Sorption Model for Dissolved Aluminium in Freshwaters

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Abstract. A series of aluminium speciation measurements were made in the freshwaters of the Yare and Great Ouse rivers (England). Samples were analysed for dissolved and particulate Al, suspended particulate matter (SPM), and other allied chemical species in order to assess the role of sorption processes on the suspended phases in controlling dissolved Al levels. Partitioning of Al occurs between solid and solution phases with a distribution coefficient (K_d) which varies over about one and a half orders of magnitude for suspended particle concentrations of comparable magnitude. A sorption model is proposed for dissolved Al concentrations in these freshwaters with most of the data fitting the model defined by a zone with K_d values of 0.316×10^6 and 10^7. However, a few data points lie outside this zone, suggesting that other processes may also influence dissolved Al distributions. Nevertheless, the model may serve as a starting point for predicting concentrations of dissolved Al in rivers where SPM levels are moderate to high (>1 mg l^{-1} but <75 mg l^{-1}), and indeed, this model works reasonably well for the Conway system (Wales). Further, the empirical distribution coefficient, K_d, decreases with increasing suspended particle concentration, which may be due in part to colloidal phenomena.

Key words: river water, dissolved aluminium, partitioning, sorption model, particle concentration effect

1. Introduction

Aluminium occurring in minerals is generally inert and is largely insoluble in weathering reactions. However, during physical and chemical weathering processes, aluminium is mobilized as (oxy)hydroxide and silicate minerals and is transported by land runoff and as aerosols into the hydrosphere. Most of it undergoes sedimentation, while the remainder is subjected to a slow dissolution process, of which only a small portion passes into solution. The solubility of Al from gibbsite and aluminosilicates is basically pH-dependent being more soluble when pH is both low and high (May et al., 1979; Drever, 1982); therefore, aluminium solubility in the usual pH range (6–7) of natural waters is quite low.

In simple aqueous solution of pH < 4, the chemistry of aluminium is characterized by hydration of highly soluble Al^{3+} ion with the formation of the Al(H$_2$O)$_6^{3+}$

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coordinated complex. At pH values above 4, the aquoaluminium(III) ion undergoes rapid hydrolysis yielding sparingly soluble hydrolysed species. Due to this speciation characteristics of dissolved Al, the solubility of Al exhibits a minimum with the production of solid phase ($Al(OH)_3(s)$) which occurs usually in the pH range 5.5–6.5 (May et al., 1979). With the rise in pH (i.e., pH > 7), the solubility of Al increases rapidly as the hydrolysis proceeds further with the formation of $Al(OH)_4^-$ species (May et al., 1979; Krauskopf and Bird, 1995).

The aqueous chemistry of Al is quite complex, and its reactivity in solution is unmatched by many other soluble metal ions. There is some similarity in the chemistries of Al and Th in natural waters, both being highly particle-reactive (Huh and Bacon, 1985). Similarly, Al^{3+} and Fe^{3+} ions in the normal pH of natural waters form complex colloidal (oxy)hydroxy species that eventually coalesce and precipitate (Bruland, 1983). Coprecipitation with Si and sorption processes at the sediment-water interface may further restrict the aluminium solubility and/or enrichment in natural waters (Willey, 1975; Paces, 1978; Mackin and Aller, 1984a; Walker et al., 1988). As a result, aluminium, the third most abundant element in the earth's crust, occurs predominantly in colloidal and particulate forms while being essentially a trace dissolved constituent of natural waters.

Aluminium forms strong complexes with natural organic matter (Lind and Hem, 1975; Stevenson and Vance, 1989), and hence, organic complexing will allow much higher concentrations of Al to be leached into solution than would be predicted simply from a consideration of the inorganic solubility of gibbsite. Dissolved Al concentrations reported by Beck et al.(1974) for the organic rich waters of the Satilla river are considerably higher than for rivers where the inorganic constituents are dominant, and indeed, a moderately good correlation ($r = 0.943$) exists between concentration of dissolved Al and dissolved organic matter (DOM) (Perdue et al., 1976). In addition, the high correlation ($r = 0.984$) between the sum of dissolved Al and Fe concentrations and DOM in this river further suggests that the total solubility of these two metals is determined by the complexing capacity of the DOM (Perdue et al., 1976).

Many other rivers rich in DOM have also been reported to contain high levels of dissolved Al (Sholkovitz, 1976; Van Bennekom and Jager, 1978; Crerar et al., 1981; Mackin and Aller, 1984b). Organic ligands bind aluminium sustaining a larger fraction of dissolved Al in acidic solution, but such complexation is weakened at pH > 6 (Lind and Hem, 1975).

Aluminium is mobilized largely in acidic surface water from shallow, acidic soils in upland regions. Organic forms of Al appear to originate in the organic horizon of soil, while inorganic Al species are mostly derived from the mineral soil fraction (Driscoll, 1989). As waters migrate over larger drainage areas, stream acidity is neutralized by the release of basic cations from the underlying bedrock/thicker deposits of soil and/or removal of strong acid anions (e.g., SO_4^{2-} or NO_3^-) through biological reduction processes (Driscoll, 1989; Andrews et al., 1996). This results in lower dissolved aluminium concentration.

The concentrations of dissolved Al in freshwaters of the world's major and minor rivers are highly variable, ranging from 0.07 to 130 μM (Gibbs, 1972; Beck et al., 1974; Hydes and Liss, 1977; Bowen, 1979; Mackin and Aller, 1984a, b; Morris et al., 1986; Upadhyay and Sen Gupta, 1995). This wide range of aluminium solubility in freshwaters is believed to be the result of differing pH conditions, occurrence of various inorganic species reacting with aluminium, and varying concentrations of DOM (Perdue et al., 1976; May et al., 1979; Cronan et al., 1986; Andrews et al., 1996).

Although it is well-known that sorption processes onto suspended phases most often govern the dissolved levels of many trace metals (Morel and Gschwend,1987), this effect has been generally discounted for dissolved Al in freshwaters due to insufficient data and because of the large influence of pH and DOM on the solubility of mineral phases of Al in natural waters. In the present study, an attempt is made to unravel the role of SPM in the distribution of dissolved Al in freshwaters.

