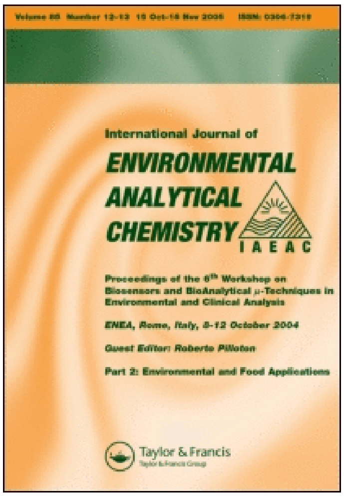

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Interaction of Certain Heavy Metals with Lake Humic Acids

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Present studies were carried out to investigate the interaction properties of humic acids with certain heavy metals—Ca, Zn, Fe and Mn by using their isotopes. Humic acids solubilized maximum portion of the calcium present (97% in case of Dal lake), of which more than 90% was present in uncomplexed form. With ^{59}Fe results were different, solubilizing less than 30% of it and most of this solubilized portion was in complex form. Results are present in detail.

KEY WORDS: Humic acid, interaction, metals, lakes, complexes.

INTRODUCTION

Humic compounds form the major part of the organic matter present in soils and sediments. They are generally high molecular weight compounds of a complex nature. Humic material can be considered largely as condensation products of phenols, quinones and amino compounds and a variety of primary monomeric organic compounds present in the environment. The products are looked upon as "random polymers",[1] wherein the monomeric composition and sequence are determined by the physico-chemical environment in which these are formed. The humic acids are negatively charged polyelectrolytes and complex with positively charged metal ions. These complexes are water soluble or water insoluble and play a significant role in migration and/or the accumulation of metal cations. The interaction of humic acids with the heavy metals has been studied by many workers.[2–7] Present investigations were carried out to study the complexation properties of lake humic acids with certain metal ions (Ca, Zn, Fe and Mn) by using their respective isotopes and is a continuation of the previous works of Desai and Ganguly[8] and Desai[1] on marine humic acids.

EXPERIMENTAL

Sampling study

Sediment samples were collected from four Kashmir Himalayan lakes, viz., Trigam, Dal, Wular and Anchar, lying within the geographical co-ordinates of 32° and 34°N lat. and 74° and 74°9′ E long. The water bodies lie in the flood plains of River Jhelum at an average altitude of 1580 m. The lakes are of post glacial origin and have probably originated as a result of meandering of the alluvial deposits. Other morphometric characteristics are given in Table I.

Materials and methods

Sediment samples were collected during the summer months (May–July) of 1982 and were wet sieved through a 200 μm mesh. They were room air dried and the humic material was isolated with a mixture of 0.2 M NaOH + 0.2 M Na_2CO_3 and then subjected to dialysis for two weeks as described elsewhere.[1] Humic acids were then precipitated from it by HCl at pH 2 and the final solution was made basic by addition of ammonia.

Carbon, hydrogen and nitrogen were analysed by dry combustion method. Potentiometric studies were carried out on humic acid

TABLE I

Selected morphometric features of the lakes.

Features	Trigam	Dal	Wular	Anchar
Trophic level	Eutrophic	Mesotrophic	Mesotrophic	Eutrophic
Basin type	N.D	D	D	D
Surface area (Km^2)	1.4	11.45	24	1.4
Maximum length (Km)	0.7	10.8	16	3.8
Maximum depth (m)	2.3	5	5.8	3.0
Length of shoreline (Km)	2.2	15.5	58	11.5

N.D. = Non-drainage type
D = Drainage type

solutions (1 gm dissolved in 500 ml of 0.02 M KOH maintained at an ionic strength of 0.2 by adding 1 M KNO_3. pH measurements were carried out on a digital pH meter (model No 5651 ECL, India) at a constant temperature. UV-visible Spectrophotometric studies were carried out on a Pye Unicam Spectrophotometer according to Kumada.[9] Infra-red spectra were recorded on KBr pellets (5 mg of HA) on a Beckman IR 4250 Spectrophotometer. Interaction of humic acids were studied with the isotopes of calcium, iron, zinc and manganese.

Following additions were done:

i) Blank: 1 ml distilled water + 2 ml of X solution (400 μg X) + 4 ml of 2.5 M NH_3.

ii) Humic acid: 2 ml of humic acid in 2.5 M NH_3 + 3 ml of 2.5 M NH_3 + 2 ml of X solution (400 μg X).

