Fluvial metal transport near sources of acid mine-drainage: relationships of soluble, suspended and deposited metal

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Abstract

The Afon Goch (Anglesey, UK) is a short (12 km source to estuary) stream highly contaminated by acid mine drainage (AMD) throughout its length, due to past-mining at the head of the stream. Metal distribution is strongly controlled by the pH, which increases downstream particularly at confluences with two unpolluted tributaries. A pH increase causes precipitation of metals, primarily Fe as hydroxide, thus altering the transport of the metal load, potentially allowing storage of metal within the river as deposited material. However, further work suggests that the controls on whether metal can behave non-conservatively, and therefore the controls on metal distribution, are more complicated than being purely pH dependent. This is because much of the Fe load, even at the low pH at the head of the stream, is not soluble Fe^{3+} but colloidal Fe hydroxide. Consequently, coagulation is a requisite intermediate step between precipitation and potential for settling. It is possible that in reaches of the stream away from tributary confluences, the process of coagulation is the predominant influence on metal distribution. Furthermore, because much of the metal load in the water column is very fine, its deposition results in a sediment in which the metals can be intimately associated with a biofilm at the sediment/water interface. Such associations change both deposition and erosion characteristics of the sediment and have implications for subsequent diagenesis and mineral morphology.

KEYWORDS: acid mine-drainage, metal transport, Afon Goch, Anglesey, Wales.

Introduction

COMBINATIONS of constructed or natural wetlands with settling lagoons, limestone filter beds and manganese oxide filter beds, are likely to become the favoured treatment systems for metal removal around mine sites (NRA, 1993). This is because of their 'low engineering' and 'low energy' status, which results from their being intended to allow metal accumulation to occur continuously and untended for an extended period. The ability to predict the state of the metal brought to these beds, the absolute amount of metal and the regime of metal and acid delivery will, therefore, be crucial in the design and management of such systems, as they will control immobilisation, potential for remobilisation, and the capacity of the bed. The research required toward this end involves both geochemistry and hydrology.

A large literature exists concerning both soluble and particulate load transport by rivers (see Walling and Webb, 1986, 1988). There is also a large literature about pollution of rivers by acid mine-drainage (AMD) (e.g. Chapman et al., 1983; McKnight and Bencala, 1989). However, few studies have examined the effect of hydrological factors on patterns of contamination (see Bird, 1987). Those that do (e.g. Grimshaw et al., 1976; Bradley and Lewin, 1982; Bird, 1987; McKnight and Bencala, 1989; and Leenaers, 1989) often relate to watercourses effected by much less contaminated drainage or more distal, and therefore more dilute, sites compared with those that might exist close to a source of AMD. The requirement exists for studies of spatial and temporal variation in metal concentration and partitioning peculiar to a heavily contaminated watercourse, which is the primary stream of a small catchment. The understanding of processes in such

heavily contaminated streams is necessary for effective remediation.

This paper summarises research into metal transport and behaviour in a watercourse which forms the primary stream of a small catchment, and is heavily contaminated by historic open-cast metal mining activity.

Study area. Copper mining at Parys Mountain (Fig. 1) has had a profound effect on the local environment. Much of the Mountain is stripped of topsoil or covered in mine spoil, laying open the high concentrations of sulphide minerals, mainly pyrite, in the rocks to rapid oxidation. Consequently, the streams that rise on Parys Mountain have been heavily contaminated by sulphuric acid, iron and various other metals. Though contamination of these streams would have probably peaked in the early eighteenth century, when mining activity was great-est, it has remained at a high level, and will continue to do so, whilst large areas of sulphide-rich rocks are open to sub-aerial erosion.

The southern Afon Goch (Red River, in Welsh) rises from the south side of Parys Mountain (elevation 115 m), drains a catchment of $35-40$ km^2, runs 11 km to its tidal limit, and has two major unpolluted tributaries.