2. Methods

2.1. STUDY AREA

The study sites were located in two rivers, the Yare and the Great Ouse, in the East Anglian region, England. The catchment areas in this region consist of basal rocks formed from the Pleistocene crag deposits and those of an earlier chalk sea (Larwood and Funnell, 1970). The solid geology is exposed only in the river valleys and elsewhere is overlain by the chalky boulder clay of the Quaternary glaciation. The lithology of the whole region is thus essentially calcareous being covered locally by sand, clay and alluvial soils. The river beds are largely covered by flint gravel with silt along the banks; chalk is exposed in a few places where scour is sufficiently strong (Edwards, 1973).

The riverine transects which were undertaken for investigation in this study comprised the freshwater region extending from the landward limit of the estuary (defined here as river-sea confluence with salinity of waters $> 0.2 \times 10^{-3}$) for over a few miles upstream. Tidal rise and fall of water levels were perceived in most parts of the sampling region and there were considerable variations in SPM levels and other geochemical parameters in these freshwaters.

2.2. SAMPLING

Monthly sampling in the Yare and Great Ouse riverine study sites was done on seven and three occasions, respectively, during 1994–1996 (see tables in the next section for sampling dates). Surface (approximately 0.5 m below the surface) water samples were collected in an acid-cleaned polyethelene bucket and stored unfiltered in acid-cleaned polyethylene bottle (for Al and Si analysis) and glass bottle (for pH and salinity determination). Samples (a 250 ml portion) for dissolved Al

and Si were filtered through acid-cleaned 0.45 μm Millipore membrane filters in an acid-cleaned all plastic Millipore filtration apparatus within 2 to 3 h of collection. The filters were dried in an oven at a constant temperature of 60 °C for 72 h, to a constant weight, and then weighed for the determination of SPM (Upadhyay, 1998).

2.3. CHEMICAL ANALYSES

pH of the water samples was measured within 2 to 3 h of collection in the laboratory with a precision of ±0.05 pH units. Salinity was measured (precision $\leq1\%$) using the Mohr–Knudsen chlorinity titration. Dissolved Si was determined spectrophotometrically with a precision of $\leq5\%$ by the ammonium molybdate-ascorbic acid method (Grasshoff et al., 1983).

Natural fluorescence (F_N) of the water samples was routinely measured as a part of the dissolved Al analysis. This fluorescence is thought to result from a component of the dissolved organic matter (DOM) present in natural waters and is believed to represent an approximate measure of DOM concentrations in river/estuarine waters (Van Bennekom and Jager, 1978; Mopper and Schultz, 1993). It is subsequently referred to as DOM. This is, however, not an absolute value, only a relative proportion, since direct measurements of DOM on these samples were not done.

Dissolved Al was analyzed using fluorescence technique within one week of sample collection by the lumogallion method of Hydes and Liss (1976), which has been described before (Upadhyay and Sen Gupta, 1995). Short term storage of a few weeks at 4 °C for dissolved Al analysis has been found to be satisfactory (Hydes and Liss, 1977). Upadhyay (1998) has also carried out the time series analysis and found one week storage is indeed satisfactory. The reagent blank was determined by the difference of the fluorescence yields between portions of deionised water containing normal and twice the normal amounts of reagents. Reagent blanks corresponded to ~0.002 μM Al. The estimated standard deviation of the reagent blank was ±0.0007 μM Al for 10 replicates. This yields a detection limit of about 0.002 μM Al (3 sd of the blank) for the method. The precision of the analysis based on triplicate measurements was usually within $\pm5\%$.

The lumogallion method does not detect Al in a more complex form such as mineral particulates (Measures et al., 1984) or strong Al organic complexes of stronger organic ligands than lumogallion (Hydes and Liss, 1976). However, the method is sensitive to monomeric and colloidal Al species (Hydes and Liss, 1976, 1977); therefore, the dissolved Al species determined in filtered sample (through 0.45 μm Millipore membrane filter) are essentially Al in true solution in addition to Al in colloidal suspension.

Particulate Al was determined on the SPM retained by the 0.45 μm Millipore filter using an acetic acid leaching technique. This method has been applied previously (Orians and Bruland, 1986; Moran and Moore, 1988) for the determination of

surface-bound exchangeable (particulate) Al for open ocean and coastal waters. For further testing the method, experiments were carried out to investigate the kinetics of dissolution of the particulate Al from the SPM of these freshwaters (Upadhyhay, 1998). In the method, the filters are treated with 25% acetic acid (pH $\sim$ 2.2) for 24 h and the leachate (5 ml) was neutralised to pH 7.2 ± 0.1 using ammonium hydroxide. The mixture was then diluted to 50 ml and centrifuged at 3000 rpm for 30 min to sediment the particles, and the supernatant was analysed in the same manner as for dissolved Al.

The blanks for particulate Al were determined on three blank filters for each set of analyses being treated similarly, except that deionised water was filtered instead of sample. Blanks for particulate Al were typically about 0.075 μM Al and the standard deviation of the blanks was similar to that measured (± 0.0007 μM Al) in dissolved Al analysis. Thus, the precision of the analysis was good ($\pm 7\% \leq$ 0.15 μM $> \pm 5\%$), as particulate Al concentrations were generally high.

The selectivity of the acetic acid leaching technique for surface-bound exchangeable (particulate) Al is an assumption in this study. This may not be a quantitative estimate of truly surface-bound reactive fraction of Al available for solid-solution exchange reactions. This measurement is potentially a function of particle size, type and amount. A portion of the Al released in such an extraction may be that which is bound into structurally associated particles. Therefore, it is stressed that the particulate Al measurement presented here is an operational reactive component of the total which is assumed to participate in dissolved-particulate interactions.

3. Results and Discussion

3.1. FLUVIAL GEOCHEMISTRY

As noted earlier, the freshwaters (salinity $\leq 0.2 \times 10^{-3}$) studied here had no interactions with seawater. The data on various geochemical parameters obtained from these waters during different surveys in the Yare and Great Ouse rivers are summarized in Table I and Table II, respectively.