X = Ca, Fe, Zn and Mn with known amount of radioactivity.

RESULTS

Elemental analysis

The carbon contents of the investigated samples were between 46.5%–58.6% which was lower than the values reported for marine samples.[1] Anchar lake showed higher carbon content and also C:H

TABLE II

Characteristics of humic acids.

Lake	Carbon %	Hydrogen %	Nitrogen %	C:H	Δ Log K
Dal	49.80	4.89	4.80	10.18	0.338
Wular	46.50	4.50	3.80	10.33	0.321
Trigam	50.80	2.80	5.57	18.14	0.305
Anchar	58.60	4.50	4.30	13.02	0.312

ratio was much higher in Trigam lake samples (Table II). Nitrogen content was between 3.8% to 5.57%.

Potentiometric studies

The titration curves of humic acids exhibited somewhat similar sigmoidal curves. The base exchange capacities of humic acids as calculated from the titration curves ranged from 40 to 120 meq/100 g of humic acids. Wular lake showed very low values. The values obtained are much lower as compared to marine humic acid samples.[1]

Spectrophotometric absorption

UV-visible Spectrophotometric curves were almost monotonous, the absorption increased with decreasing wave length. The $\Delta \log K$ values (the difference of logarithmic extinction at 400 nm and 600 nm: $\Delta \log K = \log K_{400} - \log K_{600}$; it indicates the degree of humification), showed that humic acids had almost similar degrees of humification (Table II). Deeper regions of these lakes had lower degrees of humification than the present ones (deep sites of Wular lake $\Delta \log K = 0.523$). The results are in good agreement with Flaig *et al.*[10] Our results also showed a close resemblance to the values obtained by Takamatsu and Yoshida,[11] for soil humic acids. The infra-red spectra of humic acids showed some common features. Among them are the peaks at 3362 cm^{-1} (inter-molecular hydrogen —OH) 2850 cm^{-1} (methylene groups) 1736 cm^{-1} (carbonyl stretching vibrations of carboxylic acids, cyclic and acyclic aldehydes), 1472 cm^{-1} (aliphatic C—H deformations) etc.

Interaction properties

On interacting the isolated humic acids with ^{45}Ca it was seen that the Trigam lake solubilized highest amount of calcium (97.14%). Humic acids from Dal and Wular lakes solubilized 86.67% and 78.57% respectively (Table IIIa) while the ammonia blank had only 4.37% of the metal in dispersion. This points to the fact that humic acids have good affinity for binding the calcium. Upon passing the aliquots of the filtrates through a cation exchange column it was seen that in the ammonia blank 100% of the metal was uncomplexed or cationic. In case of Dal lake humic acid about 11.9% of the calcium was complexed and the rest was uncomplexed or cationic (Table IIIa). In Trigam humic acid 92.8% and in Wular humic acid 95.3% of calcium remained uncomplexed. It is interesting to note

TABLE III(a)

Interaction of calcium with humic acids

Sample	Total volume	Activity of ^{45}Ca in Cpm Added	Activity of ^{45}Ca in Cpm Filtrate	Percent solubilized
Blank	7 ml	98356	4270	4.37
Trigam	7 ml	98356	95547	97.14
Dal	7 ml	98356	85246	86.67
Wular	7 ml	98356	77279	78.57

TABLE III(b)

Ion exchange behaviour of filtrate on Dowex-50 in NH_4 form.

Sample	Activity of ^{45}Ca in Cpm Influent	Activity of ^{45}Ca in Cpm Effluent	Percent complexed	Percent uncomplexed
Blank	1708	N.D.	N.D.	100
Trigam	38218	27218	7.12	92.88
Dal	34098	40554	11.89	88.11
Wular	30911	1460	4.72	95.28

N.D. = Non-detectable

that the interaction with ^{59}Fe showed quite different results. The ammonia blank solubilized about 10.6% of the total ions while humic acids of Trigam, Dal and Wular solubilized 21.2%, 28.1% and 23.2% of the total ion respectively. This is quite low if we compare with calcium interaction properties. On the Dowex-50 cation exchanger the trend was reverse compared to calcium. The blank showed about 2.7% in the complex form where as Trigam, Dal and Wular showed about 95.3%, 87.8% and 87.2% in the complex form (Table IV). These results are in good agreement with the marine humic acid samples[5] where it was seen that the entire iron is held up with humic acid in non-ionic form. Alexandrova[12] suggested that the iron is included in the anion part of the humic acid.