Metal distribution in the Afon Goch. Sampling of water and suspended solids at several sites through-out the catchment, twice a month for a year (Table 1), showed the river to be one of the most metal- and acid-contaminated streams in the UK (Boult *et al.*, 1994). Both solute and particulate load were found to consist of a significant proportion of pollutant metal, even after dilution by tributaries. The following spatial and temporal variation in metal distribution was apparent:
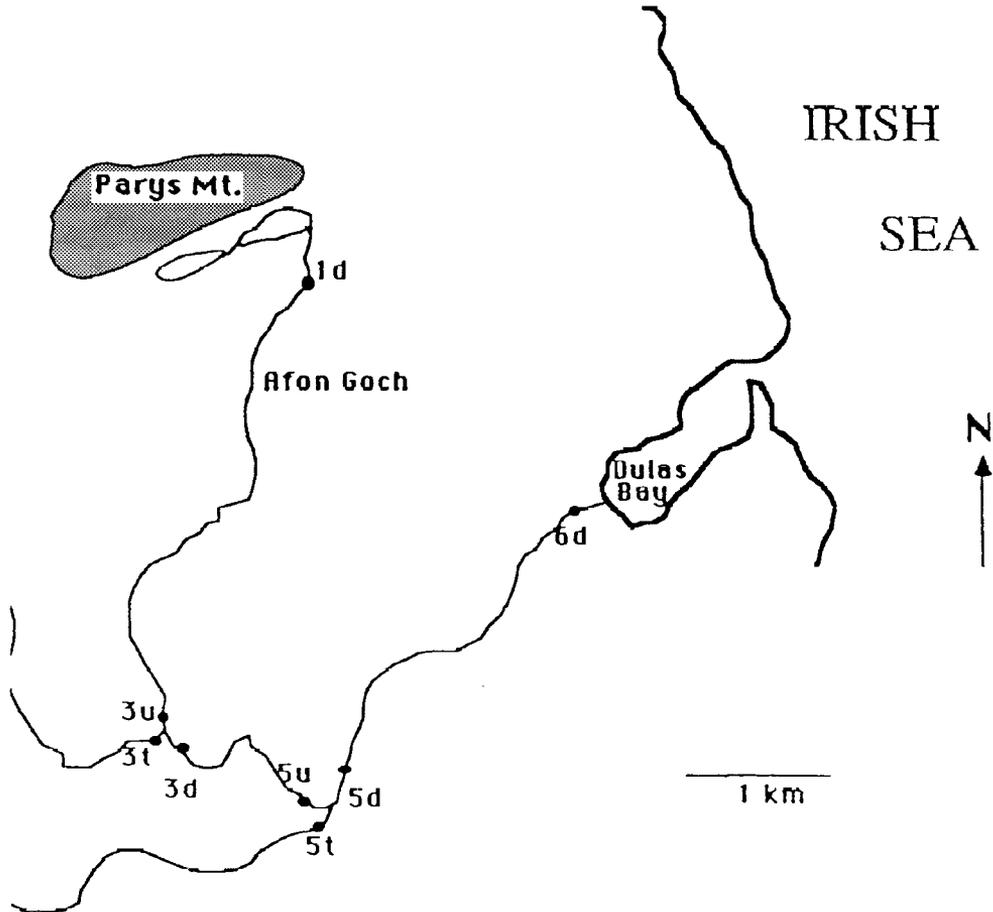
FIG. 1. Map of the Afon Goch, showing sampling sites. Site numbers increase downstream and the postscripts u, d and t refer to upstream, downstream and tributary.

TABLE 1. Range, average metal concentrations, and pH at sites along the Afon Goch, November 1990–January 1992. (from Boult *et al.*, 1994). Concentrations are in mg/l, postscript s or p indicate soluble or particulate. Site 1d is at the head of the stream, 6d just above the tidal limit, and 3t is an unpolluted tributary

Site		m^3/hr	pH	Fe s	Al s	Mn s	Cu s	Zn s
1d	Avg	83	2.40	193.24	55.56	10.80	19.23	30.03
	Max	209	3.01	259.76	166.97	49.06	59.89	41.91
	Min	4	2.27	39.28	14.41	6.14	4.48	15.78
6d	Avg	1624	5.99	1.36	1.14	0.68	1.42	1.99
	Max	4374	7.20	19.19	7.88	1.64	11.43	5.33
	Min	132	4.75	0.00	0.00	0.01	0.00	0.17
3t	Avg	144	6.49	0.15	0.12	0.06	0.67	0.23
	Max	428	7.65	0.58	0.57	0.20	12.04	1.54
	Min	6	5.45	0.00	0.00	0.01	0.00	0.00

Site		SS	Fe p	Al p	Mn p	Cu p	Zn p
1d	Avg	10.6	1.46	0.31	0.01	0.02	0.02
	Max	35.2	7.71	1.44	0.02	0.05	0.05
	Min	0.6	0.05	0.02	0.00	0.00	0.01
6d	Avg	37.8	3.91	2.15	0.02	0.18	0.04
	Max	116.0	7.23	4.89	0.06	0.52	0.12
	Min	4.0	0.11	0.75	0.00	0.01	0.01
3t	Avg	7.1	0.34	0.69	0.01	0.01	0.02
	Max	22.7	1.13	2.62	0.01	0.02	0.07
	Min	0.0	0.00	0.03	0.00	0.00	0.01

(1) maxima in the downstream particulate metal concentration profile occurred immediately below confluences of the Afon Goch and its unpolluted tributaries.

(2) the Afon Goch exhibited a very variable relationship of particulate concentration to discharge, i.e. rating relationship [this relationship is a standard tool in hydrology used both for prediction of river load, and analysis of load generation and transport processes (see e.g. Walling and Webb, 1988)].

These distributions are manifestations of the imposition of chemical processes, specifically the non-conservative behaviour of metals, onto fluvial transport, and are particularly pronounced because metal forms a substantial proportion of the total load. They result from the downstream dilution of the large amounts of acid entering the upper Afon Goch and the consequent downstream pH gradient, metal partitioning being strongly controlled by pH (Stumm and Morgan, 1981). This pH dependence is demonstrated in Fig. 2 which shows metal distribution under winter baseflow discharge. Dissolved Fe and Al precipitate as hydroxides with subsequent co-precipitation of some Cu and Zn. Metals, therefore, form a large proportion of the suspended load

(>0.45 µm), most obviously at confluences where there is effectively a stepwise pH increase.