The Yare river water was alkaline with pH of 7.8–8.9. The relatively high pH of the Yare river results from the calcareous nature of its drainage basin (Hydes and Liss, 1977). Suspended loads and dissolved Si in these freshwaters were variable ranging from 1 to 34 mg l^{-1} and 61 to 155 μM, respectively. Concentrations of dissolved Al were also variable ranging from 0.01 to 0.1 μM. In an earlier study, very similar dissolved Al concentrations (0.12–0.16 μM) were observed in these waters (Hassan, 1988). The relatively low dissolved Al in the Yare river is characteristic of the basic waters of many East Anglian rivers (Hydes and Liss, 1977).

The Great Ouse river water was also alkaline with pH of 7.6–8.7, similar to the Yare system. Suspended loads and dissolved Si in these freshwaters were variable ranging from 1 to 74 mg l^{-1} and 25 to 175 μM, respectively. Concentrations of dissolved Al in the Great Ouse river were also variable ranging from 0.03 to

Table I. Properties of the waters of the Yare river

Sampling Period	Salinity ($\times 10^{-3}$)	pH	F_N	Dissolved Si (μM)	Dissolved Al (μM)	Particulate Al (μM)	SPM (mg l^{-1})
May	0.18	7.81	16	61	0.017	0.300	1.0
1994	0.19	7.86	16	64	0.012	0.380	2.3
June	0.22	8.08	12	75	0.027	0.372	23.3
1994	0.22	7.86	12	75	0.026	0.384	21.9
	0.23	7.84	12	75	0.030	0.280	19.3
September	0.22	7.96	13	94	0.051	1.645	1.6
1994	0.16	7.97	12	130	0.049	1.274	1.9
	0.22	7.99	16	130	0.071	1.540	2.0
	0.22	7.98	15	137	0.073	1.930	1.5
	0.22	7.99	14	139	0.072	1.761	1.8
	0.22	7.99	13	139	0.067	1.544	3.0
	0.22	8.00	13	141	0.064	1.158	9.1
	0.22	8.00	13	142	0.064	1.969	34.1
October	0.10	8.32	13	130	0.086	1.046	7.3
1994	0.05	8.25	12	127	0.045	0.546	5.3
July	0.11	7.91	11	102	0.102	0.546	7.1
1995	0.11	7.92	12	145	0.032	0.591	9.6
	0.22	8.06	12	153	0.036	1.046	19.4
	0.22	8.08	12	155	0.033	1.296	26.7
	0.22	8.06	12	154	0.032	1.341	27.5
April 1996	0.11	8.13	9	–	0.052	0.507	8.8
May 1996	0.10	8.89	9	–	0.069	1.038	25.7

0.3 μM. The relatively high dissolved Al concentrations (0.2–0.3 μM) observed during July 1996 (Table II) are possibly due to the occurrence of high pH (8.2 - 8.7) in the river water which is likely to enhance the solubility of Al-bearing solid phases in these freshwaters (May et al., 1979). With the exception of these high values, the generally low dissolved Al concentrations (0.03–0.1 μM) in the Great Ouse river conform with the observations in the Yare river and are consistent with the characteristics of the East Anglian rivers (Hydes and Liss, 1977).

Table II. Properties of the waters of the Great Ouse river.

Sampling Period	Salinity ($\times 10^{-3}$)	pH	F_N	Dissolved Si (μM)	Dissolved Al (μM)	Particulate Al (μM)	SPM (mg l^{-1})
October	0.11	7.61	16	82	0.033	0.068	1.1
1995	0.15	7.72	13	101	0.097	0.429	2.2
December	0.11	7.67	15	163	0.061	0.520	1.2
1995	0.11	7.65	16	174	0.070	0.384	1.6
	0.11	7.61	15	175	0.070	0.520	1.4
	0.16	7.58	18	117	0.032	2.362	50.2
	0.16	7.58	18	117	0.033	3.717	73.6
	0.16	7.58	17	118	0.035	3.435	62.7
	0.22	7.61	16	123	0.036	1.672	47.7
July	0.16	8.21	10	30	0.250	0.741	8.0
1996	0.16	8.21	10	38	0.209	0.420	5.8
	0.16	8.47	10	52	0.238	0.618	14.1
	0.20	8.72	10	25	0.274	0.667	10.5

3.2. THE INFLUENCE OF PH, DOM, AND DISSOLVED SI ON RIVERINE CONCENTRATIONS OF DISSOLVED AL

Dissolved Al shows no regular trend with pH, DOM, and dissolved Si in the Great Ouse river (except a few high values which occur at high pH) so that no simple rationalisation with respect to these parameters is possible. In contrast, the corresponding data for the Yare river exhibit some patterning which warrants a more detailed discussion.

Dissolved Al vs. DOM, pH, and dissolved Si in the Yare freshwaters are plotted in Figure 1a–c. When the data for the individual sampling dates are considered separately, there appear to be no correlations between dissolved Al and the other variables, with the exception of F_N for September 1994. However, weak correlations are apparent when all the data are combined as a single set (the two high F_N and low dissolved Al points of May 1994 have been omitted from the linear regression (Figure 1a), with the fact that occurrence of both dissolved Al and Si at low concentrations is of some evidence for their removal through biological mechanism(s)). The covariance of dissolved Al with Si in the Yare river is similar to the observations in other rivers (Mackin and Aller, 1984a, b, 1986; Upadhyay and Sen Gupta,1995) presumably because of their common source, i.e., continental weathering whereas poor correlations with DOM and pH would suggest that these parameters do not exert a significant control on dissolved Al in these waters.

