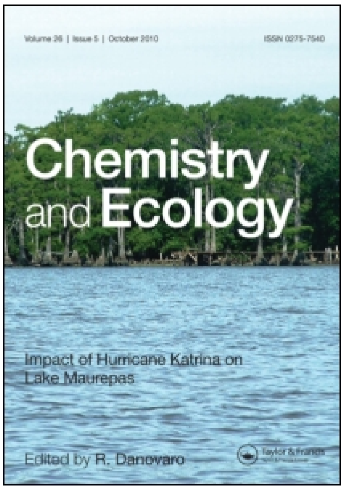

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Metal-Humic and Fulvic Acid Interactions in Fresh Water Ultrafiltrate Fractions

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Fresh water samples from Po river (Northern Italy) were filtered and characterized by measuring the most important physico-chemical parameters. The samples were subsequently submitted to ultrafiltration to separate and fractionate the colloidal particle range from $> 10^4$ to $< 10^3$ M.W. Two different types of ultrafiltration cells were tested; they yielded quite different results due to systematic errors introduced when using the cell operating under pressure.

It was found that the largest share of any metal considered was associated with the finest ($< 10^3$ M.W.) particle fraction.

Correlation analysis applied to analytical data showed that manganese is associated to organic matter in the 10^3–10^4 M.W. particle fraction. Positive correlations existing between copper and Apparent Complexing Capacity (ACC) and between cadmium content and Total Organic Carbon (TOC) in the $< 10^3$ M.W. particle fraction were also discussed.

INTRODUCTION

It is generally assumed that the organic matter in natural waters ranges in concentration from 0.1 to 10 mg l^{-1} (Stumm and Morgan, 1970); on the average about 60–80% of this matter consists of humic substances, namely humic acids (5000–10000 M.W.) and fulvic acids (300–2000 M.W.), which are derived from natural sources although a contribution may derive from sewage discharges. Despite their low concentrations, humic and fulvic acids perform many important functions in natural waters, these include metal transport, metal concentration and scavenging, leaching and dissolution of minerals and sediment formation. Humic and fulvic acids are resistant to chemical and biological destruction, maintaining their integrity and concentration which fact increases their importance in the interaction with metals. A review covering many aspects of the hydrogeochemistry of naturally occurring organic acids is presented by Jackson *et al.* (1978) and more specific aspects are treated by other authors (Gjessing, 1967; Schnitzer and Skinner, 1967; Guy and Chakrabarti, 1976; Steelink, 1977). Gjessing (1967) first posed questions not yet completely answered, regarding, for instance, the importance of humic substances in the metabolism of aquatic organisms. An attempt to study the ecological implications of humic material was first presented by Allen (1976) who also underlined the importance of the particle size effect.

The analytical separation of humic compounds from natural waters was carried out by adsorption on inorganic materials (Moed, 1971) or on macro-reticular resins (Mantoura and Riley, 1975); on the other hand when the research deals with the interactions of trace metals with natural organic compounds, separation techniques based on adsorption processes are not suitable because they change the original adsorption and complexation equilibria. The use of ultrafiltration techniques are to be preferred as pH changes or chemical processing are not required: these techniques already applied by Schindler and Alberts (1972), were also adopted in the present work.

It must be pointed out that the variables which may determine the metal distribution in ultrafiltrate fractions are not restricted to humic particles size and their complexing capacity but include complex phenomena where other components of natural waters play a significant role: in fact, humic and fulvic acids can form stable water-soluble and water-insoluble complexes with hydrous oxides, interact with clay minerals and combine with hydrophobic organic compounds such as alkanes and fatty acids.

The ultrafiltrate fractions are therefore difficult to characterize fully and in order to shed more light on the metal distribution it is worthwhile to apply a statistical treatment to analytical data, such as the correlation analysis between metal concentrations and chemical parameters or inter-metal correlations. In this work three metals, namely copper, manganese and cadmium have been investigated as far as their interaction with humic and fulvic acids is concerned.

