

Sediment quality related to discharge in a mineralized region of Wales

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ABSTRACT In many studies the quantity of suspended sediment has been related to discharge to produce "rating" curves for the river. In this study the characteristics of sediments are determined in an area of known, and previously exploited, mineralization. Suspended sediment transported by the River Ystwyth has been analysed for heavy metals, and concentrations then related to discharge. Alluvial sediments have been collected along the course of the River Ystwyth, and concentrations of heavy metals determined on a particle size basis. Analysis for metals has been conducted by X-ray fluorescence spectrometry (XRF) to determine concentrations of Pb, Zn, Fe, P, and S on suspended sediments, and Pb, Zn and Cu on channel sediments. This technique is more useful than atomic absorption spectrophotometry (AAS), as analysis of surface concentrations is important to determine bioavailability, and exchange between the sediment and dissolved load. Magnetic characteristics of the sediment have also been determined and complement heavy metal analyses.

INTRODUCTION

Rating curves describing the concentration of suspended material in relation to discharge have been produced for many rivers (e.g. Müller & Förstner, 1968; Walling, 1977). Little attention has been paid to the relationship of discharge to sediment "quality", specifically metal concentrations in polluted regions.

Studies of heavy metal transport relationships in rivers have frequently been concerned with the soluble component of mass flow (Grimshaw *et al.*, 1976), while few studies have concentrated on the transport of metals on sediment surfaces (Gibbs, 1973, 1977; Jenne, 1968).

Metal-laden sediments, derived initially from historic mining and contemporaneously from mine drainage and spoil, still provide an input of metals into the River Ystwyth in mid-Wales (Fig. 1). Suspended sediments during high flow conditions, however, are also provided from channel margins, both from the main channel and tributaries draining several defunct mines. Metal-rich sediments incorporated into alluvial soils throughout the nineteenth century, now being reworked, have contrasting environmental histories, thus conditioning the heavy metal composition of derived sediments.

To evaluate relationships between sediment levels and associated metal concentrations on their surfaces under various flow conditions,

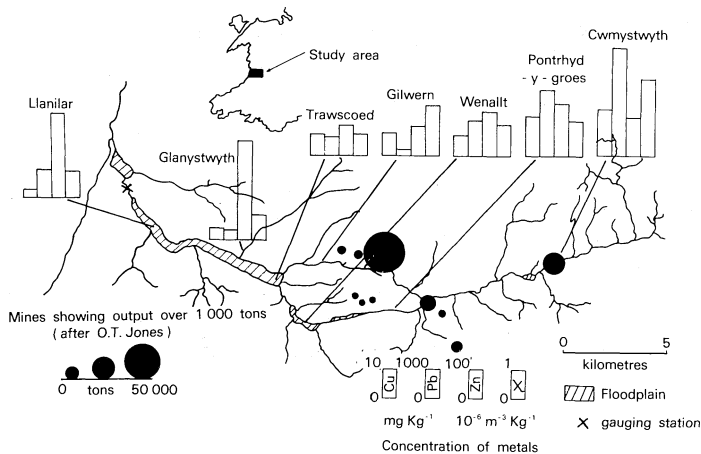


FIG.1 Mine sites on the River Ystwyth.

analyses for metals on sediments in several floods are considered. A particular flood event, occurring on the River Ystwyth from 2-3 June 1981, is examined in detail. To complement this study channel sediments likely to be sources of suspended sediment in flood, and those deposited sediments remaining from the last flood, were taken along the river and metal concentrations evaluated on a particle size basis, as were magnetic susceptibility measurements.

EXPERIMENTAL

Suspended sediment

Sampling of water from the River Ystwyth at the Water Authority gauging station at Pont Llolwen (National Grid Reference SN591 774; basin area 172 km²) was undertaken using a Rock and Taylor pump sampler set to extract samples of approximately 500 ml at 30 min or hourly intervals depending upon conditions. The Rock and Taylor sampler, in common with all automatic samplers, does not provide a depth integrated sample, and it is frequently shown that such equipment has difficulty in raising the coarser suspended sediments (e.g. Nordin & Dempster, 1963; Schneider & Angino, 1980). The samples collected therefore represent the finer "wash load" component of the river, this having a similar particle size distribution throughout the flood. Given the larger surface area to volume ratio of these sediments compared to larger sediments not sampled (Oliver, 1973), they are more important for surface metal concentrations, and hence more important in regulating the state of metals in the river.