It appears that dissolved Si, DOM and pH may have some influence on the distributions of dissolved Al in these freshwaters but these parameters are not the
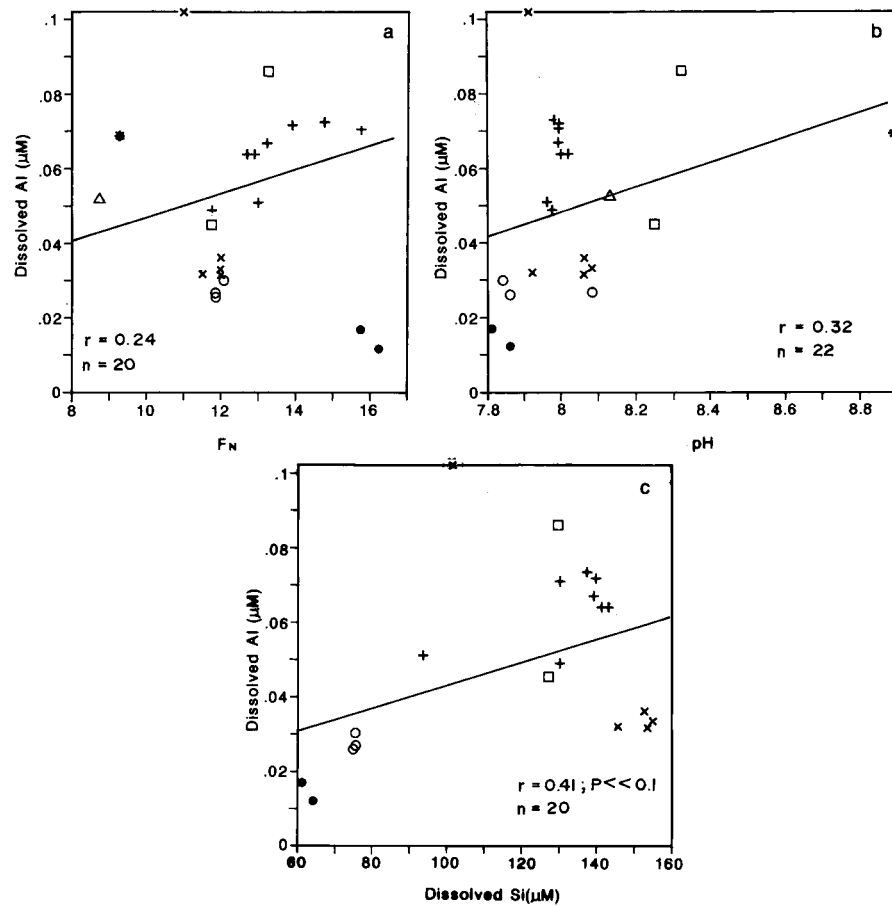
Figure 1. Dissolved Al as a function of (a) the fluorescent component of DOM (F_N), (b) pH, and (c) dissolved Si in the Yare river (symbols: ●, May 1994; ○, June 1994; +, September 1994; □, October 1994; ×, July 1995; △, April 1996; *, May 1996).

master variables. Most likely, a complex mechanism involving interaction between dissolved and particulate species operates influencing dissolved Al concentrations in these rivers. A model describing such interaction is presented in the next section.

3.3. SORPTION MODEL FOR DISSOLVED AL IN FRESHWATERS

The relationship between dissolved Al and SPM (Figures 2 and 3 insets) is of interest since it appears that dissolved Al concentrations have some kind of an interrelationship with suspended particulate load in the river water. Such a relationship suggests that soluble-particulate interactions may play a dominant role in controlling the concentrations of dissolved Al in freshwaters.

The solid line in Figure 2 (inset) is a semi-log least squares regression of the concentration of metal in solution against SPM (the two low Al data points of

May 1994 have been excluded from the curvilinear regression for the reasons cited earlier) in the Yare river. Despite some scatter in the data points, a good correlation exists which is statistically quite significant ($r = -0.52$; $P < 0.02$; $n = 20$). This is remarkable considering the wide range in background chemistry of waters in the Yare river at different times. Figure 3 (inset) depicts similar regressions (solid line for the overall data set excluding the low data point of October 1995 which is concomitant with low dissolved Si (Table II) attributable to biological removal (Rendell et al., 1997) and broken line for the data of December 1995 only) for the Great Ouse river. Although the correlation for the overall data set is poor ($r = -0.38$; $n = 12$), it is very good ($r = -0.98$; $P \ll 0.001$; $n = 7$) for the December observations. It appears, therefore, that the K_d approach (see below) may explain at least some features of the behaviour of dissolved Al in these rivers.

The partitioning of a trace metal between solid and solution phases in natural waters is often described by a conditional parameter, in terms of an empirical distribution coefficient, K_d, defined as

$$K_d = \frac{C_p}{C_d \times S} \tag{1}$$

(units ml g^{-1}), where C_p is the concentration of particulate metal (μM), C_d is the concentration of dissolved metal (μM), and S is the concentration of SPM (g ml^{-1}). This distribution coefficient has been used in several studies to address the soluble-particulate balance in the exchange of metal species in aqueous systems (Vuceta and Morgan, 1978; Nyffeler et al., 1984; Balls, 1988; Honeyman and Santschi, 1988). Indeed, K_d is relatively easy to measure in natural aquatic systems but, unfortunately, contrary to theory, the so-called equilibrium constants have been found to be variable and are not fixed ratios. Thus, this equilibrium model suffers from severe limitations; however, because of its simplicity and wide applicability, K_d continues to be a very useful geochemical tool in the study of trace metal partitioning and transport in natural waters.

This simple distribution coefficient has been shown to apply very well to solids with heterogeneous surface properties (Sposito, 1984; Campbell and Davis, 1996), and hence, this is perhaps the most appropriate approach to deal with more complex systems such as natural waters. However, the weight of sediment forming the adsorbing surface is only a poor approximation of the number of surface sites available for adsorption (Eyrolle et al., 1996). Further, the assumptions that the sorption reaction is completely reversible and an equilibrium is attained in the multiphase system may hold for open systems such as rivers/estuaries only if the time scales of interest are large compared to any physical, chemical and biological reaction times. In reality, however, kinetic constraints, imposed by reaction conditions, often prevent equilibrium from being attained (Tappin et al., 1995).

