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THE FLOCCULATION OF DISSOLVED Fe, Mn, Al, Cu, Ni, Co AND Cd DURING ESTUARINE MIXING

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A laboratory experiment was carried out in which the flocculation products, formed from the mixing of filtered (0.4 μm) river water and seawater, were analysed. This study established that Fe, Mn, Al, Cu, Ni, Cd and Co have resolvable and well-defined estuarine chemistries. Copper, Ni, Mn and Co have salinity dependences of removal which are similar to those of dissolved Fe and humic acids. The amount of removal of the above trace metals increases between 0 and 15–18‰, after which little additional removal occurs. The extents of removal from river water are very different: Fe, 95%; Al, 20%; Cu, Ni, 40%; Co, 10%; Cd, 5% and Mn, 25–45%. The basic removal mechanism appears to be the estuarine flocculation of trace metals which exist, in part, in river water as colloids in association with colloidal humic acids and hydrous iron oxides. A qualitative model, based on this mechanism, supports the observations of this flocculation study.

The results of this study give the most complete and consistent set of data presently available, from which to postulate the most important processes controlling the estuarine chemistry of trace metals. The generality of their behaviours still needs to be determined by future investigations.

1. Introduction

The chemical behaviour of trace metals during estuarine mixing may play an important part in the overall geochemical cycles of these metals [1–3]. The removal by flocculation and gain by desorption of dissolved metals are two non-biological processes operating in an estuary. For example, mechanisms controlling the almost complete removal of river dissolved Fe are now fairly well understood [2,4–7]. However, studies of other dissolved trace metals (Cu, Ni, Co, Cd) have not produced data which is either complete – or consistent – enough to establish their estuarine chemistries [8–14]. It was therefore decided to apply the product approach (i.e. use of laboratory mixing experiments coupled with the collection and analysis of removal products – flocculants – which form when river water filtered through >0.4 μm retaining filters and seawater mix), to a study of the estuarine chemistry of dissolved Fe, Cu, Ni, Co, Mn, Al and Cd in the Water of Luce (Scotland). As shown by Sholkovitz [4], this approach has distinct advantages over the generally used reactant approach (i.e. measurements of the concentration of dissolved constituents from waters collected in an estuary). It has proven valuable in establishing the extent and salinity dependence of removal of dissolved Fe, Mn, P, Al and organic matter during estuarine mixing; for these elements a principal removal mechanism is flocculation from the colloidal state in which they exist in river water [2,4–7]. This paper demonstrates that the chemical reactivity of Cu, Ni, Co and Cd during estuarine mixing can also be determined with the product approach.

2. Laboratory studies and analytical methods

The behaviour of dissolved trace metals during estuarine mixing was simulated by a laboratory mixing experiment similar to those conducted by Sholkovitz [4].

To minimize contamination the following precautions were taken. Plastic filter holders, membrane filters and all other glass and plastic ware were cleaned in hot HCl and kept in an acid bath prior to use. All filtering and handling of solutions was done in a laminar flow clean air bench.

In the mixing experiment, seawater collected off the coast of Scotland was used as the seawater end-member. This water was filtered through 0.4 μm Nuclepore filters and then passed through Chelex-100 resin to remove trace metals. River water from the Water of Luce (Scotland) was used as the fresh-water component in the mixing experiment. This water was filtered (0.45 μm Sartorius cellulose nitrate filters) within 24 hours of its collection. Immediately after filtration, varying volumes of seawater were added to 600 ml aliquots of filtered river water to produce twelve mixtures ranging in salinity from 0 to 30‰. After standing for 24 hours the mixtures were filtered through 0.4 μm Nuclepore filters to collect the resulting flocculants. The filters with the flocculants were placed in pyrex beakers to which 5.0 ml aliquots of $3N$ HNO_3 were added; the acid was completely fumed away. This step was repeated. Then 10.0 ml aliquots of $0.1N$ HNO_3 were added to redissolve the metals, and the filters were removed. This extraction procedure allowed the measurement of Cu, Ni, Co and Cd by direct injection into a flameless atomic absorption spectrometer (AAS).