Water samples were filtered through nitric acid (Analar) leached Whatman GFC filters (nominal retention >1.6 μm) and dried to constant weight. A Philips PW 1410 X-ray spectrometer operated at 60 kV and 40 mA, with LiF crystal and Cr tube was used for direct analysis of material caught on the filters. Specific conductivity measurements were also conducted on the filtered samples. Standards

for X-ray fluorescence (XRF) were prepared in accordance with Bradley & Lewin (1982).

Channel sediment

Fine sediments from the channel margins were taken between Llanilar and Cwmystwyth in the light of study areas discussed by Lewin *et al.* (1977), but included samples from tributaries thought also to provide metals. Sediments were dried, sieved to the fractions 2000–500 μm , 500–180 μm , 180–63 μm , <63 μm and analysed for Pb, Zn, Cu and Cd by XRF. Magnetic susceptibility measurements (χ) were also determined for these fractions using a Conservation Instruments MS1 instrument with 10 g sensor.

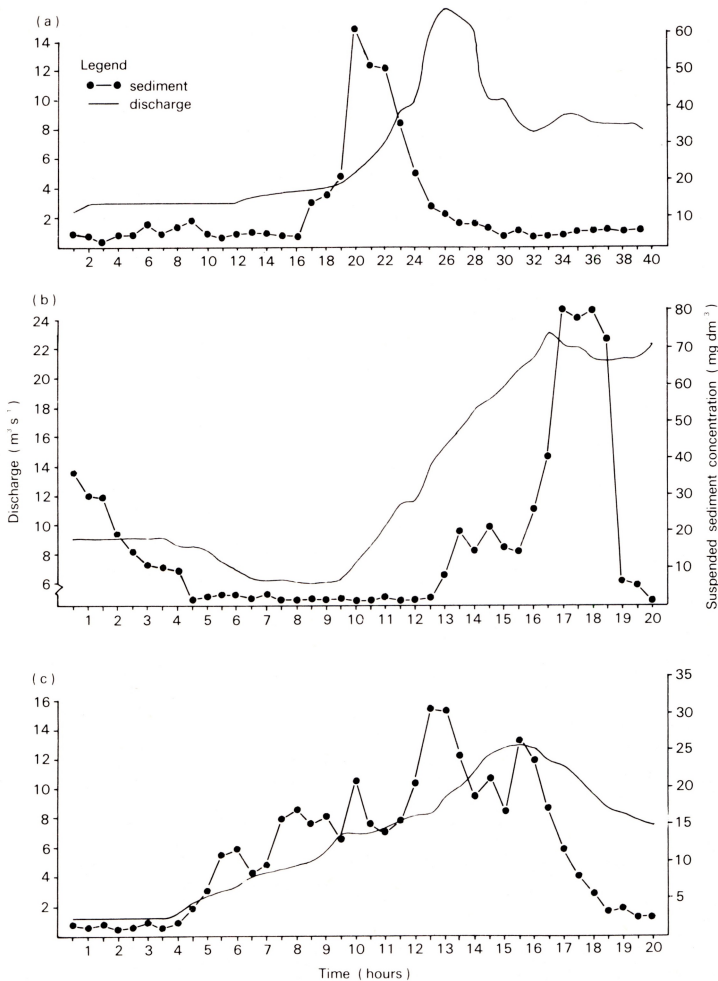


FIG.2 Sediment discharge hydrographs for the River Ystwyth: (a) 15:00 June 1 to 06:00 June 3 1981; (b) 10:30 July 22 to 07:00 July 23 1981; (c) 14:30 August 14 to 10:00 August 15 1981.

