

BEHAVIOR OF SOME TRACE CHEMICAL CONSTITUENTS IN ESTUARINE WATERS

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Abstract - The major variations in physicochemical conditions within estuaries give rise to the possibility of non-conservative (chemically interactive) behavior of some of the dissolved substances during the mixing of river and sea waters, with consequent modification of the flux of riverborne dissolved material to the open ocean. Approaches to the study of the behavior of trace constituents in estuarine systems have relied primarily upon environmental surveys of variations with salinity in the concentrations of individual constituents in the dissolved fractions. Better understanding of the processes involved in the interactions of dissolved and particulate material is obtainable from environmental studies in which a group of constituents, the behavior of which may be inter-related, is examined, with relevant measurements on particulate fractions. Complete descriptions of chemical speciation in these systems cannot be obtained for the trace constituents by present methods. Analytical resolution of dissolved and particulate material into further operationally defined fractions, and the simulation of processes in model solutions, including modified natural waters, can give valuable information, however, on the mechanisms of interactive processes. These approaches are illustrated by recent findings on trace constituents in the Beaulieu Estuary, with particular reference to the behavior of iron and selenium.

INTRODUCTION

There are several reasons for the increased attention recently given to the behavior of trace constituents in estuarine and coastal waters. The transition zone between fresh and sea waters is of intrinsic geochemical importance because of the complex interplay between major geochemical variables which occurs there. Perhaps the most important consequence in terms of the sedimentary cycle is the possible modification which estuarine interactions may bring about in the input of dissolved materials from rivers to the open seas. An understanding of the pathways of element transference in estuaries is essential also for prediction of the results of man's influence on estuaries, through waste inputs and modifications of physical and sedimentological conditions. This paper gives a brief summary of problems and approaches in estuarine chemistry, illustrated mainly by reference to recent investigations on trace constituents, undertaken in this Laboratory, on the Beaulieu Estuary and Southampton Water, which are parts of the Solent estuarine system.

PROBLEMS AND APPROACHES

A generalised framework for the consideration of estuarine reactions is shown in Fig. 1. The physical mixing of fresh and sea waters, which are very different in composition as regards both the dissolved and particulate material, may be accompanied by chemical interactions, arising through the marked changes in major variables (Ref. 1). The total dissolved salts range from a global average value of around 0.1 g l^{-1} for river waters to over 30 g l^{-1} for sea water, the ionic strength thus ranging up to > 0.6 . Sea water has a limited range of pH, usually within 7.5-8.1; river waters usually show values between 6.5-8.5 but may vary more widely. Suspended particulate concentrations are most commonly in the range $0.01-1 \text{ g l}^{-1}$. The major variations in redox potential in estuaries arise through the consumption of dissolved oxygen and, under anoxic conditions, other oxygen sources such as sulphate, in the microbial decomposition of organic matter. They occur primarily along vertical sections, with a relatively abrupt change from high to low pE generally occurring at a boundary below the interface of the sediments and overlying waters, although this boundary may sometimes occur at this interface or in the water column. Such redox variations are a major factor in establishing concentration gradients leading to exchanges of material between the interstitial waters of bottom sediments and the overlying waters.

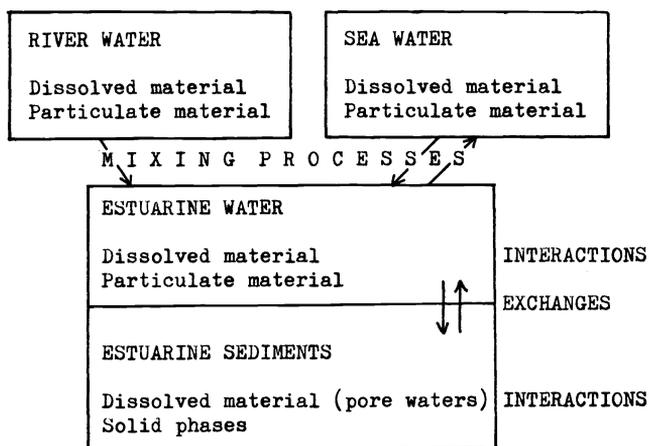


Fig. 1 Schematic representation of estuarine chemical processes.

