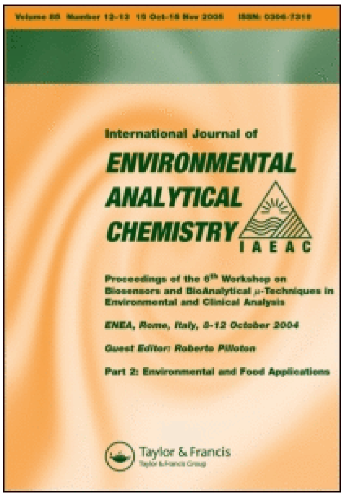

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Frimmel, Fritz H. , Immerz, Angelika and Niedermann, Helmut(1983) 'Heavy Metal Interaction with Aquatic Humus', International Journal of Environmental Analytical Chemistry, 14: 2, 105 — 115
To link to this Article: DOI: 10.1080/03067318308071612
URL: http://dx.doi.org/10.1080/03067318308071612

Intern. J. Environ. Anal. Chem., 1983, Vol. 14, pp. 105–115
0306-7319/83/1402-0105 $18.50/0

Heavy Metal Interaction with Aquatic Humus†

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(*Received August 20; 1982*)

A main part of all dissolved organic carbon (DOC) in surface waters is due to humic substances (HUS). Their complexation of heavy metals may cause biological effects and disturb water treatment steps. Because of this importance complexation capacities of HUS and any related parameters are of interest. A method for determination uses polarographic (DPP/DME) titrations in respect of copper. HUS isolated from different rivers and lakes show in general some μmol complexation capacities per mg DOC depending on the kind of original water, and on the seasonal time of sampling. Brown water and winter samples have the smallest capacities.

Many of the water quality data of the original surface waters are in good agreement with these results. Especially concentrations of dissolved heavy metals like iron, mercury and lead can be explained by taking into account the complexation ability of aquatic HUS.

KEY WORDS: Surface water, heavy metals, humic substances, complexation, polarography.

In nearly all surface waters humic substances (HUS) are the main component of the DOC (dissolved organic carbon);[1] ranging from about 50% up to 100%. The less polluted a lake or a river is, the higher is the percentage of HUS. Because of the relatively high molecular weight and their complicated composition humics cannot be described by means of a simple structural formula.[2] Therefore physical–chemical properties and the determination of functional groups are of main interest.[3-5] In addition the interaction of functional groups with cations can lead to coordination compounds.[6,7] Especially the complexation of heavy metals by HUS is one of the actual problems which have to be watched carefully in drinking-water supply. Besides these technological and toxicological aspects information is needed about the influence of the complexation of humics on the bioavailability of heavy metals. For all that a parameter which characterizes and quantifies the complexation capacity of HUS is very useful.

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†Presented at the 12th Annual Symposium on the Analytical Chemistry of Pollutants, Amsterdam, April 1982.

Sampling sites and water quality data

Water samples from different Bavarian lakes and rivers (Fig. 1) were taken and analyzed at different seasons over 2.5 years. A general characterization is given in Table I. The quality data which are of importance for heavy metal complexation are given in Figure 2.

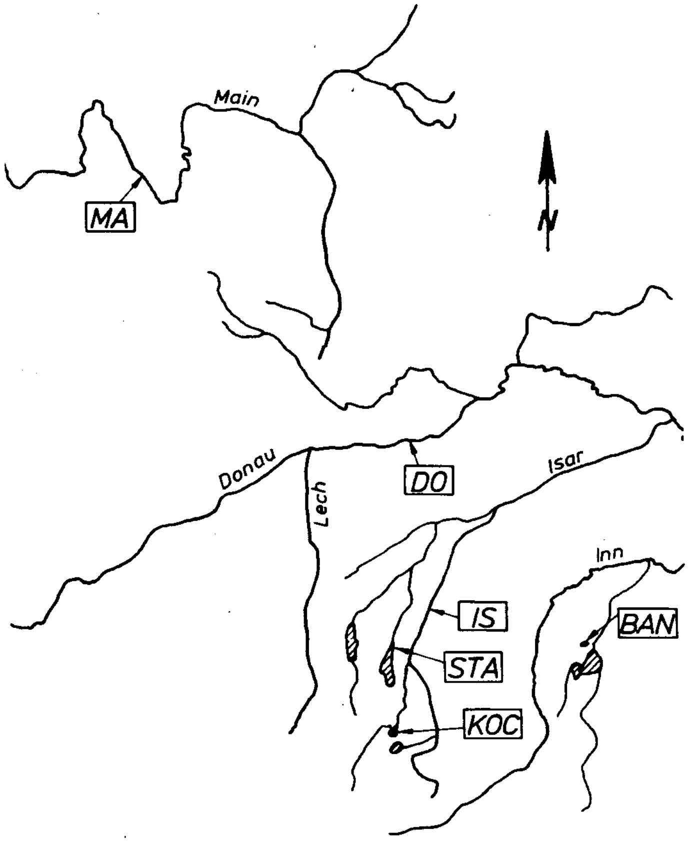

FIGURE 1 Sampling sites for the isolation of HUS.