RESULTS

Suspended sediment

The hydrograph and suspended sediment concentrations for the period 2-3 June 1981 (Fig.2a) show maximum sediment concentrations preceding maximum water discharge, as observed elsewhere by Miller & Piest (1970). At other times, however, the sediment peak exhibits a more varied response to discharge (Fig.2b and c).

XRF is rapid and non-destructive, and can be used with small samples (0.005-0.250 g of sediment were contained on the filters). In Fig.3 concentrations of Pb, Zn, Fe, P and S throughout a flood are presented in terms of XRF "concentration units" (that is, counts per second adjusted for sample weights). These units are preferred, as the changes in concentration are usefully depicted, without problems of matrix effects and standards having to be considered at this point.

Determinations from several floods have been used to compile Pearson correlation coefficients, Table 1. The changes in surface element concentration with respect to the low flow, rising and falling stages of the sediment peak are evaluated. This relationship of surface metal to sediment concentration is important as it reflects the change in total surface covering by the metals, and thus the total mass of metal transport at a given discharge on wash load sediment.

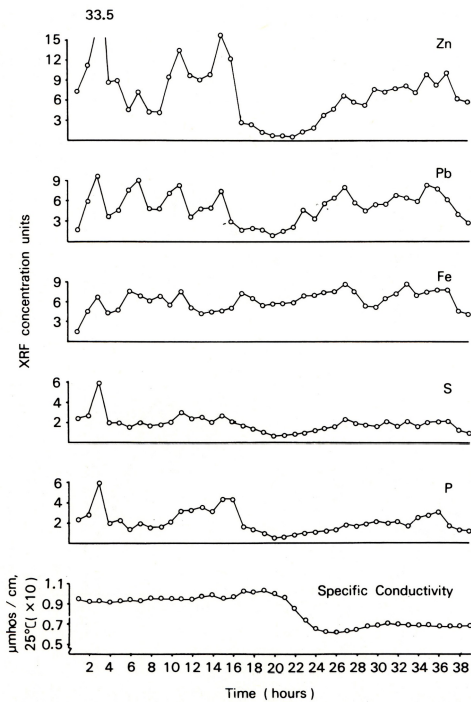


FIG.3 The variation of surface concentrations of Zn, Pb, Fe, S, and P, and specific conductivity during a flood.

TABLE 1 Correlation matrices for flood event June 1-3

	Q	SS	SC	Pb	Zn	Fe	P	S	Cd
<i>(a) LOW FLOW SEDIMENT BACKGROUND BEFORE FLOOD</i>									
Discharge	1.00	-0.18	0.43	-0.10	0.01	0.13	0.28	0.01	-0.11
Suspended solids		1.00	0.34	-0.28	0.75	0.29	-0.79	-0.73	-0.70
Specific conductivity			1.00	-0.40	-0.40	-0.03	-0.19	-0.34	-0.66
Pb				1.00	0.52	0.73	0.37	0.46	0.47
Zn					1.00	0.07	0.94	0.99	0.52
Fe						1.00	-0.05	0.02	-0.12
P							1.00	0.95	0.42
S								1.00	0.43
Cd									1.00
<i>(b) RISING LIMB OF SEDIMENT CONCENTRATION</i>									
Discharge	1.00	0.97	0.10	-0.88	-0.62	-0.49	-0.78	-0.93	-0.96
Suspended solids		1.00	0.10	-0.94	-0.64	-0.30	-0.79	-0.90	-0.99
Specific conductivity			1.00	-0.43	-0.83	0.47	-0.68	-0.42	-0.09
Pb				1.00	0.85	0.02	0.92	0.92	0.94
Zn					1.00	-0.19	0.97	0.84	0.64
Fe						1.00	0.01	0.31	0.26
P							1.00	0.94	0.78
S								1.00	0.88
Cd									1.00
<i>(c) FALLING LIMB OF SEDIMENT CONCENTRATION</i>									
Discharge	1.00	-0.39	-0.72	0.13	-0.14	0.15	-0.09	-0.03	0.32
Suspended solids		1.00	0.96	-0.87	-0.86	0.85	-0.88	-0.90	-0.91
Specific conductivity			1.00	-0.83	-0.71	-0.81	-0.74	-0.78	-0.85
Pb				1.00	0.87	0.96	0.86	0.91	0.86
Zn					1.00	0.86	0.99	0.99	0.80
Fe						1.00	0.84	0.91	0.80
P							1.00	0.99	0.80
S								1.00	0.83
Cd									1.00