While these diagenetic processes may generate locally significant fluxes and can be important in altering element distributions within the column of deposited sediment their role in supplying dissolved material to the estuary appears to be of much less importance than that of rivers (Ref. 2). There has thus been a major emphasis in estuarine chemistry on the mixing series between the riverine and marine end-members in the estuary. The compositions of individual rivers differ widely and for a given system large temporal variations may also occur (Ref. 3). Coastal sea water has a more uniform composition. With the exception of silicon, the major dissolved components in the river supply (calcium, sodium, magnesium, potassium, bicarbonate, sulphate and chloride) have average concentrations which are lower than in sea water so that the typical gradients for these elements are in the same direction as that of salinity, whereas minor constituents include some with generally a marked positive correlation with salinity and others with generally an inverse relationship. These features are illustrated in Table 1 for specific elements of interest. In considering these data the very wide variations in the compositions of individual rivers must be borne in mind.

Table 1. Estimated average concentrations of some dissolved trace constituents in the global river water supply and in coastal sea water (see Note 1)

Constituent	Concentration	
	$\mu\text{g l}^{-1}$	
	River water	Sea water
Lithium	3	170
Manganese	7	0.4
Iron	700	< 10
Copper	7	< 1
Zinc	20	2.5
Molybdenum	1	11
Barium	10	10

Note 1. Information on the selection and sources of these data is given in Ref. 1.

Behavior of dissolved constituents during estuarine mixing

The substantial changes in physicochemical conditions within an estuary give rise to the possibility that as mixing occurs the concentration of an individual dissolved constituent may show departures from the conservative, or chemically non-interactive, behavior corresponding to simple mixing (see Note a). Apart from the possible influence of other inputs, such as the diagenetically mediated inputs discussed above, and, in extreme cases, changes due to addition or removal of water itself, non-conservative behavior, if unequivocally established, is an indication of exchanges of material between dissolved and particulate forms. The behavior of the suspended particulate material is more difficult to interpret than that of dissolved material, mainly because of the complicated pattern of gravitational settling and sediment resuspension.

Information on behavior during estuarine mixing has mostly been obtained using a survey approach. Samples of water are collected over the whole range of salinities and the relationship between the concentration of the constituent of interest and the salinity, or other index of conservative mixing, is compared with the theoretical dilution line which describes the conservative mixing of the riverine and marine end-members. This approach has been discussed and reviewed by a number of workers (Ref. 1, 4 & 5).

Evidence on the behavior of a number of constituents has been obtained in this way. The removal of the operationally defined fraction of dissolved iron when iron-rich river water mixes with more saline water has been particularly well established (Ref. 4, 6 & 7) and there is evidence for reversible sorption reactions of phosphate in some circumstances (Ref. 8). The behavior of dissolved silicon may be somewhat variable between estuaries; despite numerous studies it is not clear whether typically it behaves entirely conservatively but recent evidence (Ref. 4 & 5) is generally against the occurrence of large scale removal in non-eutrophic estuaries.

The main limitations of the survey approach are:

- (1) It is informative, in practice, only for those constituents which show a marked inverse relationship with salinity. Although a constituent which is enriched in the marine end-member may show conservative or non-conservative behavior, it is not possible to make deductions as to the fate of the river input in such a situation.
- (2) In some estuaries uncertainties arise because of hydrographic factors. The presence of subsidiary input sources with concentrations which differ from that in the primary source can render interpretation difficult. In estuaries with long residence times or with rapid fluctuations in input concentrations the presence in the estuary of various water masses which are not part of a constant mixing series can be a further complication.
- (3) Even with a suitable gradient of concentration and a favourable environment for study, it is often difficult to establish removal unequivocally if the extent is small (less than about 10-15% of the input concentration). This is because of the scatter of environmental data and remaining marginal uncertainties stemming from the hydrographic factors already discussed.

The alternative approach of examining concentrations in particulate phases is, as previously indicated, more difficult to apply, although it can be of value in complementing measurements of dissolved material. For many elements changes in particulate concentrations due to estuarine processes, which are significant in terms of the dissolved concentrations, are too small to be detected with certainty against the background concentrations already present in the solid phases. Selective analysis of authigenic phases may be helpful in this respect. The complexity of sediment transportation processes in many estuaries also makes the approach equivocal. Changes in the concentrations of trace metals in the particulates accumulated in bottom sediments have been advanced as evidence for large-scale desorption processes in certain estuaries (Ref. 9). They are also explicable, however, in terms of a sediment mixing model (Ref. 10). Variations of concentrations in solid phases with factors such as particle size and mineralogy must be borne in mind in any comparisons of their compositions.