TABLE IV(a)
Interaction of iron with humic acids.

Sample	Total volume	Activity of ^{59}Fe in Cpm Added	Activity of ^{59}Fe in Cpm Filtrate	Percent solubilized
Blank	7 ml	37180	3952	10.62
Trigam	7 ml	37180	7910	21.28
Dal	7 ml	37180	10458	28.13
Wular	7 ml	37180	8694	23.18

TABLE IV(b)
Ion exchange behaviour of filtrate on Dowex-50 in NH_4^+ form.

Sample	Activity of ^{59}Fe in Cpm Influent	Activity of ^{59}Fe in Cpm Effluent	Percent complexed	Percent uncomplexed
Blank	2272	54	2.4	97.60
Trigam	2260	2153	95.28	4.72
Dal	2988	2620	87.70	12.30
Wular	2484	2165	87.16	12.84

Upon interacting zinc with humic acids it was observed that while ammonia blank solubilized 33.7% of the zinc, Trigam, Dal and Wular humic acids solubilized about 75.7%, 86% and 85% of the total added zinc. Thus zinc also showed great affinity for humic acids. Upon passing a portion of the solubilized fraction through a strong cation exchanger Dowex-50, most of the zinc was retained on the exchange column indicating that appreciable quantities of zinc humate was present in cationic form. The Trigam, Dal and Wular humic acids showed 3.1%, 9.7% and 1% of the zinc in complex form. (Table V.)

TABLE V(a)
Interaction of zinc with humic acid.

Sample	Total volume	Activity of ^{65}Zn in Cpm Added	Filtrate	Percent solubilized
Blank	7 ml	10662	3597	33.72
Trigam	7 ml	10662	8182	76.73
Dal	7 ml	10622	9218	86.45
Wular	7 ml	10662	9049	84.87

TABLE V(b)
Ion exchange behaviour of filtrate on Dowex-50 in NH_4^+ form.

Sample	Activity of ^{65}Zn in Cpm Influent	Effluent	Percent complexed	Percent uncomplexed
Blank	9597	N.D.	N.D.	100
Trigam	8182	225	3.11	96.89
Dal	92.18	899	9.7	90.3
Wular	90.49	94	1.03	98.07

N.D. = Non-detectable.

TABLE VI

Interaction of manganese with humic acid (Anchar Lake).

Humic acid used = 13.45 mg		
Sample	Blank	Humic acid
Added Mn (Ug)	400	400
Solubilized	0.55	11.48
Cationic effluent	11.00	7.63
Non-Cationic (%)	0.0	66.5

In natural lake water systems manganese is mostly present as $MnCO_3$ or $Mn(OH_2)$[13] but its retention and deposition in the sediments could be due to both the processes viz., partly being fixed by organic matter and partly deposited as coagulate. The possible role of humic acid in its binding was studied by using isolated humic acid from Anchar lake. Manganese practically precipitated out in ammonia (Table VI). Out of 400 μg, only 55 μg were in solution in ammonia and rest of it was in the cationic form. Humic acid dissolved out 11.48 μg out of which 7.63 μg were added as non-cationic complex forms.

DISCUSSION

It is interesting to note that Ca^{2+} and Zn^{2+} are complexed by humic acid in non-cationic forms at about 5–10% and 1–10% respectively. Although percent solubilized Ca and Zn are high, the complexed fractions are low. In case of Fe^{3+} and Mn^{3+}, the percent solubilized is low whereas complexation was high (66–90%). This is not a new observation, but it should be of interest to note that lake humic acids also behave chemically similarly as do the marine humic acids.[8]

Quinones and quinone containing compounds are believed to complex with various transition metals to form stable chelates[6] Fe^{3+} and Mn^{3+} having $3d^5$ and $3d^4$ configurations respectively have strong co-ordinating capacity as compared to Ca and Zn (d^{10}). Thus a higher proportion of iron and manganese remain complexed. Calcium and zinc are solubilized more because of the ionic nature of their linkages with humic material. Solubilization reactions are in agreement with Rashid[6] who observed a two fold increase in solubilization by zinc over manganese. Our results suggested that about 66% of the solubilized manganese was held up in non-cationic complex form. Desai and Ganguly[14] observed that almost 100% of the solubilized manganese was present in the non-cationic forms in case of marine humic acid samples.

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