To determine the concentration of Cu, Ni, Co and Cd in the river water end-member, aliquots of 100 and 150 ml were evaporated to dryness. The residue was heated with $3N$ HNO_3 until this acid fumed away. The metals were then redissolved into 10.0 ml of $0.1N$ HNO_3. Iron, Mn and Al concentrations were determined using the original river water (stored acidified). Working standards of all the metals were prepared in $0.1N$ HNO_3 from primary standards.

All analyses, except Al, were performed by graphite heated atomisation (GHA coupled with AAS, using an Instrumentation Laboratory Model No. 151 AAS and No. 455 GHA system. The extracted solutions required dilution (with $0.1N$ HNO_3) by factors of 150 and 4 for the determination of Fe and Mn respectively. The extracted solutions were also diluted by 35 times before Al was measured colorimetrically [15].

Experiments (using standard additions) showed that the sensitivities of the atomic absorption measurements for Cu, Ni, Co and Cd were the same in the evaporated-oxidized-acid extracted river water samples as in the acid working standards. Similarly, the presence of small amounts of seasalt on the unwashed flocculants did not alter the sensitivities.

3. Results

The flocculation of Fe, Mn, Al, Cu, Ni, Co, Cd and humic acids are shown as a function of salinity in Figs. 1–7. At S = 0‰ the data points labelled (*) are termed the zero salinity blanks, and they indicate (1) the extent to which metal-containing particles form when filtered river water is stored for 24 hours and (2) contamination during the flocculation and analytical steps. Excluding Cd, these blanks are low relative to the maximum amounts of trace metal removed.

The error bars shown in Figs. 1–7 give the precision of the analytical measurements. The reproducibilities of the overall salinity dependences are not known since only one complete mixing experiment was run. However, the relationships between the removal of iron and humic acids and salinity are very similar to those previously found for the Water of Luce and other estuaries [1,4,6,7,9,10,12,16–19]. This suggests that we are dealing in this experiment with removal processes which are common phenomena during estuarine mixing.

The relationships between flocculation and salinity are similar for Fe, Ni, Co, Cu, Mn and humic acids (Figs. 1–4, 7). The amount of humic acids, Fe, Ni and Co removal increases as salinity increases from 0 to 12–15‰, above which little or no removal occurs. Copper flocculation increases steadily from 0 to 18‰ after which there is little additional removal. Mn removal levels off between 15 and 25‰ with additional removal at 27 and 30‰. Iron, Mn and humic acid behaviour of this same type was observed in other laboratory mixing experiments [4,7].

A maximum in the amount of Al flocculated occurs at the salinity of 12‰ (Fig. 3); above 20‰ removal has reached a constant value. Previous flocculation studies of Al for the Water of Luce and other estuaries show increasing removal from 0 to 15‰ after which there is little additional removal [4,7]. The reason for the maximum in this experiment is not known.

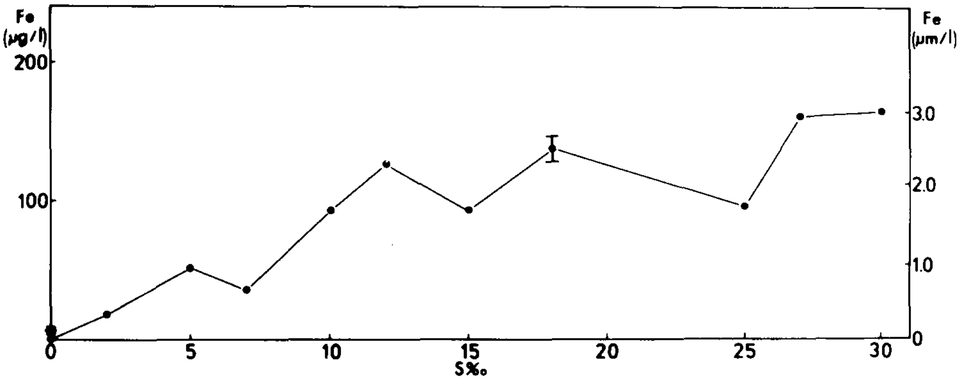


Fig. 1. Iron flocculation vs. salinity for the Water of Luce. Concentrations, corrected for the zero salinity blank (*), in amount (μg and μmol) of Fe flocculated per litre of river water.