Difficulties in the interpretation of environmental findings led Sholkovitz (Ref. 11) to adopt a "product" approach. In this, filtered samples of river and sea waters were mixed

Note a. The term interactive is used here with respect to the analytical concentration of the constituent and refers to transfer to or from the analytically defined dissolved fraction. Interactions within the dissolved fraction, which are important in relation to the activities of constituents, are not considered in this context.

to give samples of intermediate salinities and subsequently any flocculated material formed after mixing was removed and analysed. This approach usefully complements environmental studies but two points should be noted. First, the interactions leading to removal may be considerably modified in the presence of previously existing solid phases; this has been demonstrated in laboratory experiments on iron (Ref. 12) and silicon (Ref. 5). Secondly, the experimental mixing procedures do not simulate the continuous gradient of salinity actually encountered by river inputs in estuarine mixing.

Chemical speciation

Most of the information available for trace constituents in river and estuarine waters is for dissolved and particulate fractions resolved by conventional filtration techniques, usually employing cellulose ester membrane filters of approximately 0.5 μm average pore diameter. Such filters will under all circumstances retain particles much smaller than the specified pore diameter and their properties of retentivity vary according to sample volume and particulate concentration. The arbitrary nature of the distinction has always been recognised but for many purposes it is adequate and alternative approaches are impracticable for any kind of routine analysis, such as in monitoring surveys. For some components, however, the operational definition of a dissolved fraction in this way is unsatisfactory, since macromolecular, polymeric and colloidal species are included along with species in true solution for which the cut-off lies between 1 and 10 nm. Examples of such components are considered in detail in the subsequent account of the relationships between iron and dissolved organic material in natural waters.

Analytical procedures are usually intended to measure, within the arbitrarily defined dissolved fraction, the total concentration of the element, but it has become recognised that for some elements a fraction may be present which is only measured by the method if specific steps are introduced to render it available. For many analytical purposes an initial concentration and separation stage is essential since sensitivities are frequently inadequate for direct determination and selectivity is often insufficient to cope with matrix effects. In such a procedure chelating groups, for example in a chelating resin or a complexing agent dissolved in an immiscible solvent, may be used to achieve selective concentration. Fractions of elements may occur which are very strongly complexed, held in thermodynamically non-labile complexes, in colloidal associations, or in the form of compounds which do not react with the ligands employed, and which are thus unavailable. Perturbation of the system, for example by destroying organic material or by drastically altering the pH, can render such fractions available. Comparisons of the values of treated and untreated aliquots thus enables fractions to be defined in an operational sense. These fractions cannot be identified unequivocally with specific chemical entities, however, partly because the nature of the species present is itself uncertain, and partly because the resolution is operationally rather than fundamentally defined.

Copper affords an excellent illustration of these points. Information on this element has been summarised in more detail elsewhere (Ref. 1). It shows that the analytical decomposition of the organic material in a sample of river or estuarine water leads to an increase in the available concentration of copper. The best method available for this process is photo-oxidation with ultraviolet radiation. The fraction of copper thus defined by difference may represent that part of any organically associated copper which is not available to the complexing agents used for concentration. Another fraction of organically associated copper can be measured by extraction of the element into an organic solvent, such as chloroform, without the addition of a complexing agent. These operationally defined fractions are, not surprisingly, different in magnitude and it appears that neither represents the total organically associated copper. The gradients of copper in the Beaulieu Estuary and Southampton Water are not sufficiently marked to enable deductions to be made as to the extent of any non-conservative behavior (Ref. 13 & 14). The larger values for these fractions in estuarine and coastal waters (Ref. 1) as compared with open ocean waters (Ref. 15), however, show that there is a difference in speciation between these zones.

The use of such analytically defined fractions in studies of speciation is of value only in the absence of techniques for the identification and determination of individual chemical species or groups of similar species. The difficulties in determining these species for trace constituents arise in two ways. First, the concentrations concerned are generally very low and are outside the range of most direct methods of investigation. Secondly, there is an inadequate theoretical basis for modelling the speciation as a guide to analytical approaches. This largely reflects the fact that there is a considerable concen-

tration (usually 1-10 mg l^{-1}) of dissolved organic carbon in natural waters much of which is uncharacterised in terms of its detailed chemical structure. In river waters the uncharacterised material consists of terrestrially derived humic substances whereas in the ocean it is dominated by material produced in situ which has some structural

resemblances to such compounds. Despite advances in characterising the metal-binding properties of these compounds (Ref. 16) their role in complexation has not been fully clarified. A primary reason for this is that the equilibrium modelling approaches used to consider associations with inorganic ligands have uncertain applicability to systems containing organic molecules of this kind (Ref. 1). An additional consequence of the complexity of the dissolved organic material is the general use made of measurements of the total dissolved organic carbon, rather than of individual compounds or groups of compounds, in studies on natural waters.