These metals were selected because they occur as a natural component of colloidal fractions (Mn) or as highly toxic pollutants (Cd) or as common pollutant particularly toxic to aquatic life (Cu).

Preliminary experiments showed that iron, ranging from 40 to 170 μg/l, concentrates to a very large extent in the nominal molecular weight fraction $> 10^4$ and presents a distribution trend in the ultrafiltrate fractions which is markedly different from Total Organic Carbon (TOC). These findings are consistent with the results of Moore *et al.* (1979) which obtained 90% or more of "dissolved" Fe in the nominal molecular weight fraction $> 10^5$ together with a small fraction of the organic material. The study of this metal, which may influence the distribution of others, is therefore worthy of consideration, but requires that colloid fractioning be made according to a cutoff scheme different from the one adopted here, which, on the other hand, appears rather suited to describe behaviour of manganese.

EXPERIMENTAL

Reagent and Apparatus

All chemicals were of reagent grade. Water used in these experiments

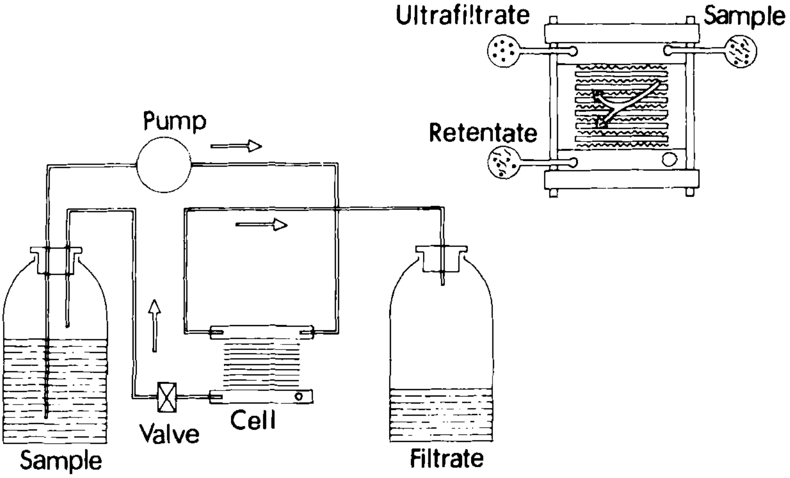

FIGURE 1 Schematic diagram of the High Flux Ultrafiltration Cell and connected equipment.

was obtained from a Milli Q-2 deionizer system (Millipore Co.) equipped also with an activated carbon cartridge adsorbing trace organics and giving a blank less than 0.1 mg C dm^{-3}. The deionizer was fed with double distilled water.

The equipment used included 2 types of ultrafiltration cells: the first was a Millipore 90 mm High-Flux ultrafiltration Cell with a vibrating stirrer working under a 70 psi N_2 gas pressure, the second a Millipore High Volume Cassette System Cell through which the water was kept circulating with a peristaltic pump. Both cells were loaded with membrane filters retaining molecules of Nominal Molecular Weight Limit (NMWL) 1000 (PSAC) and 10.000 (PTGG). Schematic diagram and features of the Cassette System Cell are presented in Figure 1.

Trace metals were determined by Atomic Absorption Spectrometry (Jarrel Ash Model 82–365). A C. Erba gas chromatographic equipment was used for Total Organic Carbon (TOC) measurements.

Apparent Complexing Capacity (ACC) was determined, towards Cu^{++} and Cd^{++}, by measuring free divalent cations with ORION solid-state specification electrodes Models 94–29 A (Cu^{++}) and 94–48 (Cd^{++}) connected to an ORION Model 801 pH/mV meter in combination with a single junction reference electrode Model 90–01.

Procedures

The procedure adopted for TOC measurement was based on oxidation with potassium persulphate in the presence of perchloric acid according to Menzel and Vaccaro (1964).