Samples for DOC (dissolved organic carbon) and metal analysis were passed through a 0.45 μm membrane filter in a stainless steel respectively all plastic pressure filtration apparatus. The pointed columns refer to the sampling points 1–6 (Table I) and show the range of the determined values.

The relative standard deviation for the individual determinations is mostly smaller than 5% for the general parameters and smaller than 10%

TABLE I
Sampling sites and general water quality

No.	Rivers	Abbrev.	Character
1	Main (Randersacker)	MA	fairly polluted
2	Donau (p. Ingolstadt)	DO	moderately polluted
3	Isar (a. München)	IS	moderately polluted
	Lakes		
4	L. Starnberg	STA	mesotrophic
5	L. Kochel	KOC	mesotrophic
6	Bansee	BAN	dystrophic (brown water)

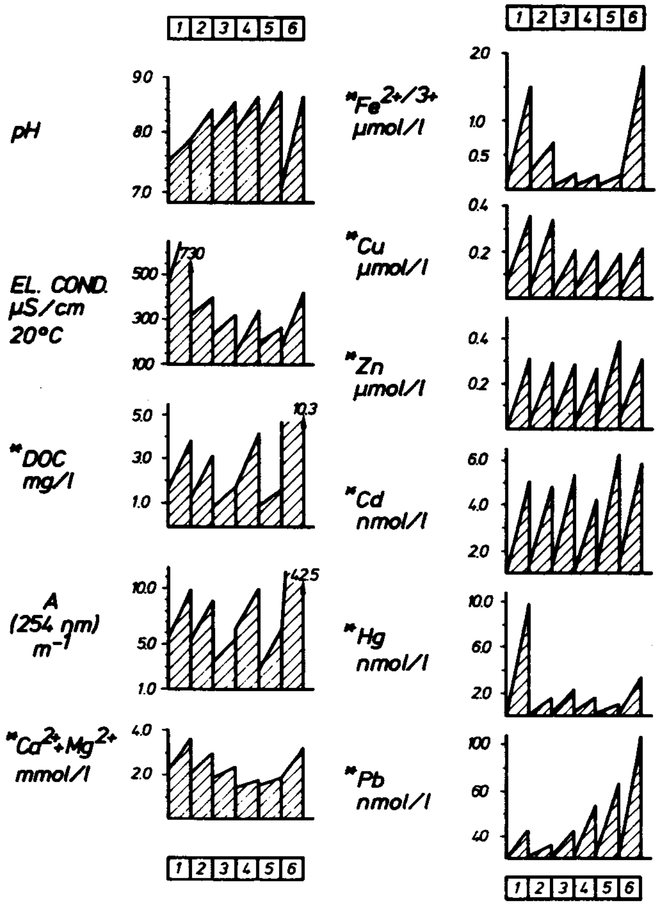

FIGURE 2 Water quality data at the different sampling sites (*dissolved $<0.45\,\mu m$).

for the trace metals (Table IV). In case of some heavy metals the inhomogeneity of the natural waterbody and the sample treatment add up a deviation of ±30%.

The results show clearly that the brown water (Bansee) and the river Main are fairly different from the other waters. There exist good correlations between pH, electric conductivity and the earth alkaline ion concentration, and between the UV-absorption and the DOC. In addition some heavy metal (Pb, Hg, Fe) seem to be correlated with DOC. This effect can be seen more clearly by taking the values of the individual samples especially from the bog lake.

Isolation of humic substances

Humic substances were isolated from the water acccording to the scheme shown in Figure 3. It is derived from a generally accepted procedure using a polystyrene resin as stationary phase.[8,9]

For alkaline conditions can influence the humic molecules,[10,11] the final effluent should be neutralized immediately. The effectivity of the sorption and desorption can be seen from Table II, which shows the mass balance for the isolation of HUS from Isar water.