There is also a major interest in the oxidation states of certain trace constituents in natural waters. The limitations of equilibrium modelling are compounded in this area with additional uncertainties arising because the redox potential in such systems, and its control, are poorly comprehended (Ref. 17). The presence of complex organic material, among other factors, affords possibilities for the kinetic stabilisation of thermodynamically unstable oxidation states. Selective techniques for the measurement of particular oxidation states are thus of great value in environmental studies, especially for those elements, such as selenium and chromium, which show redox speciation which clearly differs from that corresponding to an equilibrium system.

The particulate material in natural waters comprises a wide variety of phases of diverse origins - for example, living and detrital organic material, lithogenous and authigenic inorganic phases. Selective chemical leaching techniques can be used to make partial resolutions of the components and to examine the related associations of trace constituents, but the limitations of their selectivity must be appreciated (Ref. 18).

STUDIES ON THE SOLENT ESTUARINE SYSTEM

The remainder of this paper summarises some recent investigations which illustrate the general aspects discussed above and the value of more detailed analytical resolutions within the dissolved and particulate fractions.

Most of the work described was undertaken on the Beaulieu Estuary. The River Beaulieu is a minor stream entering The Solent. It drains heathlands and bogs of the New Forest and shows concentrations of dissolved iron and organic matter which are fairly similar to global average values and a high concentration of dissolved manganese. The marked gradients of concentration which arise in the estuary afford suitable opportunities for studying interactive processes. In an earlier study (Ref. 7) the behavior of dissolved iron was shown to be markedly non-conservative with extensive removal in early mixing and almost complete removal of the element, relative to the river input concentration, by the time the salinity reaches 15‰. The River Beaulieu contrasts markedly with the larger rivers, the Test and Itchen, discharging to The Solent through Southampton Water. These drain dominantly limestone areas and have much lower concentrations of the above constituents.

It is obvious on the basis of solubility equilibria that concentrations of iron as high as

$100 \mu\text{g l}^{-1}$ or more, as found in the River Beaulieu, must reflect the presence of iron in a colloidal or complexed form. Observations that such high "dissolved" concentrations are commonly associated with high levels of dissolved organic matter have suggested the involvement of this material in the mobilization of iron. Some workers, notably Shapiro (Ref. 19) have considered that organic matter may stabilize inorganic colloidal forms of iron. It has also been suggested that iron is transported in rivers dominantly as organic complexes (Ref. 20). Removal of iron on mixing with more saline waters could occur by several processes, depending upon the speciation in the fresh water input. Any flocculation of organic material occurring as a result of changes in ionic strength could lead to removal of associated iron. The presence of increased concentrations of ions such as calcium could lead to displacement of iron from labile complexes, with subsequent precipitation. Iron initially in the form of colloidal hydrous oxide would likewise precipitate as a result of destabilization with increase in ionic strength.

In order to elucidate the behavior of iron in relation to that of organic matter a study (Ref. 14) has been made in which samples from the River Beaulieu were analysed for dissolved organic carbon (DOC), using photo-oxidation in conjunction with non-dispersive infra-red analysis of carbon dioxide (Ref. 21), and for dissolved iron and manganese by atomic absorption spectrophotometry. These dissolved fractions are defined on the basis of filters of $0.45 \mu\text{m}$ average pore diameter. Ultra-filtration with Diaflo ultra-filters was used to fractionate the dissolved organic material on the basis of molecular weight cut-offs (these are necessarily of somewhat arbitrary significance for complex material of this type) and the distributions of the DOC and iron between these fractions were examined. Corresponding measurements for DOC were made on the River Test. In addition the behavior

of DOC during mixing in the Beaulieu Estuary was examined. That of dissolved iron was known from earlier work (Ref. 7).

The distributions of the dissolved organic material between the different molecular weight fractions are similar for the two rivers despite their distinctly different concentrations of DOC (see Table 2). A small but significant fraction of the organic material has an apparent molecular weight range above 10^5 . Most of the material falls in the molecular weight range 10^3 - 10^5 . There is a marked difference in retention between the PM10 and UM10 ultra-filters which have the same nominal cut-offs. This is probably attributable to a somewhat higher cut-off in practice for the PM10 membranes and this, together with gel-filtration experiments (Ref. 14), suggests that much of the DOC is accounted for by material with a molecular weight distribution centred around 10^4 .