Variation in stream-load rating relationships in unpolluted streams is controlled by variations in supply of erodible material, which cause characteristic hystereses in the rating curve (typically for any discharge event, load at a particular discharge will be greater whilst discharge is increasing than at the same discharge whilst discharge is declining). In streams less polluted than the Afon Goch significant amounts of metals do not change their partitioning and supply remains the primary control, any deviations between rating relations of pollutant and non pollutant particulates arising only because of differences in availability of these different components of load (e.g. Grimshaw *et al.*, 1976, Bradley and Lewin, 1982). However, because particulate production in the Afon Goch is not solely controlled by discharge-dependent erosion (including wash-in), which is responsible for particulate load in less contaminated waters, production is continuous even when discharge is such that deposition dominates erosion. Consequently, stream-bed deposits have the potential to build up to a greater degree in the Afon Goch than in less metal- and acid-polluted streams (Boult and
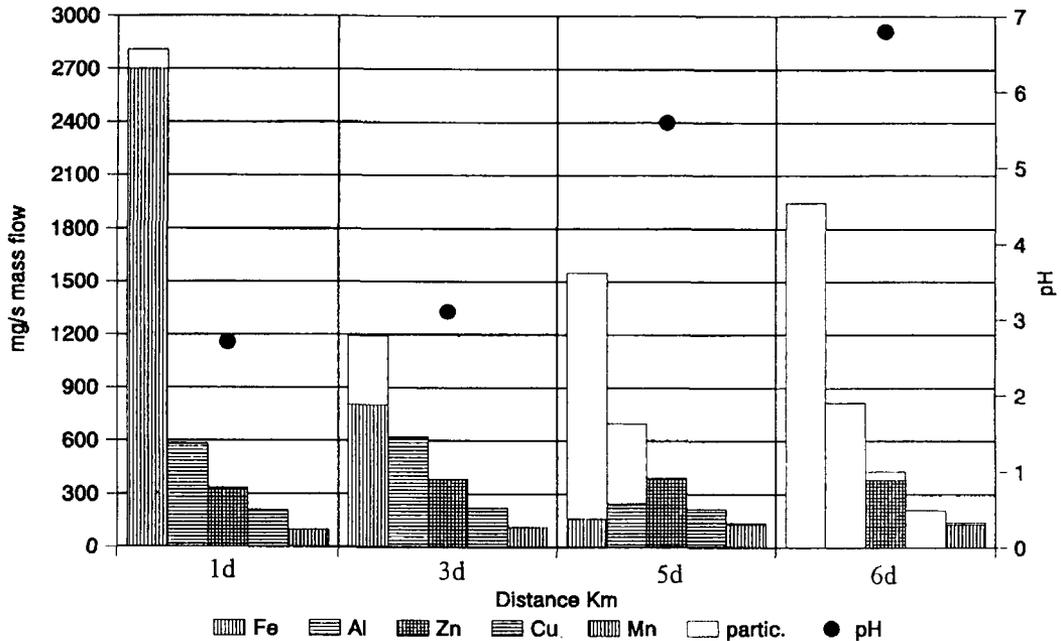
FIG. 2. Downstream metal distribution, partitioning, and pH in the Afon Goch under winter baseflow discharge. At this discharge metal flux remains constant downstream (except Fe), but changes from soluble to particulate as pH increases (portions of bar that that are unshaded represent particulate), because of circum-neutral tributaries entering at site 3 and site 5. (From Boult *et al.*, 1994).

Curtis, 1994). This potentially greater instream storage of load results in particulate rating relationship hystereses, and therefore variability, that are exaggerated compared with those of other streams. In highly AMD contaminated streams, therefore, the potential for metal transport to occur as high magnitude/low frequency events is greater than in less contaminated streams.

It is apparent that the proportions of soluble, suspended and deposited metal are constantly changing, and understanding the processes involved is central to a realistic description of metal transport in these highly AMD contaminated systems.

Relationships of soluble and particulate metal

Metal removal from the water column would be expected to occur as a result of physical and chemical processes and via the partitions shown in Fig. 3a. The significance to load transport of differentiating between soluble and particulate matter is that the latter is subject to gravitational settling, and therefore storage within the system. Consequently, fine metal colloids produced by precipitation, though particulate are not distinct from solutes in their transport behaviour. Furthermore, if colloids are produced,

the production of (non-colloidal) particulates from solutes will be by a two stage process, precipitation then agglomeration, each controlled by different variables. Should pollutant load be composed of a large proportion of colloidal material, metal transport behaviour will be different from that when precipitation results directly in the production of a potentially non-conservative (i.e. subject to gravitational settling) metal load. The relationships between the various partitions in such a case are shown in Fig. 3b.

The following Sections assess whether Fig. 3a or 3b gives a more realistic description of metal behaviour in the Afon Goch, the first Section is concerned with metal behaviour within the water column, the second with water sediment interaction.