Trace metal K_d values are highly sensitive to particle type and can vary over several orders of magnitude as the chemistry of the aqueous phase changes (Leckie and Tripathy, 1985). The magnitude of K_d is also dependent on accurate measurement
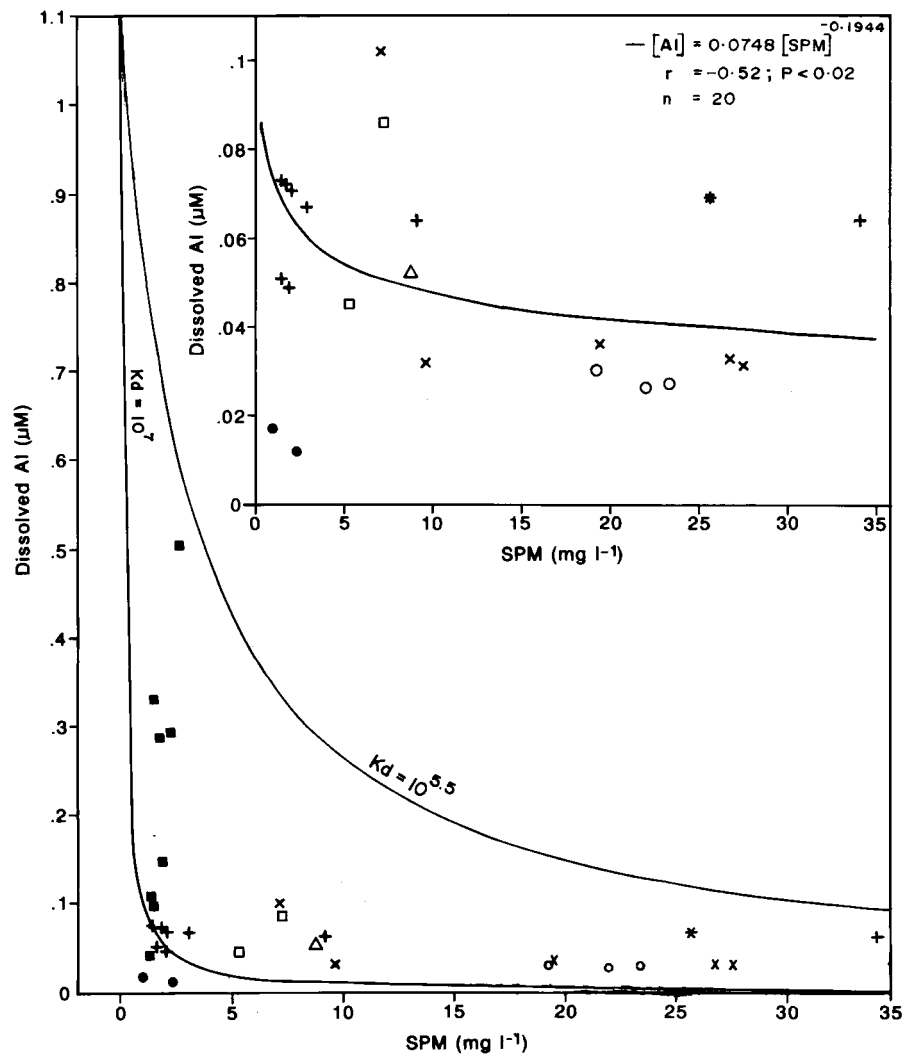
Figure 2. Dissolved Al as a function of SPM in the Yare river (the inset corresponds to the observed dissolved Al concentration in an expanded scale) (symbols as in Figure 1 with additional inclusion of the Conway data (■)).

of exchangeable particulate metal species, which is conditional on the type and strength of the chemical leaching agent used in the chemical determination of the particle-bound fraction (Tappin et al., 1995). In addition, because of the potential complexity of the speciation of metals in solution, especially in association with dissolved organic ligands, the analytical measurement of the dissolved metal may also not truly reflect the concentration which is available to enter into particle-water interactions (Tappin et al., 1995). Thus, K_d is both an empirical and a conditional parameter; it is simply a chemically intuitive approximation applicable only to the
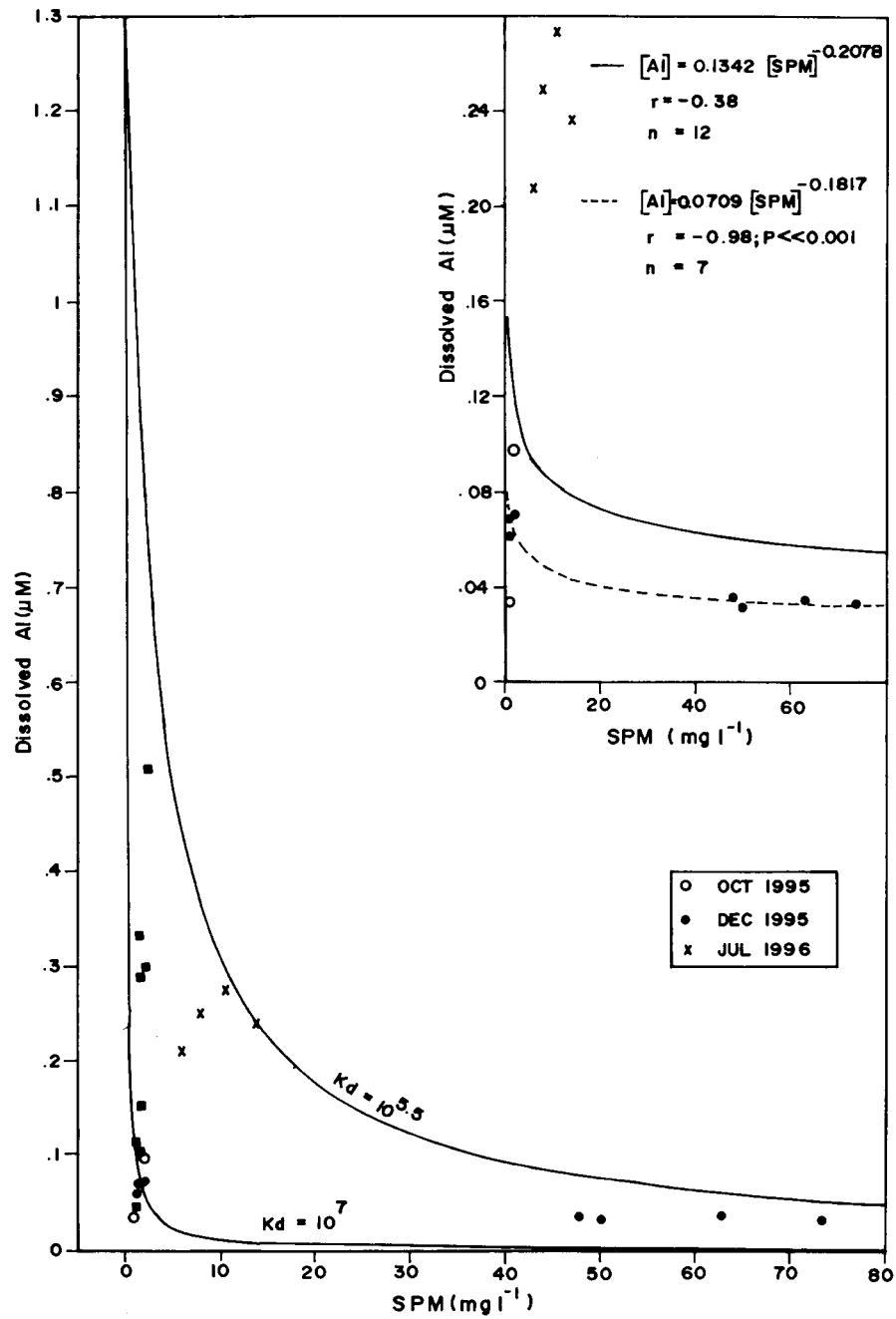
Figure 3. Dissolved Al as a function of SPM in the Great Ouse river(the inset corresponds to the observed dissolved Al concentration in an expanded scale) (additionally included the Conway data are symbolized as ■).

