of Cu, Co, Mn, Zn, Mg, Ca, Ba, Sr,  $Hg^{2+}$ , Al,  $Fe^{3+}$ , rare earths, Y, In, Cr, Sb, As, Th and  $U^{6+}$  ( $UO_2^{2+}$ ), in the pH range of 4 to 6 (2.5 or less for Fe, Th, Zr, U, etc.) a precipitate appeared with about 0.88 mg of fulvic acid with most of these metal ions whereas these metal ions did not precipitate in distilled water under similar pH conditions. This suggested the possible association of metal ions with fulvic acid in a manner different from normal aqueous solutions.

## EXPERIMENTAL

Two ml of ammonia (6N) was added to one ml of fulvic acid (0.11 mg). A known volume of the radioisotope solution (of known carrier content except Zr) was added to this solution as well as to a blank containing 2 ml ammonia (6N) and one ml double distilled water (DDW). An equal volume of the radioisotope solution was counted. The solutions were made up to a known volume (5 ml or 10 ml). These were mixed well and kept for a week with intermittent shaking. The blank and the sample were filtered. One ml filtrate of each was counted. Another one ml aliquot of each was separately passed through Dowex-50W  $\times$  8 cation column conditioned to  $NH_4^+$  form with about 2.5 N ammonia solution and the column washed with two column volumes of ammonia. The interstitial volume, effluent and the ammonia washings were collected and counted under the standard geometry.

$^{65}Zn$ ,  $^{54}Mn$ ,  $^{60}Co$ ,  $^{59}Fe$  and  $^{95}Zr$ — $^{95}Nb$  were counted for gross gamma activity on a single channel analyser with a NaI(Tl) crystal.  $^{234}Th$  was counted for beta and  $^{239,240}Pu$  for alpha. Results are given in Table 1.

## RESULTS AND DISCUSSION

Table 1 shows the amounts of the elements (mg) solubilized per g of fulvic acid. Comparative values are also included in the table for humic acid obtained from a coastal marine sediment. Fulvic acid solubilized all the elements significantly and from the table it is clear that the solubilizing capacity of fulvic acid is at least 2 to 3 times higher than that of the marine humic acid. The exchange capacity values obtained by potentiometric titration were 147 meq/100 gms of the fulvic acid and 383 meq/100 gms of the humic acid. The exchange capacity value of the fulvic acid is thus less than half while solubilizing capacity is more than twice (weight to weight). This indicates the relative importance of fulvic acid (which is more mobile and soluble) in relation to the influence on the state of trace elements. It is also interesting to note that in case of Zn and Mn, the amounts of these elements solubilized by fulvic acid and retained on the cation column were almost equivalent to the exchange capacity of the fulvic acid. Table 2 gives the ionic nature of the solu-

bilized elements in fulvic acid. Values for humic acid are given for comparison. Zn forms an exchangeable complex while all the other elements such as Mn, Co, Fe, Zr, Th, U and Pu form significant quantities of non-cationic complexes. Particularly trivalent and heavy elements form mostly non-cationic complexes. These were also comparable with the complexes formed with humic acid also.

TABLE 1. Solubilization of certain Metal Ions by marine Humic and Fulvic Acids

Element	Solubilization (mg/g)	
	Humic acid	Fulvic acid
Zn	5.97	41.51
Mn	—	85.7
Co	33.8*	22.8*
Fe	15.4	34.22
Th	2.85	8.72
U	6.0	—
Pu	$0.042 \times 10^{-3}$	$0.14 \times 10^{-3}$

\* Non-cationic fraction only.

Humic acid used : 0.95 mg, Fulvic acid used : 0.11 mg.

Trace element used : HA : Zn, 21.92  $\mu\text{g}$  ; Co, 50  $\mu\text{g}$  ; Fe, 53.3  $\mu\text{g}$  ; Th, 3  $\mu\text{g}$  ; U, 9.8  $\mu\text{g}$ .

FA : Zn, 14.62  $\mu\text{g}$  ; Mn, 10  $\mu\text{g}$  ; Co, 10.0  $\mu\text{g}$  ; Fe, 21.3  $\mu\text{g}$  ; Th, 1.83  $\mu\text{g}$ .

TABLE 2. Nature of Metallic Complexes of Humic and Fulvic Acids

Element	% Non-cationic in solubilized fraction	
	Humic acid	Fulvic acid
Zn	12.4	0
Mn	100*	66
Co	64	35
Fe	100	90
Zr-Nb	95	94
Th	100	100
U	70	—
Pu	100	100

\* Sorbed on humic acid in sea water.

Humic and fulvic acids were found to contain sugars, phosphate and amino acids and it may well be assumed that these ligands may, to some extent at least, be responsible for such complexation processes. It is also important to note that in case of Mn, Fe and Zr-Nb, at least a small fraction (about 5-10%) is still cationic. This indicates that there are different reactive sites at which the metal ions are bound as cationic and non-cationic. A support to this view was provided by the authors (Desai, *et al.*, 1970) wherein the studies of the interaction of humic and fulvic acids with alkaline earth and rare earth radioactive pairs showed that alkaline earth elements were bound at an exchangeable cationic site while the rare earth elements were bound as non-cationic species. Such complexation processes may very well

affect the physico-chemical states of a wide spectrum of elements thus affecting their distribution in the marine environment.

## REFERENCES

- DESAI, M. V. M. and GANGULY, A. K. 1970. BARC—488.
- , MATHEW, E. and GANGULY, A. K. 1970. *Curr. Sci.*, **39** : 429.
- DUURSMA, E. K. 1965. *In* : J. P. Riley and H. Skirrow [Eds.] *Chemical Oceanography*. Academic Press, 1965, **1** : 433.
- GANAPATHY, S., PILLAI, K. C. and GANGULY, A. K. 1968. BARC—376.
- HOOD, D. W. 1963. *In* : H. Birnes [ed.] *Oceanography and Marine Biology*. George Allen & Unwin Ltd., **1** : 129.
- KOSHY, E., DESAI, M. V. M. and GANGULY, A. K. 1969a. *Curr. Sci.*, **38** : 555.
- , —————, —————, 1969b. *Ibid.*, **38** : 582.
- , and GANGULY, A. K. 1969. BARC—402.
- PILLAI, T. N. V. and GANGULY, A. K. 1970. *Curr. Sci.*, **39** : 501.
- , DESAI, M. V. M., MATHEW, E., GANAPATHY, S. and GANGULY, A. K. 1970. Presented at IAEA Symposium on Distribution of Chemical Species in Marine Environment at Tokyo, Japan.