Metal behaviour within the water column. The passage of Fe and Al colloids through 0.45 μm filters is a well known phenomenon (e.g. Kennedy *et al.*, 1974), the simplest colloids being the hydroxides formed by the tri-valent ion's stepwise hydrolysis of water. When water samples are analysed by inductively coupled plasma optical emission spectrophotometry, (ICP-OES) or any other spectrographic method, soluble and particulate metals are determined in composite, therefore the passage of such colloids will result in positive deviation from neutrality of the solution.

a)

b)
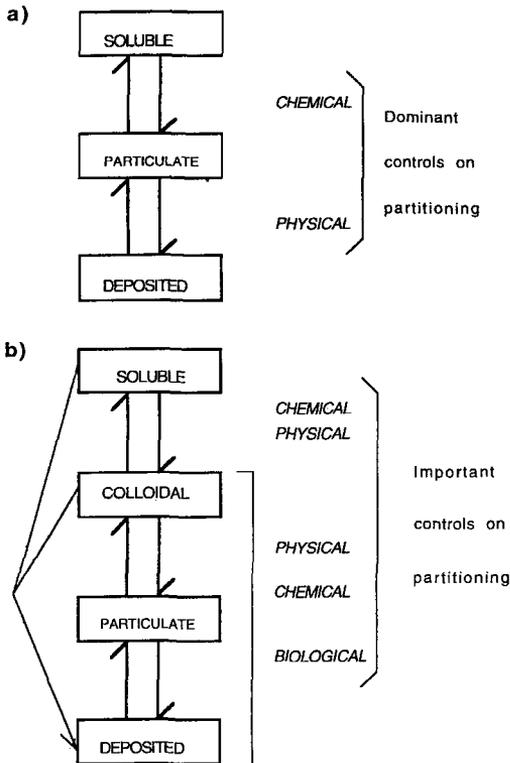
FIG. 3. (a) Simple scheme of metal partitions and processes controlling partitioning. (b) Partitioning and controls that may be important in the Afon Goch, a more complex scheme than (a) because of the recognition of the colloidal state and biotic effects on deposited material. The line on the left shows a pathway that must be present but may be from either the soluble or colloidal state.

Water samples were taken from the Afon Goch and stream pH measured under different discharges, and at various sites downstream (Fig. 1.) (as detailed in Boult et al., 1994; Boult and Curtis, 1994). The samples were immediately filtered through 0.45 μm membranes and acidified. They were subsequently analysed by ICP-OES for all cations at detectable concentrations and total S. Analysis of anions was initially done by Dionex ion chromatograph, but discontinued after the first set of samples as SO_4^{2-} was the only anion of significance relative to the cation concentrations, and this correlated well with total S measured by ICP-OES. Charge balance was calculated using the following assumptions:

(a) at the sites studied the waters were or had been oxygenated sufficiently to preclude the presence of Fe^{2+}. This has been confirmed by Walton and Johnson (1992).

(b) soluble Fe was present in the stream as Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe_2(OH)_2^{4+}$, the relative proportions being controlled by pH according to standard equilibria (e.g. Stumm and Morgan, 1981).

(c) soluble Al was present as Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$, the relative proportions being controlled by pH according to the equilibria determined by Martin (1986).

(d) all other cations (Mn, Cu, Zn, Pb, Cd, Ca, Mg) were present as free divalent ions, except Na which was monovalent.

(e) as the pH of the stream was consistently below 5.5 at the sites studied (Boult et al., 1994), HCO_3^-, which is the commonest anion in unpolluted waters but could not be analysed for directly, was assumed to be of negligible concentration (e.g. Stumm and Morgan, 1981).

(f) all dissolved S was assumed to be present as SO_4^{2-}.

The charge balance calculated (Fig. 4), suggests sub 0.45 μm (colloidal) metal makes a contribution to total metal load in the Afon Goch, most obviously at the upstream sites and declining in significance downstream.

The charge imbalance of 18 meq/l recorded at site 1, is equivalent to either 336 mg/l of Fe or 108 mg/l of Al ions at the prevalent pH. ICP-OES analysis of filtered (0.45 μm filter) waters from site 1 showed Fe and Al concentrations to be 200 and 45 mg/l. Consequently charge neutrality of the water sample could be achieved at site 1 only if nearly all 'dissolved' Fe and Al were colloidal. Equilibrium solubility data provide a degree of independent support for the predominance of colloidal metal;

$$[Fe^{3+}] = [H^+]^3 * 9.1 \times 10^3$$

(Stumm and Morgan, 1981)

Therefore at pH 2.6, the average for site 1d (Table 1), solubility of Fe should be only about 50 mg/l, considerably less than the average 200 mg/l recorded after filtration (0.45 μm filter) and ICP-OES analysis of site 1 waters.