particular set of conditions for which it is measured (Benes and Steinnes, 1995; Stumm and Morgan, 1996). Nevertheless, sorption models are a powerful means of describing solid-solution (quasi-) equilibria in aquatic systems (Moran et al., 1996).

If a dilute solution of a surface-active substance (such as an aqueous aluminium solution which is highly particle-reactive under some conditions) is brought in contact with a large adsorbing surface, extensive adsorption will occur with an accompanying reduction in the concentration of the solute in solution.

Let C_o be the concentration of metal in solution in the absence of suspended particulate matter, C_p is the concentration of particulate (adsorbed) metal in the suspended solid concentration of S equilibrated with the solution, and C_d is the equilibrium concentration of the solution.

The assumptions are that sorption exchange reaction will occur to attain equilibrium, and the suspended particulates, mostly clays and organic detritus of recent to very recent origin, are undersaturated with respect to adsorption at surface sites. In addition, clay and organic components possess a high degree of adsorbing capacity due to their high cation exchange capacity and high specific surface area (Karickhoff et al., 1979; O'Connor and Connolly, 1980). Applying mass balance to the sorptive equilibrium,

$$C_o = C_d + C_p. \tag{2}$$

Rearranging Equation (2) and incorporating values for C_d and C_p in Equation (1) yields,

$$K_d = \frac{(C_o - C_d)}{(C_o - C_p) \times S}. \tag{3}$$

Solving Equation (3), C_o is calculated for individual samples and averaged to obtain riverine Al concentration in the absence of SPM, which is 1.1 μM for the Yare and 1.3 μM for the Great Ouse in the present case. Equations (2) and (3) can then be rearranged to calculate dissolved Al concentrations at varying SPM concentrations :

$$C_d = \frac{C_o}{1 + (S \times K_d)}. \tag{4}$$

Using Equation (4), curves are generated (Figures 2 and 3) with K_d values 0.316×10^6 and 10^7 (ml g^{-1}). It can be seen that in both instances most of the data fall in the zone defined by the K_d values of 0.316×10^6 and 10^7, with only a few points as outliers. It is suggested that most of these extreme values represent unusual local conditions, and could not be predicted by even the most sophisticated model. The changing particle characteristics are attributed as the single major factor and this is quite obvious in a dynamic aquatic system, such as a river. Unfortunately, there are no measurements available on the steeply rising part of the

curves which hinder the prediction of high dissolved Al at low SPM. However, it may be that at low SPM, phytoplankton blooms occur and remove dissolved Al and hence the K_d formulation becomes inappropriate.

Although there are some deficiencies in this model, its characteristic feature is indicative of occurrence of relatively higher dissolved Al concentrations at low SPM compared to those at greater SPM levels, and perhaps, this could be a reality at least in some freshwater environments. For instance, the model output (Figures 2 and 3) is tested by using data from the Conway system (Wales) (collected during December 1995; Upadhyay, 1998) which drains a very different geological system. These data points with SPM < 3 mg l^{-1} fit reasonably well in the steeply rising part of the model (the data at greater SPM levels are not available for comparison). The observation in the very low salinity ($< 0.2 \times 10^{-3}$) region of the Tamar river (England) by Morris et al. (1986) of occurrence of very high dissolved Al at low SPM and low dissolved Al at high SPM levels (see their Figure 5) is in conformity with the model proposed. Considering the broad range of geochemical characteristics of these rivers, this agreement is noteworthy and attests to the wider applicability of this model.

These results suggest that adsorption reactions may be important (also see next section) and aluminium adsorption onto suspended particulates (Walker et al., 1988) can be a significant factor in controlling aluminium concentrations in rivers. It may, however, be stated that an unambiguous interpretation of the apparent trend in the low SPM region of the Yare and Great Ouse rivers is not possible since the data are far from conclusive. Hence, it is emphasized that the model needs further testing prior to its wider application in riverine systems. Nevertheless, as the trend suggests, the model does provide a starting point for predicting concentrations of dissolved Al in rivers where SPM levels are moderate to high.

3.4. PARTICLE CONCENTRATION EFFECT FOR ALUMINIUM IN FRESHWATERS

Adsorption of solutes onto solids in natural waters is often thought of as a process which occurs in the linear region of the Langmuir isotherm. This suggests that K_d should be independent of surface adsorption density, hence of S, provided that the solute concentration is low compared with the concentration of particle surface sites. Thus, in a given environment, K_d should ideally remain constant for a given composition of the suspended particles and of the solution, if a steady-state condition is achieved, although the ratio between solid phase (C_p) and dissolved (C_d) concentrations will vary with S.

Instead of remaining constant, it is commonly observed that K_d decreases with increasing SPM concentrations, and that this effect spans many orders of magnitude (Honeyman and Santschi, 1988). This tendency of declining adsorption isotherm with increasing particle concentrations has been termed the "particle concentration effect" (O'Connor and Connolly, 1980). The reasons for this apparently

anomalous observation are unclear but several different mechanisms are generally invoked to explain it.