The balance suggests that nearly 60% of the original DOC contribute to the HUS. 7.4% remain immobilized at the resin. For the other samples results are similar. Only the brown water shows a much higher percentage of HUS (about 80%) and a seasonal variation (winter to 90%). The neutralized eluents can be analyzed and examined by gel chromatography to get detailed information about their composition.

Determination of the complexation ability

The titration of Cu^{2+} with increasing amounts of the isolated HUS is used for quantifying their complexation properties. Differential pulse polarography measures the free and labile Cu^{2+}.[7,12,13] Figure 4 shows the current-potential curves for the original Cu^{2+} concentration (0) and the curves for the titration steps (1–6). The graph gives the current of the polarographic maximum according to the added HUS also expressed as DOC.

The 50% line is derived from a theoretical reaction equilibrium (a).

$$Cu^{2+}\cdot aq + HUS^{n-} \rightleftharpoons Cu\,HUS^{2-n} \quad \text{(a)}$$

This includes a general problem, for the measured Cu^{2+} curve gives operationally defined values. They can be compared with one another, but the interpretation towards complexation has to be proved in detail.

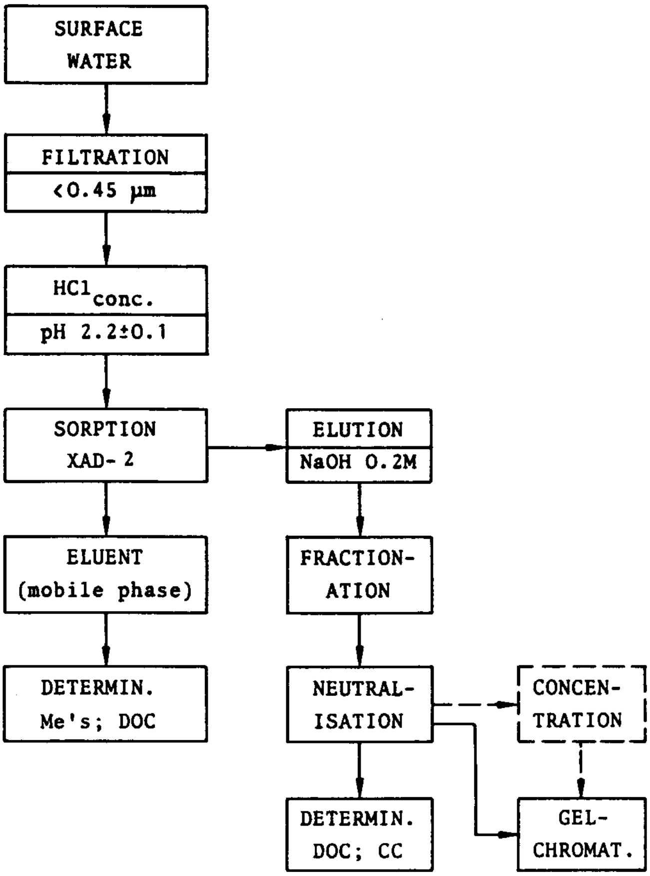

FIGURE 3 Isolation scheme for aquatic HUS.

TABLE II
Mass balance for the isolation of HUS from Isar water on a polystyrene resin

	Vol. l	DOC mg/l	org. C %
Original water	50	1.43	100
Eluent (mobile phase)	50	0.60	42.4
Eluent (NaOH, 0.2 M)	0.3	140	50.2

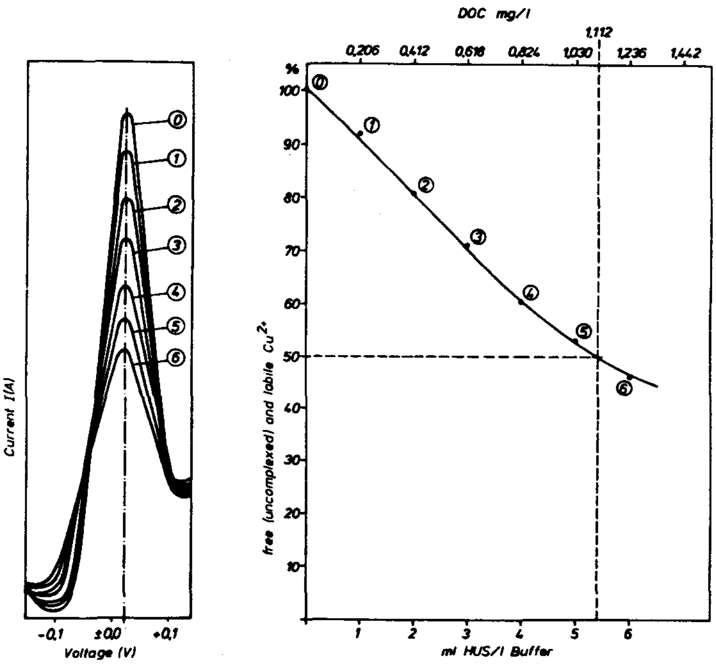

FIGURE 4 Polarographic titration curve for the complexation of Cu(II) by HUS.