Dilution of the colloid-forming pollutant metals is probably the most important factor in reducing the charge deviation downstream. The reduction may also be partly a result of progressive coagulation to particle sizes >0.45 m. Unfortunately, available data do not allow quantification of the importance of each process. Furthermore, various sources of negative charge such as organic acids, and clay minerals that enter the stream from the catchment, may no longer have negligible concentrations at the distance downstream of the lowest two sites. Such anions were not
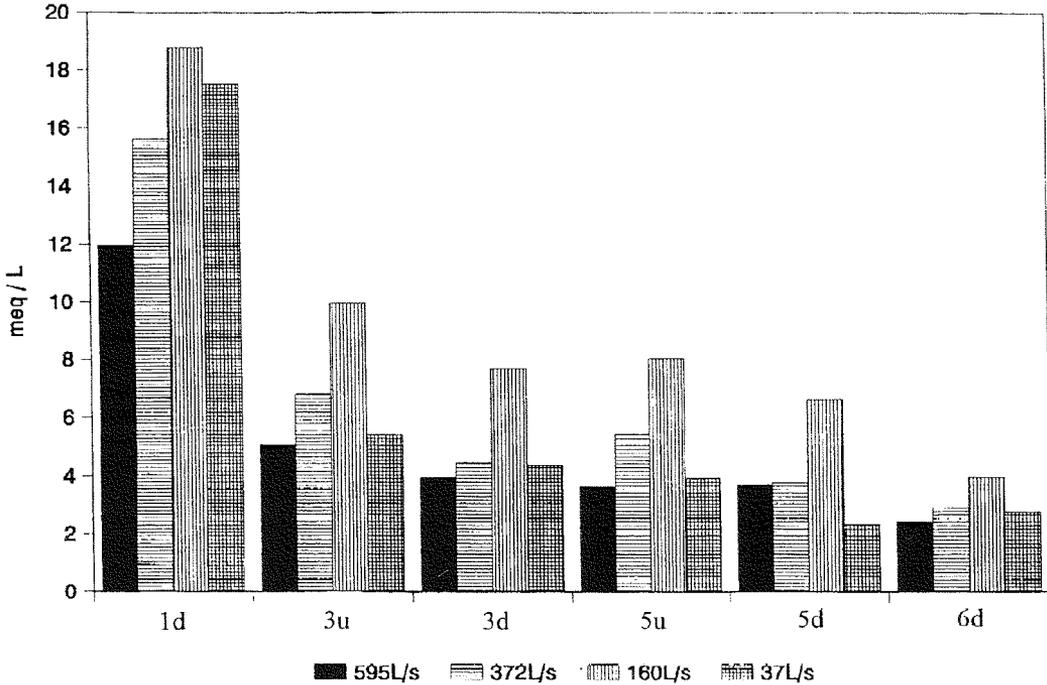
FIG. 4. Deviation from charge balance downstream, under four discharges recorded at different times of the year (discharge measured at site 6d).

analysed for and consequently may begin to make a contribution to the charge deviation, further obscuring the behaviour of metal colloids.

The rate of coagulation of colloids, which controls the rate of their loss by sedimentation, depends on the frequency of collisions and the efficiency of particle contacts. The former is controlled by the particle size distribution and the shear forces within the water column, the latter a combination of electrostatic forces and the presence of different functional groups on the colloidal particle, allowing different coordination of electrolyte. Consequently, a model of coagulation would either be highly complex requiring large amounts of high quality data or be applicable only to very specific situations. It is recognised that adequate theories and sufficient empirical information do not exist to provide quantitative and generally valid predictions of the rate of settling of colloidal material when solution parameters are changed in the natural environment (Stumm and Morgan, 1981). Observed values of metal concentrations of particular size fractions cannot, therefore, be compared with expected values to assess the relative importance of agglomeration directly. However, some inferences can be made from the limited data-set available.

The increase in positive charge deviation from neutrality as discharge declines from 595 to 160 l/s (Fig. 4), may be a result of the increasing transit time, which would allow removal of metal ions from solution, by sorption onto existing colloids, to occur to a greater extent. The reversal of this increase at very low discharge (37 l/s measured at 6d), may be because the transit time was sufficient to allow coagulation of the colloids to such a degree, that they could no longer pass through the 0.45 µm filter.

River water samples studied in a field laboratory immediately after extraction, showed an increase in the >0.45 µm Fe and Al fraction on standing. However, electrical conductivity during the same period remained constant, therefore the increase in >0.45 µm particulate Fe and Al concentrations is probably due to coagulation of colloidal material, rather than precipitation from solution. The production of >0.45 µm Fe and Al continued for the 18 hour monitoring period, though the rate of coagulation declined after the first 6 hours. Similar trends indicative of coagulation were apparent at all sites down the river, however the predominance of coagulation was sensitive to agitation. Stirring (by magnetic stirrer turning at 300rpm) caused conductivity to increase, presumably by providing a

sufficient velocity gradient for disaggregation forces to be greater than those causing flocculation, resulting in predominantly smaller particles more prone to solvation.

In an unstirred system the equilibrium between production by coagulation and removal by settling, determines the concentration of particulate metals *in vitro*. In the river, however, other controls may dominate, such as the variation with discharge of shear rates and resuspension/settling rates; resuspension of previously deposited sediment may also be important. However, in-river sampling below confluences suggests it is possible nevertheless, that the processes of coagulation and settling may be a significant control on metal particulate concentration under at least some conditions of discharge. This is because, if the distance downstream is divided by the flow velocity at the time of measurement, to give an average transit time, the relationship of particulate metal concentration and time is of the same order as the coagulation rates measured *in vitro*. For example, when the average flow velocity at site 3d was 0.23 m/s, water and load sampled 1.2 km downstream of 3d had aged by (1.2 km/0.23 m/s) 1.5 hours, whilst the increase in >0.45 μm metal particulates was 7.5 mg/l. Though the *in vitro* particulate production rate was 5 mg/l in 6 hours the behaviour of the system over the 18 hour monitoring period suggests production would have been fastest initially. Consequently, it is possible that for the flow velocity mentioned above, which corresponds with the average (November 1990– January 1992) discharge of the Afon Goch, the process of coagulation is an important control on particulate metal distribution.