The ACC determination was based on the addition, at pH 5.5 and $I = 0.05$ (KNO_3), of known amounts of Cu^{++} or Cd^{++} 10^{-3} or 10^{-4} M and on the potentiometric measurement of the uncomplexed metal (Ramamoorthy and Kushner, 1975; Buffle *et al.*, 1977; Stella and Ganzerli, 1980).

Free copper or cadmium ion concentrations down to 10^{-8}–10^{-9} M may still be measured with the electrodes due to the metal ion buffer effect played by the organic ligands and provided that electrode calibration is regularly checked with metal buffered standard solutions and the electrode response is recorded at least five minutes after each addition of 0.1 cm^3 of titrating metal solution. Care must be taken in standardizing the whole procedure to allow comparison between samples: ACC data are therefore useful as relative parameters. This technique was preferred to the anodic stripping voltammetry first proposed by Chau (1973): ASV diagnostic parameters are in fact strongly affected by sorption of organic substances, occurring in natural waters, onto hanging mercury drop electrodes (Brezonik *et al.*, 1976).

Sampling

Thirteen water samples from Po river (Northern Italy) were collected over a period of two years, under uncontrolled flow rate and seasonal conditions, in several sampling stations approximately located at mid-course of the river. Plastic containers were repeatedly washed with 1M HNO_3, terdistilled organic-free water and river water before collecting the samples.

After sampling alkalinity, hardness and pH measurements were performed. Aliquots of about 30 l were immediately submitted near the sampling station to a multistep filtration using Millipore membrane packets of decreasing porosity, 8 to 0.45 μm, to reduce the clogging that would affect a single step filtration: ACC and TOC were measured on the obtained filtrate.

Ultrafiltration followed with minimal delay and three fractions were obtained: the first (A) containing colloidal particles of Nominal Molecular Weight Limit (NMWL) $>10^4$, the second (B) of NMWL 10^4–10^3 and the final filtrate (C) which is assumed to bear particles of the maximum NMWL $= 10^3$. All filtering membranes were washed, before using, with large volumes of terdistilled organic-free water to avoid any contamination. Ultrafiltrate fractions were stored partly in plastic bottles for metal analysis and partly in glass bottles for TOC and ACC measurements. The C fraction, before analyzing for trace metals was concentrated 10 to 20-fold by evaporation under an infrared lamp in a laminar flux hood in order to achieve the same concentration gain factor obtained, as a result of ultrafiltration, on first two fractions.

RESULTS AND DISCUSSION

Ultrafiltration fractioning was accomplished by applying the two different techniques described in the previous section.

The ultrafiltration system working under pressure presents serious shortcomings and gives poorly reproducible results because the filtered

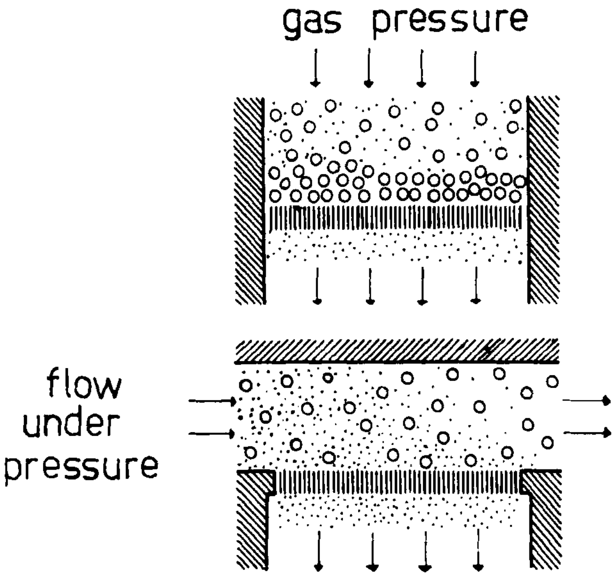

FIGURE 2 Basic principles of under pressure and tangential ultrafiltration techniques.

matter is packed over the filter in a compact layer which clog the pores and changes the working features of the filter itself. Moreover nitrogen gas must be carefully cleaned of the trace elements, mostly copper, released from the tank pressure valve, before entering the cell. The Cassette System Cell is to be preferred because the sample-retentate fluid flows horizontally over the membrane packets through woven mesh spacers. The liquid snakes its way over and under the mesh fibers in a sinuous flow pattern thus avoiding the above-mentioned effects; also the water flowing in a sealed circuit is shielded from all external contaminants. It was therefore adopted as the most reliable technique. The principles of the two ultrafiltration systems, are schematically illustrated in Figure 2.