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The data indicate that, immediately preceding a flood, the surface metal concentrations on the sediment are relatively constant, being influenced by quantities of "clean" sediment brought into the system by minor disturbances. Under flood conditions, when the peak of sediment arrives before the discharge peak, the river system is "flushed" of fine material, its source being exhausted before maximum discharge. Wash load material flushed through the system has low values of Pb and Cd, while Zn is least affected.

Iron coatings have a particularly strong scavenging affinity for heavy metals (Cross *et al.*, 1970; Grieve & Fletcher, 1977), and will influence metal equilibria between solution and precipitate, in turn influencing "dilution" and other effects as observed by Grimshaw *et al.* (1976).

Using the Pearson coefficients of correlation as indices of relationships, then under low flow conditions Pb appears bound to sediments in a Fe-Pb form, with Zn probably present as a phosphate with particulate sphalerite (ZnS). With the inclusion of channel-side sources for sediment at the onset of the flood, Pb is present as a phosphate (Nriagu, 1974) with particulate galena (PbS). Iron plays a minor role. On the falling limb Fe is again important and sorbs metal complexes to the sediment surfaces.

Channel sediments

Suspended sediment taken from the river at Pont Llolwen show metal equilibria between solution and precipitate prevailing at that point in time, while analysis of metals on the channel sediments afford a time integrated record due to the "reservoir" qualities of the sediment for heavy metals.

Pagenkopf & Cameron (1979) utilized the decrease in trace metal content of the sediments downstream of a lead smelter to predict how rapidly transfer of metals from solution to sediment takes place. Such studies on the River Ystwyth, however, are complicated by the number and variety of mines downstream, providing variable sources, as does the reworking of alluvial soils from floodplain sites.

Concentrations of Pb, Zn, Cu, with χ in the sediments downstream from Cwmystwyth are shown in Table 2. Lead concentrations decline downstream from Cwmystwyth to Llanilar as does Cu, although there is some input of metals from the disused mill race at Wenallt. Zinc exhibits a more variable response, chemically more mobile than Pb, the ratio Pb to Zn declines downstream, reflecting the leaching of Zn from the Cwmystwyth source to downstream sampling points (Fig.1). The ratio of Pb to Cu declines in a similar fashion to that of Pb and Zn, suggesting that the downstream gradient represents a sorption process and is not solely determined by the composition of the upstream ores, and the proportion of "clean" sediment from low-metal sources feeding in sediment downstream of the mine inputs.

Samples from tributaries draining the Frongoch mines, entering the Ystwyth between Trawscoed and Llanilar, reveal metal ratios different to those in the main channel. The ratio of Zn to Cu is greater in the tributaries, while the Pb to Zn ratio declines. The Frongoch mines provide less Pb and Zn to the system than those on the Ystwyth, but comparable concentrations of Cu. Clearly there is some change in the chemical composition of the mineral ores between