TABLE 2. Dissolved organic carbon in river waters and its fractionation by ultra-filtration (see Note 1)

Origin	Total concentration mg C l ⁻¹	Percentage retained by Diaflo ultra-filters				
		XM100	PM30	PM10	UM10	UM2
River Beaulieu	7.7	18	23	30	78	92
River Test	2.1	10	20	21	76	86

Note 1. Values shown are means of measurements on a number of samples collected on different occasions. The nominal molecular weight cut-offs of the ultra-filters are as follows: XM100, 10^5 ; PM30, 3×10^4 ; PM10, 10^4 ; UM10, 10^4 ; UM2, 10^3 .

The distribution of iron in ultra-filtrates (see Table 3) shows the element to occur dominantly (> 90%) in the molecular weight fraction above 10^5 . It is difficult to account for the difference in the molecular weight distributions of organic carbon and iron on the hypothesis that iron is mostly complexed with organic molecules since humic materials over a wide range of molecular weights all show metal-binding capacity. The most probable explanation for the distributions is that the iron is mainly present as a colloid stabilised by a small fraction of the DOC, which may be of lower molecular weight than is indicated by ultra-filtration. Further evidence for this view was obtained by laboratory model experiments (Ref. 14) which showed that ultra-filtered river water can maintain added iron in a "dissolved" state at levels two orders of magnitude above those in photo-oxidised aliquots.

TABLE 3. Fractionation of dissolved iron in River Beaulieu water by ultra-filtration (see Note 1)

Total concentration µg l ⁻¹	Percentage retained by Diaflo ultra-filters		
	XM100	PM30	UM10
136	98	98	99
138	93	-	-
314	90	91	-

Note 1. Values are shown for three different samples. The nominal molecular weight cut-offs are given in Table 2.

The data in Fig. 2 together with other similar results (Ref. 14), show the essentially conservative behavior of DOC in the Beaulieu Estuary. A small loss of DOC would not, however, be apparent in this approach and it is possible that the large scale removal of iron in the estuary is accompanied by the removal of some associated DOC, as might be predicted from the ultra-filtration data. This would accord with the results of mixing experiments carried out with other systems (Ref. 11).

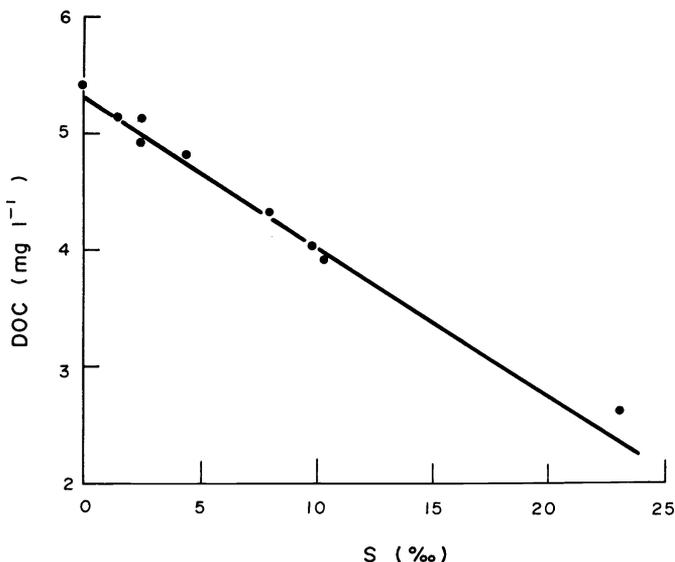


Fig. 2 Relationship between the concentration of dissolved organic carbon and salinity in the Beaulieu Estuary. Survey on 31st January, 1977 (Ref. 14).

The above findings also have considerable implications for our understanding of the fate of riverborne DOC in estuaries and in more open waters and these will be discussed elsewhere.