Two important parameters connected with the organic nature of the colloidal material are TOC and ACC. Through ACC one obtains an empirical measurement of the concentration of all chelating and complexing sites, which, regardless of their nature, are available for metals in the humic material molecules: this concentration is not actually physical but reflects the behaviour of the reference metal towards the chelating agents in the river water. It is potentiometrically measured

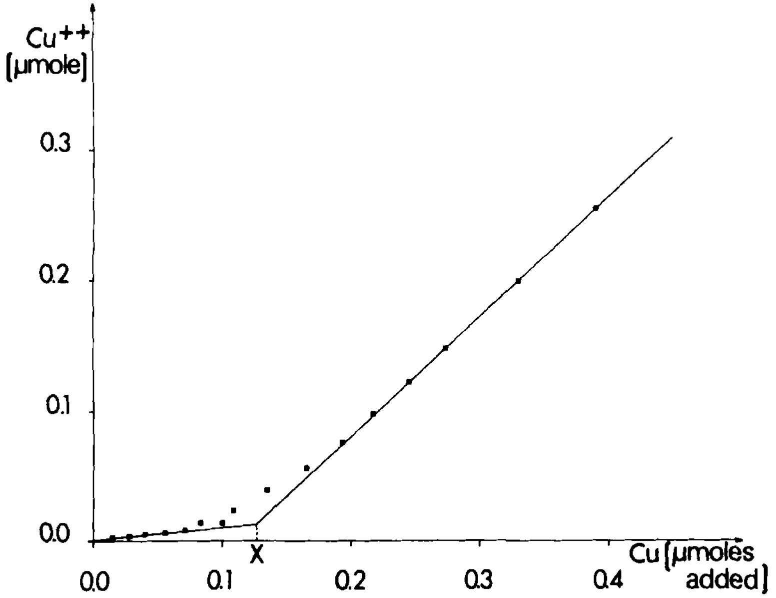

FIGURE 3 Potentiometric measurement of ACC (Cupric Ion-Selective Electrode).

using copper as reference metal and graphically evaluated as shown in Figure 3.

For four samples the measurements were repeated using cadmium as reference metal and applying the same potentiometric procedure (Table I). Contradictory results have been reported on the binding strength of Cu^{++} and Cd^{++} with organic matter in river water: Ramamoorthy and Kushner (1975) found that ACC, measured through different metal ions, decreases in the order Hg^{++}, Pb^{++}, Cu^{++}

TABLE I
Apparent Complexing Capacity (ACC) (μmole . dm^{-3}) evaluated through Cu^{++} (ACC_{Cu}) and Cd^{++} (ACC_{Cd}) addition

	SAMPLE			
	5	9	11	13
ACC_{Cu}	0.74	1.02	1.13	0.81
ACC_{Cd}	0.82	1.14	1.55	0.90

TABLE II

Total and fractionated trace metal content ($\mu g.dm^{-3}$) and chemical parameters (ACC = $\mu mole.dm^{-3}$; TOC = $mg C.dm^{-3}$) in 13 Po river samples T = total sample (0.45 μm filtrate); A = $> 10^4$ M.W.; B = 10^3–10^4 M.W.; C = $< 10^3$ M.W. particle fraction