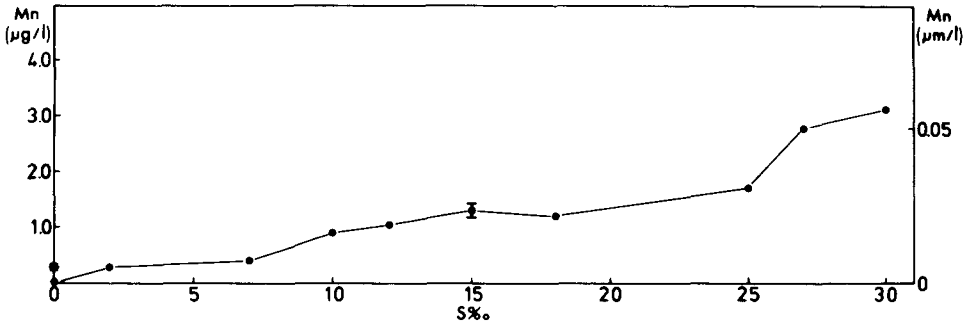


Fig. 2. Manganese flocculation vs. salinity for the Water of Luce. Concentrations, corrected for the zero salinity blank (*), in amount (μg and μmol) of Mn flocculated per litre of river water.

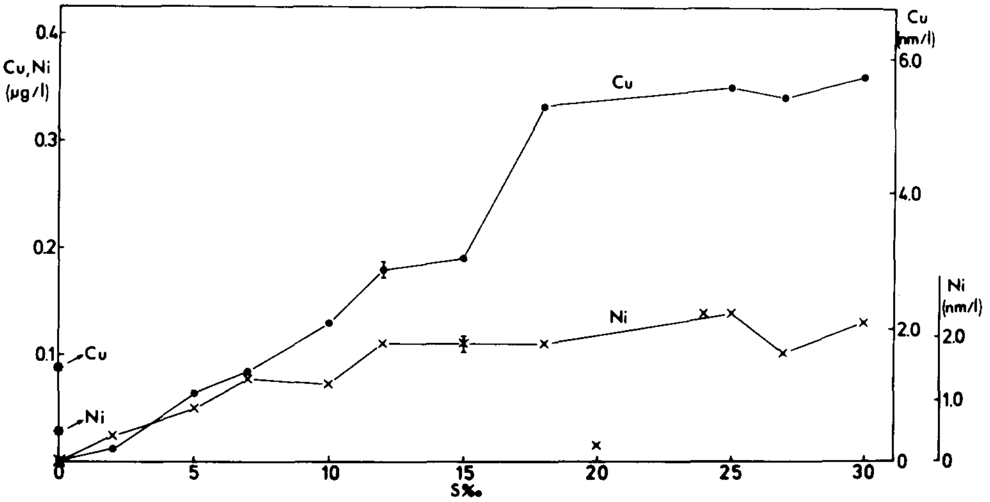


Fig. 3. Copper and Ni flocculation vs. salinity for the Water of Luce. Concentrations, corrected for the zero salinity blank (*), in amount (μg and nmol) of Cu and Ni flocculated per litre of river water.