Besides the possible disturbances from surface interactions at the electrode other sorption effects[14] have to be watched carefully. Variations of the measuring conditions (e.g. drop time, drop size, modulation amplitude, measuring time), and the shape (half width) and potential of the peak are suited to give information about the above mentioned disturbances. The results from varying the drop size (area ratio) from 1 to 2.5, the drop time from 0.5 to 1s and the reaction time from 1 to 2 min showed reproducibile values within the exactness of the individual determinations. The half width and the position of the peak are constant for most of the titration rows. The shape of the titration curve and a blank polarogram of the HUS without copper showed that there were no great disturbances. We conclude from that a reliable polarographic procedure and a suitable operationally defined parameter, which shows the influence of HUS on polarographically active ("free") Cu^{2+}.

The concentration of HUS expressed as DOC which leads to a 50% reduction of "free" Cu^{2+} is a representative value (CC(Cu 50%)) for characterizing the complexation ability of the HUS under the defined conditions. The decrease of originally free Cu^{2+} at a DOC of 1 mg is called specific complexation capacity (SCC(Cu)). It can be easily calculated from CC(Cu 50%) in case of a fairly linear titration curve. Mostly the exact value has to be taken from the non-linear curve itself.

RESULTS

The CC(Cu 50%) and the SCC(Cu) for HUS from the different waters are given in Table III.

TABLE III

Cu-complexation capacities of HUS (as DOC)

	Summer sample		Winter sample	
HUS origin	CC(Cu 50%) mg DOC	SCC(Cu) μM Cu	CC(Cu 50%) mg DOC	SCC(Cu) μM Cu
1	0.74	6.0	1.61	3.3
2	0.54	7.7	1.58	3.5
3	1.14	4.6	1.70	3.3
4	2.01	2.8	2.80	2.1
5	0.76	5.7	1.21	4.3
6	1.76	3.3	2.82	2.3
6[a]	1.41	4.6		

[a]Interstitial water.

Samples taken in summer show up to twice higher specific complexation capacities than the winter HUS. The capacities of the brown water HUS are in general smaller.

The reaction conditions of the titration are derived from natural aquatic systems. The acetate buffer (Cu-Komplex $K_1 < 2.5$)[15] will not compete markedly with the Cu^{2+}—HUS—complexation. Therefore the specific complexation capacity of some μmol per mg DOC can be expected for most rivers and lakes.

CONCLUSIONS

Varying results can be explained by the molecular size. In summer biodegradation leads to a higher amount of smaller molecules with relatively more functional groups which includes higher complexation ability. This is in good agreement with experimental data from ultra filtration.[16]

Brown water contains in general humics of bigger size. Interstitial water from anaerobic sediment has abviously species of higher reactivity.

The determined complexation capacities of the isolated HUS can be compared with the DOC and the heavy metal concentrations in the original surface water. This leads to the conclusion that the available functional groups determined by the applied method do not find an equivalent amount of heavy metals in natural aquatic systems and hence are not fully occupied by trace metals. The natural Ca-concentrations which are about 3 times higher than the total heavy metal concentrations suggest a competition for the metal complexation, though the Ca-HUS-complexes are expected to be 10^3 and 10^4 times less stable than the Cu-complexes. The exceeding concentrations for dissolved ($<0.45\,\mu m$) Fe and Hg in the river Main and the Bansee can be explained by pollution in the first and by complexation with HUS in the latter case. The Hg and Pb values in the Bansee can be interpreted by the input from atmosphere and by a complexation mechanism which works e.g. via the mercapto groups of the HUS.[17] For that a competitive role of the water hardness will be less important than for the Cu-complexation. The high concentration of Fe$<0.45\,\mu m$ in the Bansee is in good agreement with its high content of HUS.