Characterisation of the deposited metals. The sampling of bed deposits, in order to understand load transport, is a complex procedure (Church *et al.*, 1987). The inhomogeneity of grain-size, and chemical and mineralogical composition of stream bed deposits extends in three dimensions, making representative sampling time-consuming. The difficulties are compounded in analysing the pollutant metal content of such deposits, as different metal species tend to have affinities for particular grain sizes and mineralogies. Much of the literature concerning bed sediments in streams receiving high loadings of metals is not quantitative with respect to mass balance of contaminants. Most papers are concerned with chemical characterization and determination of solution–solid equilibria and processes. Similarly, initial bed-sediment analyses in the Afon Goch, in which bulk sediment was taken by single grabs or cores at each site, have been pertinent to a stand alone study of geochemical processes within a core (Parkman, 1994), the study of in-fauna local to the sample site (Yordanov, 1994), and as a measure of the general level of contamination. However, as demonstrated by the insensitivity of bulk sediment metal levels to discharge (Yordanov, 1994), they are insufficient on their own to improve understanding of short-term metal transport. Even if carefully sampled, the metal content of bulk sediment is either related to average concentration in the water column, i.e. buffered from short-term fluctuations, and/or related to major discharge events importing metal contaminated particulates large enough not to be moved for an extended period.

In the Afon Goch, due to the very high metal concentrations, sorption onto terrigenous material is less important than agglomeration of Fe hydroxide flocs in particulate metal production. The small grain size of the flocs results in much of the deposited metal being in the form of an apparently homogeneous coating. Deposition rates of these coatings are more amenable to quantification than is the metal content of bulk sediment. Ferric hydroxide surface coatings have been widely observed in streams contaminated by AMD (e.g. Chapman *et al.*, 1983), but have not been studied in the context of quantification of pollutant fluxes. Carpenter and Hayes (1980) successfully measured the accretion of Fe–Mn hydroxides and associated metals in an uncontaminated stream by fixing plates to blocks on the stream bed. Similar sampling methods (flat polystyrene plates attached to the streambed) were used to collect material for examination and to measure accretion in this study. Stage (stream depth) was continuously monitored in parallel with sediment collection, allowing calculation of discharge and stream velocity through the use of a previously defined stage discharge relationship (Boult and Curtis, 1994).

The sediments were examined and analysed using both electron microscopy and digestion (as in Boult, 1994; Boult *et al.*, 1994) with subsequent ICP-OES analysis to characterise structure, grain size and chemical composition (Fig. 5 and Table 2). This was done to assess the processes of sediment accumulation and resuspension, both of which might be shown to be complicated with controls other than discharge.

Biota alter both the physical and chemical properties of sediments. Until recently the former have been primarily attributed to macrobiota and the latter to microbiota. These alterations are important, both in erosional situations due to effects on transport rates, and depositional situations due to alterations in diagenesis.

The study of microbiotic effects on metal contaminated sediments have generally been concerned with the process of metal/biota interaction (reviewed in Schultze-Lam *et al.*, 1993), and not variations in the amount of biota present, and potential for alteration in metal flux *per se*.
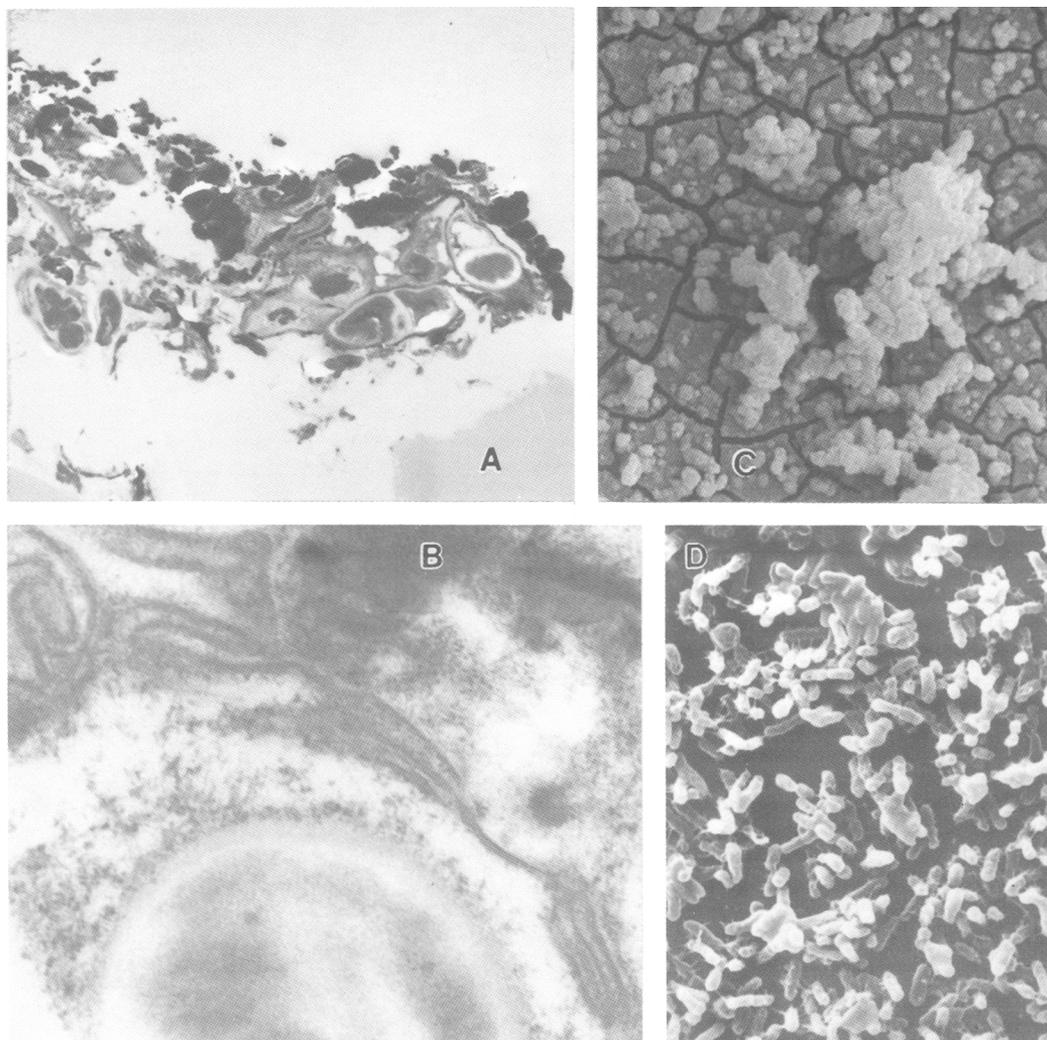
FIG. 5. (a) Transmission electron micrograph (× 4.5k) of vertical section of Afon Goch sediment (site 3d), upper surface uppermost. (b) TEM enlargement of (a) (× 100k). Endoplasmic reticulum/degenerate cell wall apparent to the left and a small bacterium to the right. (c) Scanning electron micrograph of upper surface of sediment layer (site 3d) (× 5k), showing c.1 m sized spherical to rod shaped entities, probably bacterial, covered by finer grains. Some bacteria are part of a desiccation cracked conditioning film/bacterial monolayer and some are emergent. (d) SEM of early stage biofilm grown from Afon Goch isolate in uncontaminated conditions (× 5k), a monolayer is not complete but some emergence has occurred due to clumping.