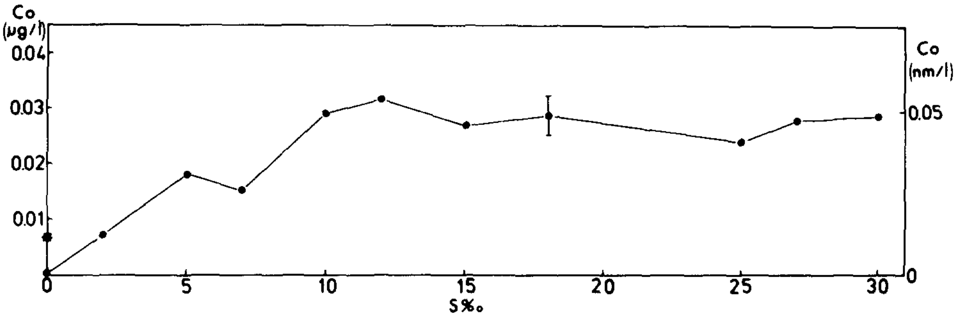


Fig. 4. Cobalt flocculation vs. salinity for the Water of Luce. Concentrations, corrected for the zero salinity blank (*), in amou (µg and nmol) of Co flocculated per litre of river water.

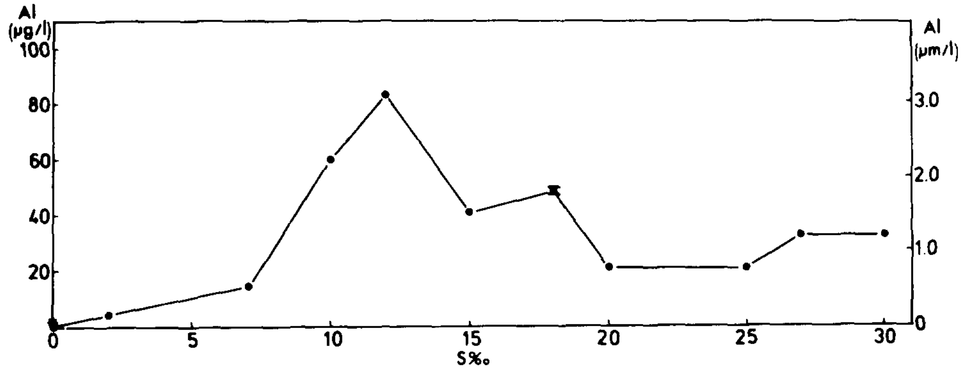
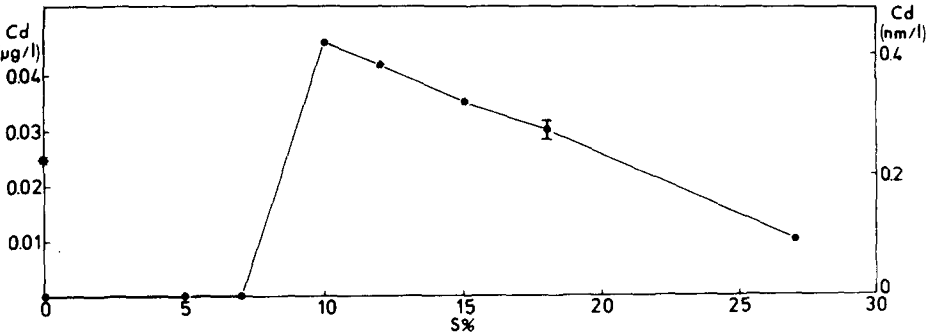


Fig. 5. Aluminium flocculation vs. salinity for the Water of Luce. Concentrations, corrected for the zero salinity blank (*), in mount (µg and µmol) of Al flocculated per litre of river water. Point at 5‰ indicates contamination.



ig. 6. Cadmium flocculation vs. salinity for the Water of Luce. Concentrations, corrected for the zero salinity blank (*), in mount (µg and nmol) of Cd flocculated per litre of river water.