						SAMPLE							
	1	2	3	4	5	6	7	8	9	10	11	12	13
Cu_T	4.3	5.1	4.2	14.8	4.8	10.1	3.8	8.2	22.8	7.9	17.0	22.1	21.0
A	2.3	0.8	2.7	2.2	0.4	1.1	0.5	0.8	0.3	0.4	0.1	0.6	0.5
B	1.3	1.8	0.8	2.0	0.4	1.9	0.6	0.7	2.2	0.2	0.1	0.8	0.6
C	0.7	2.5	0.7	10.0	4.0	7.5	2.7	5.9	19.8	7.0	17.3	18.5	20.7
Cd_T	0.13	0.17	0.44	—	0.54	0.43	1.10	0.50	0.87	0.33	0.76	0.20	0.20
A	0.05	0.02	0.09	—	0.05	0.05	0.03	0.19	0.02	0.02	0.09	0.05	0.05
B	0.05	0.02	0.06	—	0.05	0.07	0.12	0.05	0.48	0.02	0.17	0.05	0.05
C	0.03	0.13	0.29	—	0.44	0.31	0.85	0.26	0.32	0.29	0.54	0.10	0.10
Mn_T	5.0	4.5	9.4	6.2	9.2	4.6	4.2	6.2	10.1	18.5	11.3	13.8	11.0
A	0.6	0.3	1.6	0.9	0.1	0.4	0.1	1.5	0.1	0.3	0.1	0.3	0.1
B	0.5	0.3	0.3	0.1	0.1	0.2	0.5	0.4	0.1	0.1	0.1	0.2	0.1
C	4.1	3.9	7.3	4.7	8.1	4.0	3.4	3.6	9.1	17.4	11.8	13.3	11.5
ACC_T	0.50	0.58	0.34	1.21	0.74	0.70	0.20	0.33	1.02	0.58	1.13	0.81	0.81
A					0.09	0.01	0.01	0.04	0.07	0.01	0.01	0.02	0.02
B					0.10	0.10	0.01	0.01	0.08	0.02	0.10	0.02	0.01
C					0.55	0.59	0.18	0.28	0.87	0.55	1.01	0.77	0.78
TOC_T					2.5	2.0	12.7	2.3	2.3	2.5	2.8	1.9	2.1
A					0.2	0.1	0.4	0.1	0.1	0.3	0.3	0.1	0.2
B					0.3	0.4	2.8	0.4	0.6	0.3	0.1	0.1	0.1
C					2.0	1.5	9.5	1.8	1.6	1.9	2.4	1.7	1.8

and Cd^{++} and they attributed complexing capacity to soluble organic matter, perhaps fulvic acids. Similar measurements reported by Giesy and Briese (1978) showed random unpredictable results relative to copper and cadmium.

The ACC data on filtered water samples in our experience are constantly higher for Cd^{++} than for Cu^{++} (Table I). It may be supposed that adsorption phenomena, perhaps of cadmium hydroxide or of cadmium basic salts, onto the surface of colloidal particles, are superimposed upon chelating reactions and this effect may account for the increased ACC_{Cd} values. All analytical data for thirteen Po river samples are reported in Table II as total and fractional figures. General analytical parameters, such as pH, hardness and alkalinity, were typical of the true solution component of fresh water but failed to give any correlation with metal fractionation: therefore, they are not reported. Significant correlations are presented by ACC and TOC and metal concentrations.

Figures referring to total (T) filtered samples, thus $Cu_T < 5.0$, $Cd_T < 0.5$ and $Mn_T < 2.0\ \mu g\ dm^{-3}$, were obtained as sums of A, B and C concentrations, the latter being always over detection limits due to the already mentioned concentration factor.

Pearson correlation coefficients, calculated through the SPSS computer programme, were compared with the corresponding theoretical values ($P = 0.05$). The results are reported in Table III where only significant correlations are given.

The following observations may be drawn from the set of correlations obtained:

a) for any given metal, the total content in water before ultrafiltration correlates strongly with the dominant C fraction.

b) Manganese associated with the 10^4–10^3 M.W. particle fraction (B) (mixed fulvic and humic acids) correlates positively with the corresponding fractional TOC_B, but not with ACC_B.