Some type of particle-particle interaction is usually invoked to explain the effect of particle concentration on partition coefficients. For example, an increase in the aggregation of particles at high concentrations could result in a decrease in surface area and available sorbing sites (Di Toro et al., 1986). In addition, the nature of the particles and their size (e.g., coarser material having low adsorbing strength) may explain some of these effects. Irreversible adsorption or incomplete desorption can also lead to such observations (Di Toro and Horzempa, 1982). Other factors such as kinetics (Nyffeler et al., 1984; Hering and Morel, 1988, 1990; Jannasch et al., 1988), the presence of a non-aqueous dissolved phase (Voice et al., 1983; Voice and Weber, 1985), and filtration artefacts (Horowitz et al., 1992) are equally in contention for this phenomenon. Recently, a metastable-equilibrium adsorption theory (Pan and Liss, 1998a, b) has been proposed which indicates that experimentally measured equilibrium adsorption constants for a given adsorption system decrease as the actual metastable – equilibrium adsorption states deviate from the ideal equilibrium state or as the adsorption reversibility decreases.

There is, however, evidence to suggest that in some cases the existence of colloidal forms of metals included in the dissolved fraction may also be an important factor for the apparent discrepancies between experimental results and theory (Morel and Gschwend, 1987; Benoit et al., 1994; Benoit, 1995; Benoit and Rozan, 1999). In addition, it is now widely recognized that the colloidal phenomena are a dominant process affecting the behaviour of trace substances in natural aquatic systems. This colloidal theory is based on the concept that the concentration of colloids increases in proportion to the quantity of suspended macroparticles so that the particle concentration effect is a consequence of metals bound to colloids that pass through conventional filters and are included with the dissolved fraction when calculating K_d.

In the colloidal theory, sorption is viewed as occurring both on macroparticles and colloidal particles, with the partitioning of metal between these solids and in true solution, apparently two spheres of partitioning being encompassed in the traditional sorption model. To represent these equilibria, K_p and K_c are defined as the coefficients for the distribution of metal between the truly dissolved state (C_u) and macroparticles and colloidal particles, respectively:

$$K_p = \frac{C_p}{C_u \times S} \tag{5}$$

and

$$K_c = \frac{C_c}{C_u \times S*}, \tag{6}$$

where C_c is the concentration of metal bound to colloids and S^* represents the concentration of colloidal particles. Then the dissolved metal concentration, C_d, is the sum of truly dissolved metal and that which is bound to colloids:

$$C_d = C_u + C_c. \tag{7}$$

Combining Equations (7) and (1) yields

$$K_d = \frac{C_p/S}{C_u + C_c}. \tag{8}$$

Incorporating Equations (5) and (6) into Equation (8) yields

$$K_d = \frac{K_p}{1 + (K_c \times S^*)}. \tag{9}$$

Equation (9) is similar to that derived by previous workers (Morel and Gschwend, 1987; Moran and Moore, 1989; Benoit et al., 1994).

If $K_c \times S^* \ll 1$, then $K_d = K_p =$ constant (i.e., not a function of SPM level). This implies that if colloids are quantitatively unimportant, the experimentally observed K_p will equal the thermodynamically defined value (Morel and Gschwend, 1987). Conversely, if $K_c \times S^* \gg 1$ then:

$$K_d = \frac{K_p}{K_c} \frac{1}{S^*}. \tag{10}$$

Equation (10) indicates that for the solutes that have a strong propensity to sorb, when colloids are abundant, K_d for such system will be inversely proportional to S^*. For the sparingly soluble metals, the amount of the sorbed fraction associated with small solids (colloids) that pass through the filter may lead to an overestimation of the solute concentration. If, as might be expected, the unfilterable solid (colloids) concentration covaries with the total solid concentration ($S^* \propto S$), then this effect will be maximized at high solid concentrations, resulting in a decrease in the distribution coefficient (Morel and Gschwend, 1987) with increasing solid concentrations, as is commonly observed.

The values of K_d for Al in freshwaters of the Yare river are estimated to be in the range $0.5 \times 10^6 - 2 \times 10^7$ ml g^{-1} for the sediment loads of 1 to 34 mg l^{-1}. The same for the Great Ouse river are in the region of $0.2 \times 10^6 - 0.7 \times 10^7$ ml g^{-1} for the SPM levels 1 to 74 mg l^{-1}. In the Conway system, K_d values range between 0.8×10^6 and 4.3×10^7 ml g^{-1} (SPM 1 to 3 mg l^{-1}). These results are similar to those reported (10^5 – Morris et al., 1986; 0.4–7.9×10^6 – Moran and Moore, 1989; 10^5 – Hydes and Kremling, 1993; 0.3–7.9×10^5 – Upadhyay and Sen Gupta, 1995) from riverine, estuarine and marine environments .