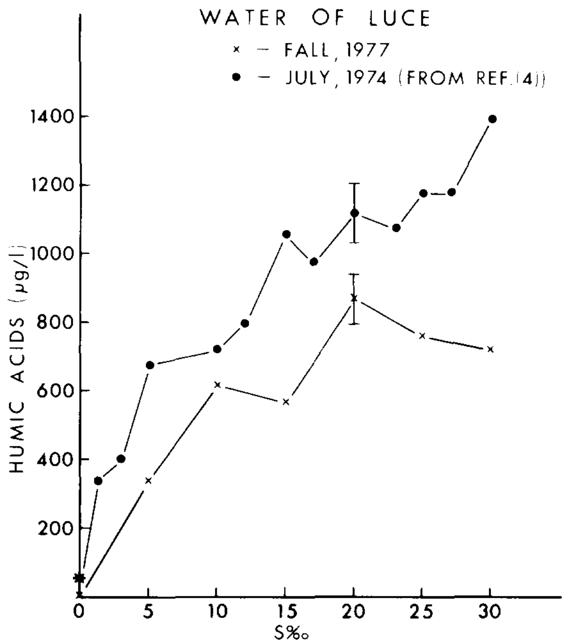


Fig. 7. Humic acid flocculation vs. salinity for the Water of Luce. Results from two studies are shown. Concentrations in amount flocculated per litre of river water. Analytical method given in Sholkovitz [4].

Cadmium behaviour contrasts sharply with that of the other metals (Fig. 6); there is negligible removal until 10‰ where the maximum flocculation takes place. This is followed by a continuous decrease to 27‰. The Cd-*S*‰ profile does not include data for *S* = 2, 25 and 30‰ since these samples were contaminated. A preliminary study, based on only four data points between 0 and 15‰, also showed a maximum in Cd removal between 5 and 10‰. For arguments in this paper I will assume that the general type of salinity dependence in Fig. 6 holds for Cd. Obviously, more detailed work on Cd is needed.

4. Discussion

4.1. General observations

The laboratory mixing experiments and analytical techniques used in this study permit the measurement of trace metals in the flocculants at very low concentrations (e.g. 0.01 μg/l for Cd and Co). Thus the relationships between salinity and trace metal flocculation have been resolved with only a few ambiguities (see last section).

The removal of dissolved Fe and humic acids shows a salinity dependence of the general type observed in estuaries, using both the reactant and product approaches [1,2,6,7,9,10,12,16–19]. An important feature of previous studies [4,6] is the similar salinity dependences for the removal of Fe and humic acids in both the Water of Luce and Amazon estuaries. The results of the present work indicate that Cu, Ni, and Co also have a salinity dependent removal which follows that of Fe and humic acids. This implies that (1) similar processes may govern the flocculation of Fe and humic acids and Cu, Ni and Co, and (2) this type of trace metal removal may be a general phenomenum of estuarine mixing. The latter implication will need to be verified by other investigations while the former implication will be developed in the last section of this paper.

4.2. Percentage removal of trace metals

Table 1 compares the concentrations of the trace metals in the river water with the amounts flocculated. The latter values, taken from Figs. 1–6, represent removals at high salinities (25–30‰). The percentage removals of the river metals are as follows: Fe, 95%; Mn, 25–45%, Cu, 40%, Ni, 40%, Al, 20%, Co, 10%, and Cd, 5%. The removal of Mn is better represented by the range 25–45%; the smaller value results if the flocculation value at 25‰ is used instead of those at 27 and 30‰.

The above results indicate the almost total removal of Fe, appreciable losses of dissolved Cu, Ni, Mn and Al, and the removal of very small quantities of Co and Cd.

It must be emphasized that these percentage removals come from only one laboratory mixing experiment which does not contain suspended material. Desorption of metals from river suspended matter [20,21] and/or the addition of dissolved trace metals from pore solutions of estuarine sediments [22] may both counterbalance their removal by flocculation.

The almost total removal of river dissolved Fe has been demonstrated to be a normal occurrence during estuarine mixing [1,2,4,6,7,9,10,12,16–19].