However, two expanding areas of recent research have brought about a requirement for a change of emphasis in the study of biota/sediment interaction. These are the recognition of structured surface associated microbial communities, biofilms, and their ubiquity in the aquatic environment (Costerton *et al.*, 1985; Austin, 1988), and independent studies on fine grained marine sediments, which have shown the microbial in-fauna and microalgal mats to be very important in sediment stabilisation (Patterson, 1989). Consequently, in both erosional and depositional situations, the microbiota may be exerting a more

TABLE 2. Some examples of composition of sediment accumulated after a 10-day period on polystyrene plates. Results are given only for toxic metals with depositions greater than 1 mg/m^2 at one site. Composition of sediment from site 3d is also given after 25- and 96-day collection periods

Period days	Site	mg/m^2 Total	% metal	mg/m^2 Fe	Al	Mn	Cu	Zn
10	1	3846	16	527	15	0	2	4
10	3u	427	109	48	24	0	3	35
10	3d	17094	22	2895	217	14	59	46
10	5u	403	51	94	0	0	1	5
10	5d	41026	46	15865	32	0	18	14
10	6d	540	25	11	45	0	2	3
25	3d	23077	42	7952	148	0	33	9
96	3d	275356	42	100344	748	10	78	40

significant control than previously thought, potentially preventing prediction of metal flux from chemical and physical measurements.

This change of emphasis is potentially relevant to all studies of load transport, but particularly transport of non-conservative components. It is also relevant to consideration of diagenesis, particularly the prevalence of certain types of mineralisation, mineral composition and morphology. The non-conservative aquatic transport behaviour and complicated mineral formation of heavy metals, makes their behaviour a good candidate for reassessment, as does their importance as environmental contaminants and economic resources.

Biofilms are known to occur in the vast majority of aquatic habitats (Costerton et al., 1985; Austin, 1988), and play an important role in the ecology of rivers. They are composed of bacteria, algae, protozoa cyanobacteria and a variable amount of inorganic detritus. They are complex and diverse communities, individual members interacting to cycle nutrients and wastes, resulting in a heterogeneous organisation of cells. The growth and activity of the biofilm is controlled by the rate of nutrient diffusion through to the lower layers (Kinniment and Wimpenny, 1992), and hydrodynamic stresses (Rouxhet, 1991) which may result in sloughing.

The predominant products of bacteria and algae are extracellular polymeric substances (EPS) (Geesey, 1982). These are highly hydrated and through their diffusion properties and/or presence of anionic reactive groups, maintain a micro-environment within the film different from that in the water column. EPS secretion has profound consequences for the biofilm community. EPS concentrates nutrients from the water column (Marchesi et al., 1991), which is particularly advantageous in flowing waters. The nature of EPS also causes diffusion gradients within the film to be enhanced, increasing the number of micro-habitats and leading to the establishment of anoxic and reducing conditions close to the substrate. Variable rates of EPS production and composition due to nutrient status and other stresses (e.g. Uhlinger and White, 1983), are responsible for temporal heterogeneity of the biofilm. EPS secretion also results in protection of the embedded micro-organisms from harmful factors in the aqueous phase.