Figure 4 presents the relationship between $\log_{10} K_d$ and $\log_{10}$ [SPM] in freshwaters of the Yare, the Great Ouse and the Conway rivers. Invariably, K_d decreases
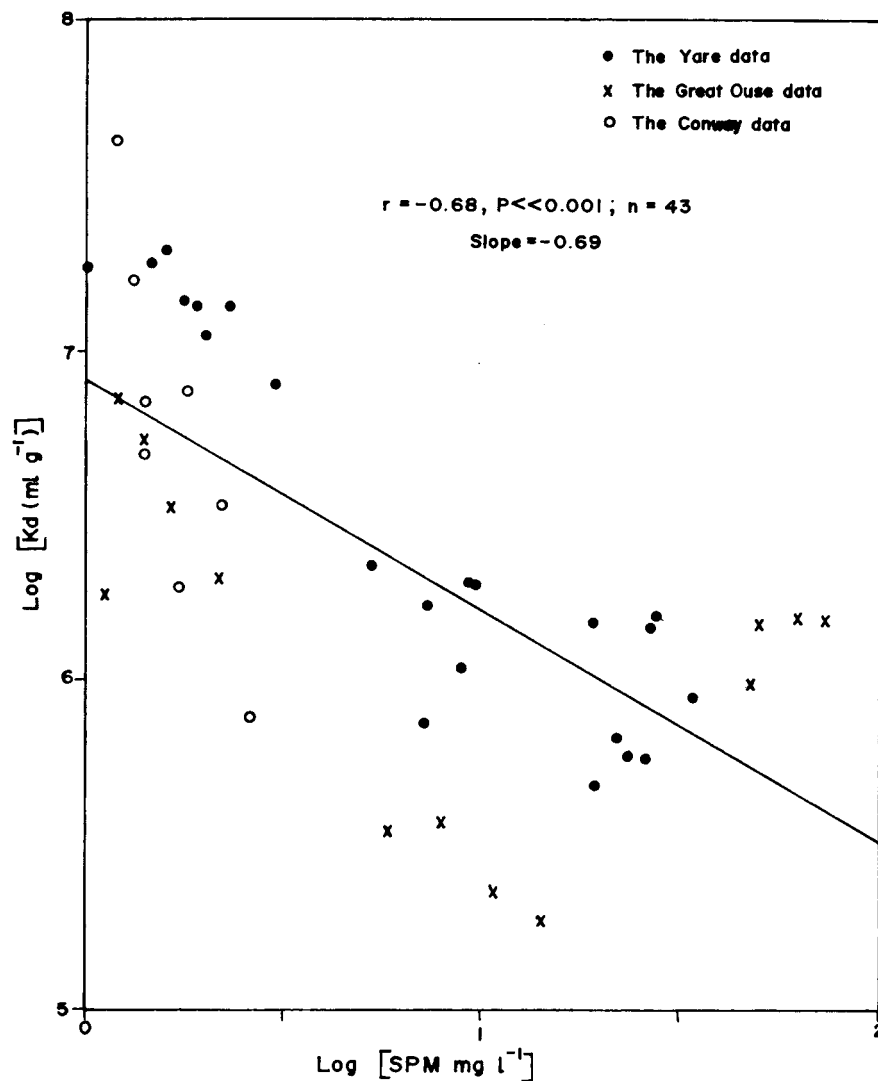
Figure 4. $\text{Log}_{10}K_d$ vs. log_{10} [SPM] for aluminium in the Yare, the Great Ouse and the Conway rivers.

with increasing SPM concentration, and indeed, the particle concentration effect is quite pronounced in these rivers. This is the first reported evidence of the particle concentration effect for Al in freshwaters.

The K_d data show scatter around the mean trend, and this is probably related to factors such as local differences in particulate matter composition and physicochemical characteristics and measurement uncertainties (Benoit et al., 1994). Although the correlation for the Great Ouse data set is poor ($r = -0.41$; $n = 13$), it is remarkably good for both the Yare ($r = -0.92$; $n = 22$; $P \ll 0.001$) and

Conway ($r = -0.84$; $n = 8$; $P < 0.01$), and there is a smooth decline in K_d indicating a strong inverse relationship with SPM. The overall data set ($n = 43$; all data points) for all these rivers also shows a similar trend and this relation is significant well above the 99.9% confidence level and provides very useful empirical information on partitioning of Al between the solid phase and solution. The slope of the regression line is -0.69 and is consistent with observations in estuarine systems (Benoit et al., 1994; Upadhyay and Sen Gupta, 1995).

Because of the very low concentration of Al observed in this study, the effect of the filter on the dissolved Al probably needs attention. Sorption will artificially increase and decrease the measured concentrations of particulate and dissolved Al, respectively. For Al, much of which occurs in the form of colloids will be removed with increasing efficiency as filters are progressively overloaded. This is especially likely for circumneutral river waters (like those studied here which are slightly alkaline), with pH values near the solubility minimum for such Al-bearing solids. Further, since filter loading is likely to increase with SPM, a steady decrease in dissolved Al level (in the filtrate) should result with increasing SPM. These trends would, however, cause the opposite of the particle concentration effect, and hence, the filtration artefacts can be disregarded.

Gschwend and Wu (1985) in their study have shown that colloid concentration covaries with solids concentration. The observations by Benoit et al.(1994) for Fe and Al associated with colloids and their increase with SPM in Texas estuaries are some indications that the level of colloids may be correlated with the amount of suspended macroparticles in rivers/estuaries. Hence, the particle concentration effect for Al in freshwaters observed in this study is thought to be linked at least to some degree with colloidal phenomena, rather than being merely an artefact of either reduction in surface density or other processes.

In a recent study, Benoit and Rozan (1999) have reported strong manifestation of particle concentration effect for Pb, Cd, Cu, Ag, and Zn in four Connecticut rivers. On discriminating dissolved fractions from colloidal metals (3,000 MW $-$ 0.45 μm), this effect was either nearly eliminated or reduced in virtually all cases. This is a compelling evidence that colloidal metals passing through 0.45 μm filters are an important cause of the particle concentration effect.

Given the techniques employed for the determination of surface-bound exchangeable Al in the current study, the observed inverse trend between K_d and SPM may also be expected if lower SPM coincides with a particle size distribution shifted to lower values. Smaller particles would be more soluble during extraction, giving rise to higher "apparent" adsorption and an elevated "apparent" K_d. On the other extreme, the drop in K_d with increasing SPM might have resulted from a lower adsorption onto the larger particles with low specific surface areas and surface complexation site densities. Also, some bias might have been imparted to K_d expressions consistently by inclusion of structurally associated un-reactive Al fractions in the "particulate" side of the equation. The degree to which these various

factors contribute to the observed trends is, however, not possible to assess without more detailed physico-chemical analysis of the SPM itself.

4. Conclusions

The Yare and the Great Ouse rivers drain similar geological systems, and hence, a comparable fluvial geochemistry of Al is to be expected. The sorption model proposed for dissolved Al in these freshwaters is indeed in reasonably good agreement for both systems. The Conway river data also fit the model reasonably well. In addition, the data from the low salinity ($< 0.2 \times 10^{-3}$) region of the Tamar river conform with this model. There is also a broad similarity in the variations of K_d as a function of SPM in these waters. Considering the wide variations expected in inter-riverine particle characteristics and water composition, these results are fairly good. This lends support to the model proposed and implies that sorption reactions may be important in the geochemistry of Al in rivers.

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