TABLE 1

Water of Luce (Scotland) – summary of results of trace metal flocculation

Element	River water conc. ($\mu g/l$)	Flocculated amount * ($\mu g/l$ of river water)	Removal * (%)
Fe	174 (±6)	165	95 (±3)
Mn	6.5 (±0.5)	1.7–3.0	25–45
Al	170 (±5)	32	19 (±1)
Cu	0.85 (±0.05)	0.35	41 (±5)
Ni	0.28 (±0.04)	0.12	43 (±10)
Co	0.25 (±0.02)	0.028	11 (±3)
Cd	0.21 (±0.03)	0.01	5 (±1)

* At high salinities. See text for details.

The 20% removal of Al is in agreement with that estimated by Hydes and Liss [23], and it is also within the range of values found in previous mixing experiments using Scottish rivers [4].

Subramanian and D'Anglejan [17] and Holliday and Liss [16] show that Mn behaves conservatively. Evans et al. [22] show that Mn can be added to estuarine waters by diagenetic solubilization in sediments. In contrast, Mn removal appears to occur in southeast U.S. estuaries, but the extent of removal is difficult to assess from the data presented [12]. This and the previous work [4] on Scottish rivers show that Mn is flocculated during estuarine mixing. The 25–45% removal reported in this study is more accurate than the previously estimated 90–100% removal because of better analytical methods. In summary, Mn can behave very differently in estuaries all exhibiting large-scale Fe removal. All available evidence indicates that the independent behaviour of Fe and Mn is real.

Studies of other dissolved trace metals (Cu, Ni, Cd, Zn and Co) have not been able to establish their estuarine chemistry [3–14,16]. Boyle [24] in a study of the Amazon estuary, suggests that Ni is conservative whereas Cu may be removed from solution. Windom [12] also suggests that Cu and Cd are removed but it is impossible to tell from his data how these metals behave in any one estuary at any one time. Using a product approach, Lowman et al. [25] show that Fe, Co and Zn (to >90%), Ni and Mn (30%) and Cu (20%) are rapidly and appreciably removed from solution when river water is mixed with seawater (at 15‰).

4.3. Mechanisms of trace metal flocculation

The estuarine reactivity of trace metals is governed by the physical and chemical relationships between trace metals, organic matter, hydrous iron oxide and the major anions and cations of seawater. These components can exist as dissolved, colloidal and suspended matter and can be involved in flocculation, precipitation, chelation, complexation and adsorption. The complexity of this system (particularly when organic and colloidal matter is involved) has meant that it is not adequately understood [26–28]. There are, however, some theoretical and experimental studies on different combinations of the above components and processes (see Table 2). These are used along with the observations of this study to develop (below) a qualitative and generalized model whose purpose is to try to identify the most important geochemical processes controlling the removal of trace metals. Another aim is to show that chemical properties of trace metals are sufficiently different to account for their different estuarine reactivities.

Field and laboratory studies indicate that the main process affecting iron and humic acids during estuarine mixing is their rapid flocculation, with both constituents having similar salinity-dependent removal [2, 4–7]. Large-scale removal (80–100%) of Fe is accompanied by the flocculation of only a small amount (5–10%) of river dissolved organic matter (DOM). The organic fraction, which flocculates, consists of high-molecular-weight dissolved humic acids [6]. The concentration and estuarine reactivity of Fe

TABLE 2

Experimental studies on the association of trace metals with humic substances and iron oxides