EPS is the biofilm's first, and most important, line of defence against heavy metal toxicity. This is due to several factors. Perhaps the most important is metabolism-independent biosorption, which is the non-directed physico-chemical interaction between metal species and microbial biomass, including components of cell envelopes, walls and EPS (Schultze-Lam et al., 1993). It is a rapid process, which results in a much reduced subsequent rate of transport into the cell. The process occurs equally well if living cells, dead cells or cell fragments are present.

The presence of a persistent biofilm as the uppermost layer of sediment in the Afon Goch is therefore possible, and highly likely in view of studies done by Macaskie and Dean (1987) of waste streams in uranium processing. Furthermore, Johnson (1995) has isolated and cultured, in unpolluted media, certain of the biotic components of a layer from the Afon Goch. He found biofilms developed after a period of between a week and a month, from 1 μm thick 'conditioning' films of humic acids with sparse bacterial attachment to dense 'species films' of several hundred μm thickness.

Figure 5a is a transmission electron micrograph (uranium and osmium stained, see Boult, 1994, for

sample preparation) of a vertical section through the accumulated river sediment, and Fig. 5c is a scanning electron micrograph of the surface of the sediment; in both cases the underlying shapes cannot easily be attributed to processes of abiogenic sediment deposition. The vertical section is heterogeneous and composed of a high proportion of round to rod-shaped objects of 1–1.5 µm length bound by thin lines of high electron density, which are highly suggestive of bacteria. Figure 5b, an enlargement of a region near the bottom of the section, shows an electron-dense structure typical of degenerated cell membrane or endoplasmic reticulum, and what is almost certainly a small bacterium. Comparison of the surface in Fig. 5c with those of Johnson (e.g. Fig. 5d) suggests that the underlying shapes are a microbial film, but coated in EPS and accumulated metal. The latter was confirmed by microprobe analysis. Therefore, the sediment layer is best described as a highly contaminated biofilm.

Given that the sediment–water interface may be substantially biotic, it is probable that redox and ion activity gradients are maintained (i.e. chemical conditions prevailing in the bulk liquid will be very different from those within the film), such that the biofilms may well dictate metal removal from the water column. The metal removal pathway direct from solution or colloidal suspension to deposited material without passage through a phase liable to physical settling (Fig. 2), noted by Chapman et al. (1983) and Boult et al. (1994), may be a result of biofilm action. Involvement of the surface activity of the biofilm is likely as removal was most apparent when the wetted perimeter to discharge ratio was high (Boult et al., 1994). Metal behaviour will therefore be further complicated, because any biofilm control on metal behaviour will be modulated by ecological concerns, growth cycles of the biota, nutrient supply, predation, etc. The process of biofilm mineralisation and its relative importance to metal removal from AMD is the focus of continuing study. Some aspects of metal removal are reviewed by Lion et al. (1988) and Schultze-Lam et al. (1993).

In addition to altering metal removal from the water column, the biota will effect the subsequent transport behaviour and diagenetic fate of deposited metal, the former as a result of sediment stabilisation (which is discussed further below), and the latter because the close association of metal and organic material forms an excellent substrate for sulphate reducing bacteria when deposited in the marine environment or a reed-bed. There is a literature on microbial sediment stabilisation, but this has so far been concerned mainly with the marine environment (e.g. de Boer, 1981; Patterson, 1989). No sediments studied so far are comparable with those in a metal polluted stream. The role of microbiota in physically stabilising particulate metal has, therefore, never been studied directly.

The behaviour of deposition/resuspension with flow velocity is likely to lie between a constant function and purely threshold value relationship. The characterisation of the sediment as a contaminated biofilm makes the behaviour more likely to tend toward the latter, than if it were an abiotic deposit (Patterson, 1989). Other apparent differences are likely to be quantitative.

Insufficient sampling was done to fully describe the relationship of erosion/accumulation to discharge. However, it was apparent that the sites of greatest deposition (Table 1) corresponded to the positions of maximum suspended solids concentration, i.e. sites 3d and 5d. It was also noted that 96 day old collection plates had not been depleted by flow velocity peaks occurring after 60 days, which were of sufficient magnitude to erode 10 day old sediment. This suggests the stabilisation of the sediment against erosive forces and/or the occurrence of higher rates of sediment accumulation as the sediment layer ages and increases in depth. Such behaviour is consistent with the establishment of a mature emergent biofilm. In addition, it was apparent that the velocities necessary for net erosion were similar for sediments at sites below the first and second tributaries, whilst the velocities for net deposition differed. This is consistent with deposition being more reliant on chemical processes than is resuspension, and therefore likely to be influenced by the metal concentration gradient and other chemical differences between the two sites.

Conclusions

In highly acid mine-drainage contaminated streams, in which metal forms a significant part of total load, the transport behaviour of metals is different from that in less polluted streams. This is because of the production of metal particulates within the water column, which is not directly controlled by discharge. The particulates are largely colloidal, producing a load subject to different controls on its subsequent transport than would occur in a less polluted stream. Furthermore, deposition of this load results in a sediment in which the metals can be intimately associated with surficial micro-biota, and consequently become chemically and physically altered.

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