It may be supposed that manganese is not chelated to humic material but is associated with it as amorphous hydrous oxide, which depending on pH and oxidizing conditions, may be both of manganese (II) and manganese (IV) (Jenne, 1968).

The associations of iron hydrous oxides with colloidal organics have so far received more attention than those of manganese and were investigated by Shapiro (1964) and Jenne (1968): the latter author found that the two components provide mutually protected coatings.

TABLE III

Significant pairwise correlation coefficients (P = 0.05) between total and fractionated trace metal concentrations and physicochemical parameters in Po river samples

	Cu_T	Cu_A	Cu_B	Cu_C	Cd_T	Cd_A	Cd_B	Cd_C	Mn_T	Mn_A	Mn_B	Mn_C	ACC_T	ACC_C	TOC_T	TOC_A	TOC_B	TOC_C
Cu_T				0.99							−0.62		0.74					
Cu_A										0.64								
Cu_B																		
Cu_C											−0.62			0.85				
Cd_T							0.61	0.90										
Cd_A										0.72								
Cd_B																		
Cd_C															0.83			0.83
Mn_T												0.99						
Mn_A																		
Mn_B												−0.57	−0.62				0.79	
Mn_C																		
ACC_T																		
ACC_C																		
TOC_T																		
TOC_A																		
TOC_B																		
TOC_C																		

More recently Moore *et al.* (1979), deduced from their quantitative measurements, that the adsorption of iron hydrous oxides onto organic material was an improbable explanation for the observed differences in the fractionation of the metal and of DOC (Dissolved Organic Carbon) and suggested that organic material plays the role of colloid protector.

The correlation observed in this work between Mn_B and TOC_B leads to the view that manganese oxides, unlike those of iron, are adsorbed onto the organic matter: a hypothesis which fits the observed proportionality.

c) Rather surprising is the positive correlation of ACC_C with Cu_C, but not with Cd_C concentration, in the *C* fraction ($M.W. < 10^3$), in which fulvic acids are predominantly present; in the same fraction however Cd_C, but not Cu_C, is positively correlated with TOC_C. The fact that ACC is measured through copper addition is not, by itself, sufficiently explanatory.

Copper binding capacity, defined and measured by Giesy and Briese (1978) in analogous studies, though obtained through a different experimental procedure, corresponds in principle to the ACC concept and similarly well correlates with copper, but not with cadmium, at the same probability level ($P = 0.05$). A number of papers (Sunda and Hanson, 1979; Ellis and Knezek, 1972; Schnitzer and Skinner, 1976) report that organics account for essentially all of the Cu binding capacity and that Cu forms more stable complexes with naturally occurring organics than most of other metals do: furthermore, as already shown by Reuter and Perdue (1977), Cu can be complexed by fulvic acids even in the presence of a 40000-fold excess of Ca, which represents a rather common situation in natural waters.

Another aspect which is evidenced by Ramamoorthy and Kushner (1975), is that low molecular weight particles are responsible for the highest percentage share of cadmium. In this respect their data show that the best parameter describing this behaviour is TOC, as is also confirmed by our data. It seems very appropriate to consider, that, even in this case, the significant role of the organic matter may well be confined to the adsorption of very finely dispersed particles of hydrolyzed cadmium species and simple inorganic complexes. Therefore it may be assumed that ACC and TOC values are indicative of two different ways by which a metal may associate with soluble or very fine colloidal organic particles: the first through chelating reactions and the second through more complex adsorption phenomena.

On the other hand no correlation exists between TOC and ACC in any ultrafiltrate fraction.

d) Manganese oxides in the largest molecular weight colloidal fraction (A) ($> 10^4$ M.W.) seem to play a role in adsorbing trace metals such as Cd and Cu as shown by the positive correlation between Mn_A and both Cu_A and Cd_A. The role of iron may be dominant in this fraction and the observed correlations, far from denying this assumption, would indicate that manganese and iron are present in a rather constant ratio in the colloidal particles.

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