I *Relative order of trace metal-fulvic acid stabilities*	
Ref. [41]	$Fe^{3+} > Al^{3+}, Cu^{2+} > Pb^{2+} > Fe^{2+} > Ni^{2+} > Mn^{2+} > Co^{2+} > Ca^{2+} > Zn^{2+} > Mg^{2+}$ @ pH = 5
II *Relative order of trace metal-humic acid stabilities*	
Ref. [44]	$Fe^{3+} > Al^{3+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$
Ref. [45]	$Fe^{3+} > Al^{3+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Fe^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$
Ref. [46]	$Cu^{2+} > Zn^{2+}, Ni^{2+} > Co^{2+}, Mn^{2+}$
Ref. [47]	$Cu^{2+} > Pb^{2+} >> Cd^{2+} > Zn^{2+}$
III *Irving-Williams order*	
Ref. [36]	$Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+}$
IV *Absorption onto freshly precipitated hydrous iron oxide + goethite*	
Ref. [27,48,49]	$Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+} > Ba^{2+} > Ca^{2+} > Mg^{2+}$
Ref. [50]	$Pb^{2+}, Zn^{2+} > Cd^{2+}$
Ref. [51]	$Cu^{2+} > Pb^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+}$

and humic acids (from studies of particle size fractions (0.45–0.001 μm) of river water) demonstrate their colloidal nature [2,4–7]. In addition, DOM in river water is necessary to maintain Fe in the dissolved-colloidal state [2,4,29].

In analogy with the behaviour of Fe and humic acids, the following model is proposed to qualitatively predict the estuarine reactivity of trace metals.

(1) In river water, some fraction of dissolved trace metals exist as a colloid in physical-chemical association with colloidal humic acids (HA) and hydrous iron oxides (HIO).

(2) Removal of trace metals results from their flocculation as colloids and/or from their subsequent adsorption onto HA and HIO flocculants.

(3) The extent and salinity dependence of removal during estuarine mixing will be determined by the relative affinities of trace metals for seawater anions and for HA and HIO in the presence of seawater cations.

Evidence to support this model is presented in the remainder of this section.

The capacity of DOM (particularly humic substances) to keep trace metals in solution (dissolved and colloidal) is known for river and lake waters [2,4, 29–37]. Particle size separation studies also indicate the existence of trace metal–organic colloids in fresh waters [2,6,19,35–38]. As demonstrated for Fe, Mn, P, Al and humic acid [2,4–6], perhaps the best evidence of their colloidal nature is the salinity dependences observed in flocculation studies of this paper (Figs. 1–6).

The affinities of trace metals for humic and fulvic acids have been studied in detail. As summarized in Table 2, Fe^{3+} has the strongest affinity (stability constant) whereas Mn^{2+}, Co^{2+} and Cd^{2+} show the least affinity. Cu^{2+} is consistently the most strongly associated of the divalent trace metal cations.

The adsorption of trace metals onto goethite and hydrous iron oxides has received some attention. As shown in Table 2, Co^{2+} and Cd^{2+} have the least affinity whereas Cu^{2+} has the greatest, followed by Ni^{2+}.

The sequences shown in Table 2 are derived from a variety of laboratory studies in solutions of low ionic strength. Although the sequences shown are fairly consistently observed, there are variations depending on the pH and the reacting components [39–42]. However, the sequences support the idea that the relative affinities of trace metals for humic substances and hydrous Fe oxides may be controlling their extent of removal during estuarine mixing.

Stumm and Brauner [28] present one of the latest mathematical models which attempts to establish the extent of organic–trace metal interactions in seawater. A condensed version of their results is shown in Fig. 8 which compares the concentration of metal-inorganic and metal-organic ligands in seawater. Under the conditions of this model (see Fig. 8), Cu^{2+} can exist as Cu-citrate. Fe^{3+}- and Ni^{2+}- organic ligands can also compete with the inorganic complexes. In contrast, Cd^{2+}, Mn^{2+} and to a lesser extent Co^{2+} should exist as Cl complexes. As seen in Table 2, these three metals also show the weakest affinities for humic acids and hydrous Fe oxides.