Measurements have also been made on particulate material in the Beaulieu Estuary (Ref. 22). Some data for particulate iron are shown in Fig. 3. A selective chemical leaching technique (Ref. 23) was used to resolve the lattice held material from other phases. The removal of iron from the dissolved input is reflected in the markedly non-linear changes in the percentage of non-lattice held iron in the particulate material over the range of salinities. The concentrations of particulate iron vary with salinity in a much less systematic way because of the substantial variations along the estuary in the amounts of particulate material in suspension. Their magnitudes, however, are greater than those for dissolved iron. In contrast, manganese is dominantly present in the dissolved form. River water concentrations

are high, typically around $100 \mu\text{g l}^{-1}$, and significant removal does not occur during estuarine mixing (Ref. 7 & 22). In the estuary, the percentage of non-lattice held manganese in

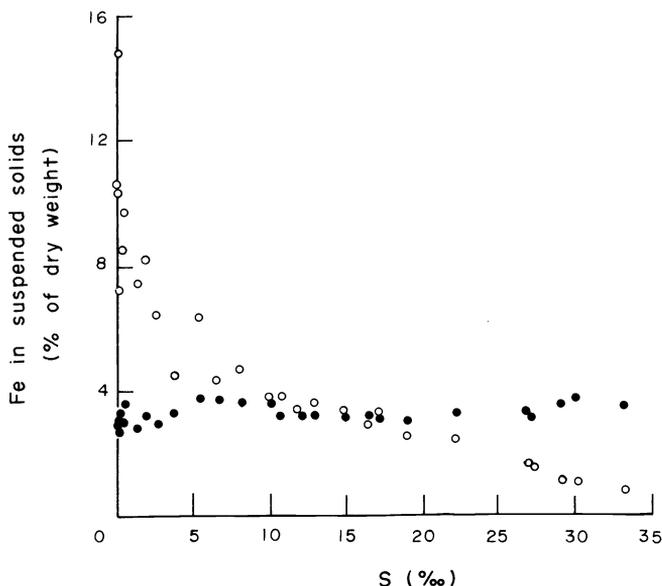


Fig. 3 The leachable (○) and non-leachable (●) iron contents of suspended material in the Beaulieu Estuary and their relationship with salinity (Ref. 22).

particulate material varies in an approximately linear manner with salinity reflecting simple mixing of riverborne and marine particles (Ref. 22). On ultra-filtration of the river water (Ref. 14) a negligible fraction of the dissolved manganese is found with the iron in the molecular weight range above 10^5 , according with the essentially independent behavior of the two elements in the estuary.

An example of analytical resolution of a single oxidation state of an element is afforded by recent measurements of selenium in rivers of the Solent system (Ref. 24). Determinations using a gas-liquid chromatographic method based upon, but considerably modified from, that of Shimoishi (Ref. 25) are specific for the selenium IV available for reaction with 4-nitro-o-phenylenediamine at pH 1. On photo-oxidation of natural waters there is a disproportionation between selenium IV and selenium VI and hence the total dissolved selenium may be measured.

The results (Table 4) show that concentrations of total dissolved selenium in the chalk rivers are considerably higher than in the more acidic River Beaulieu. With these higher concentrations the presence of available selenium IV can be detected but it amounts to < 10% of the total. The total dissolved selenium shows essentially conservative behavior during

mixing in Southampton Water with sea water containing about 130 ng l^{-1} . While the fractions measured are operationally defined they probably correspond well to the selenite and selenate species. The dominance of Se(VI) is expected from equilibrium calculations and the presence of a small fraction of Se(IV) is an interesting non-equilibrium phenomenon.

TABLE 4. Selenium in river waters

River	Calcium mg l^{-1}	Total selenium ng l^{-1}	Available selenium IV ng l^{-1}
Test	82	370	20
Itchen	85	250	18
Hamble	83	390	31
Meon	84	280	20
Beaulieu	28	85	< 2

CONCLUDING COMMENTS

In these investigations detailed resolutions of certain components have been made with an emphasis on constituents which either behave in a related way (e.g. iron and DOC) or show differences which can give insights into estuarine geochemical processes (e.g. iron and manganese). The complementary role of experimental modelling of the effects of organic material on chemical speciation has been briefly mentioned and is discussed more fully elsewhere (Ref. 1 & 26). The use of photo-oxidation to prepare organic-free natural waters with minimal perturbation of other chemical properties affords a powerful tool for such experiments. Recreation of environmentally observed phenomena by addition to such a solution of specific organic compounds or organic material separated from natural waters can give important information on the nature of these phenomena. The use of ultra-filtration for the separation of naturally occurring organic material on a basis nominally of molecular weight suggests a valuable extension of approaches. Thus a natural medium may be simplified by the breakdown of organic matter and then reconstituted stepwise for experiments on its effects on inorganic constituents using a variety of techniques, among which radio-chemical and electrochemical methods are especially valuable.

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