Though the proposed method shows the limitations of an operationally defined parameter it is a helpful tool for getting information about the interaction of HUS and heavy metals. The results are in good agreement with many of the quality data for the original surface waters.

EXPERIMENTAL DETAILS

Sampling

Water samples were taken in polyethylene bottles. Filtration was performed immediately at the sampling site. Samples for heavy metal analysis were acidified (5 ml HNO_3 conc. per liter) direct after filtration.

Sampling from anaerobic parts of the brown water was performed under N_2 atmosphere.[9]

Water quality determination

The water quality parameters were determined according to standardized methods.[18] Table IV gives the methods used and the standard deviation in routine analysis ($n = 12$).

Isolation of HUS

Water samples of 50 l were treated as indicated in Figure 3. A glass

TABLE IV
Quality criteria for the analytical methods used

Parameter	Method	Value ± Stand. Dev.
T	Hg-Thermometer	10 ± 0.05°C
pH	Electrode	7 ± 0.02
El. cond.	Electrode	150 ± 2 μS/cm
A (254 nm)	Spectrometer (cell: 1 cm)	$\pm 0.2\,m^{-1}$
$Ca^{2+} + Mg^{2+}$	Titration	2 ± 0.01 mM/l
$Fe^{2+/3+}$	Photometer (Bathophenanthroline)	6 ± 0.4 μM/l
	AAS (flame)	6 ± 0.3 μM/l
Cu	AAS (flame)	0.2 ± 0.015 μM/l
	DPAS/HMDE	0.1 ± 0.01 μM/l
Zn	AAS (flame)	1 ± 0.1 μM/l
	DPAS/HMDE	1 ± 0.1 μM/l
Cd	AAS (C-furnace)	15 ± 1 nM/l
	DPAS/HMDE	10 ± 0.9 nM/l
Hg	AAS (cold vapour)	0.5 ± 0.05 nM/l
Pb	AAS (C-furnace)	10 ± 3 nM/l
	DPAS/HMDE	10 ± 1 nM/l
DOC	O_2/UV-Degradation	1 ± 0.07 mg/l

column of 20 mm diameter and 46 cm height was filled with Servachrome XAD 2 (300–1000 μm particle size) analytical grade. The bed volume was 150 ml and the void volume 47 ml. The column was rinsed with H_2O dest. (500 ml), followed by 0.2 *n* NaOH (600 ml), H_2O dest. (1200 ml) and 0.01 *n* HCl (200 ml) before the sample was applied. The columns were run by 10 ml/min and protected against sunlight. After rinsing with 50 ml 0.01 *n* HCl and 50 ml H_2O dest. the alkaline elutions were started with portions of 20 ml 0.2 *n* NaOH and a flow rate of 1 ml/min.

In the case of the interstitial water from the Bansee all operations were performed under N_2 atmosphere and in oxygen free solutions. The alkaline eluent was stored in a Schlenk-tube. All samples were stored in the fridge.

Polarographic titration

The polarographic determinations were performed under N_2 atmosphere and in oxygen free solutions according to the operating conditions given in Table V.

Instrumentation

pH-meter: Digi 550, Wissenschaftlich-Technische Werkstätten, Weilheim.

TABLE V

Experimental setting of the polarographic titration

Analytical method:	DPP/DME (Differential Pulse Polarography/Dropping Mercury Electrode)
Total sample volume	10 ml
Buffer	Acetate, 10^{-2} M
pH-value	6.8
Temperature	25°C
Initial (= total) Cu-Concentration	10 μM/l
Volume of HUS-solution added (one step)	5–100 μl
Initial potential	−0.15 V
Final potential	+0.20 V
Scan rate	5 mV/s
Mod. ampl.	50 mV
Current range (max.)	2 μA
Drop size	medium
Reference electrode	Ag/AgCl/KCl (3M)

Atomic absorption spectrometer: SP 9 Pye Unicam.
Polarography/Voltammetry: PAR 174 A, 315 A, SMDE 303.
UV-VIS-spectrometer: Pye Unicam SP 8–100; 1 cm cell.
DOC-Analyzer: UV-DOC Maihak, Integrator Mai II.

Chemicals

All chemicals were of grade "pro analysi" (Merck), acids and organic solvents were of grade "selectipur" (Merck). Distilled water was twice distilled in an all quartz apparatus. N_2 was highly purified and for polarography especially deoxygenated. Hg for polarography was special quality III (99.9995%, Degussa).

For quantitative determinations ion standard solutions of Fluka were used for calibration. Diluted samples were prepared shortly before use.

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