The model calculations of Stumm and Brauner suggest that trace metals should have quite different extents of association with organic ligands in seawater. However, such models at present do not realistically cover the river-estuary system since they do not consider colloids, trace metal–humic substances interactions and the adsorption onto solids (e.g. HA and HIO flocculants). Nevertheless, the general observations of Stumm and Brauner's model and of experimental studies with HA and HIO support the results of this flocculation study and lead to the *following conclusions.*

(1) Iron removal is almost complete as the result of the flocculation of strongly associated Fe-humic acid colloids [2,4–7].

(2) Copper and Ni show appreciable extents of removal (40%) as their affinities with HA and HIO are "competitive" with seawater cations. They are flocculated as metal-HA-HIO colloids and show salinity dependence of removal which are very similar to those of dissolved Fe and humic acids.

(3) The flocculation of Al (20% removal) occurs because it exists in river water as colloidal clay [7,23, 43] and as organically associated colloids [31,38].

(4) Cadmium and Co are removed to only small extent (5 and 10% respectively) as they form very strong Cl complexes in seawater. The maximum in the amount of Cd flocculated (Fig. 6) may result from the formation of soluble Cd-Cl complexes as salinity increases.

(5) The estuarine behaviour of Mn is partly resolved. Its lack of affinity with organic ligands suggests that it should show little removal, as is the case in some estuaries [16,17]. However, in estuaries where there is extensive mobilization of Mn from reducing sediments, dissolved Mn (in the form of Mn^{II} is added to the estuarine waters because the oxidation of Mn^{II} is slow as compared to that of Fe^{II} [12,52,53]. Results of the laboratory mixing experiments using Scottish rivers ([4–7], this study) sug-

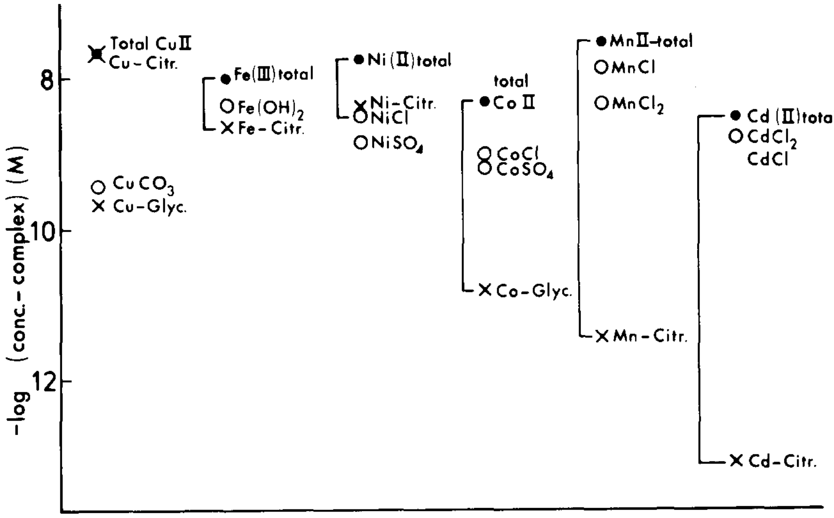


Fig. 8. Synthesis of data from a chemical speciation model of seawater (S = 35‰) by Stumm and Brauner [35]. Concentrations [–log(mol/l)] of only the most dominant inorganic- and organic-trace metal ligands are shown for Fe^{3+}, Cu^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+} and Co^{2+}. Total dissolved organic carbon equals 2.3 mg C/l. The dissolved organic carbon consists of a mixture of acetate, citrate, tartrate, glycine, glutamic acid and phthalate, each present at 7 × 10^{-6} mol/l. Citr = citrate; Gly = glycine.

gest that the removal of a certain fraction (25–45%) of dissolved Mn is a result of the catalytic effect which ferric hydrous oxide substrates have on the oxidation and precipitation of Mn^{II} from aerated water [52,53]. The question remains why Mn behaves conservatively in certain estuaries which have large-scale removal of Fe [16,17]. The answer may lie in the fact that the river waters of these estuaries have significantly higher ratios of dissolved Mn/Fe than do the Scottish rivers (0.28 compared to 0.037 and smaller).

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