TABLE 2 Metal concentrations on channel sediments

Site and Particle size (μm)	% Fines	Pb	Zn	Cu	χ	Pb/Zn	Pb/Cu	Zn/Cu
		(mg dm ⁻³)						
<i>Cwmystwyth</i>								
2000-500	17.88	4975	126	32	5.0	39	153	3.9
500-180	63.03	3656	132	30	2.3	28	118	4.3
180-63	12.08	3275	119	31	1.9	27	104	3.8
<63	2.01	2936	109	39	1.9	27	75	2.8
<i>Pontrhyd-y-groes</i>								
2000-500	11.97	4033	303	39	1.0	13	104	7.8
500-180	51.96	2303	183	25	1.2	13	94	7.5
180-63	29.88	1828	162	24	1.3	11	75	6.7
<63	6.20	1254	142	26	1.4	9	48	5.5
<i>Wenallt</i>								
2000-500	10.90	1478	177	16	1.0	8	92	11.0
500-180	74.12	1284	151	12	1.0	9	111	13.0
180-63	12.91	1067	152	21	1.3	7	51	7.3
<63	2.07	1512	157	34	1.6	10	45	4.7
<i>Trawscoed</i>								
2000-500	6.88	1805	110	24	0.7	16	74	4.6
500-180	67.81	599	103	13	0.7	6	46	7.8
180-63	22.00	583	105	13	0.6	6	47	8.4
<63	3.31	653	109	17	1.1	6	39	6.6
<i>Llanilar</i>								
2000-500	40.27	828	163	28	0.8	5	29	5.7
500-180	53.23	1141	156	25	1.0	7	45	6.2
180-63	6.03	800	152	36	1.6	5	22	4.2
<63	0.46	801	141	30	1.9	6	27	4.8
<i>Gilwern</i>								
2000-500	50.79	100	108	11	1.8	1	9	9.9
500-180	41.95	188	105	18	1.5	2	10	5.8
180-63	6.56	175	107	29	1.9	2	6	3.8
<63	0.70	311	107	53	4.1	3	6	2.0
<i>Glanystwyth</i>								
2000-500	37.96	237	415	25	1.4	0.6	10	16.9
500-180	18.71	152	477	36	1.2	0.3	4	13.4
180-63	8.21	201	486	40	1.2	0.4	5	12.2
<63	35.12	158	461	52	1.3	0.3	3	9.0

the two main mines, coupled with this is the different success rate in winning the metals from the ore, which has left some spoil heaps relatively rich in heavy metals.

Considering metal concentrations on a particle size basis, greater concentrations of metals are found in the coarser fractions (Table 2). Usually the fines exhibit the greatest metal concentrations due to sorption on their greater surface area (Oliver, 1973); the coarser fractions studied may have fine particulate metal inclusions. However, the fines are more mobile within the system,

being deposited on the recession limb of floods. As has been seen for wash load suspended material, the concentration of heavy metals decline in the flood, the fine channel side sediments analysed represent suspended sediments from the preceding flood.

It appears then that two processes are operating simultaneously; firstly, ore particles are being transported attached to less dense material, the critical entrainment velocity for particles of galena (specific gravity 7.5 g cm^{-3}) results in the rapid deposition of "pure" particulates, and secondly, chemical equilibria prevailing under flood conditions within the river determine concentrations of metals sorbed to the surface of suspended materials.

Magnetic properties

The relationships of heavy metals to magnetic susceptibility are also studied, without considering Fe concentration, which it undoubtedly reflects. A certain degree of masking of χ from different particle sizes obviously exists, and bulk sample data are used to counter this effect. Considering the sample sites from the main channel only, the tributaries have metal ratios characteristic of the Frongoch ore-field, then the relationship of χ to Pb, (Pearson coefficient of correlation, $r = 0.951$), suggests that Pb within the channel is fixed in a Pb-Fe complex, and not as an organic-metal complex as suggested by Davies (1975), although within the alluvial soils such as organic-metal complex is more probable. Of the other metals considered, Cu to χ exhibits a correlation coefficient of 0.763, while Zn provides a poor correlation ($r = -0.084$). In principle, therefore, monitoring of stream sediments contaminated from a point source, for Pb and Cu can be undertaken cheaply and quickly by χ , and further work is continuing (Bradley *et al.*, unpublished data).

CONCLUSIONS

The mobilization and transport of heavy metals has often been considered in terms of soluble loads in river water. In the River Ystwyth, however, it is demonstrated that surface coatings of Pb, Zn and Cd also vary with discharge. The "dilution" effect as seen in studies concerned with soluble load applies equally to surface coatings, while on the falling limb, metal concentrations change according to variable sources and Fe strongly influences the equilibrium between soluble and particulate load.

From the preliminary study of metal ratios on sediments influenced by mines in different parts of the catchment, the provenance of sediments accumulating further downstream can be determined. χ measurements provide an indirect means to determine Pb and Cu contamination from a point source, both cheaply and quickly. XRF is also rapid and non-destructive, and does not rely upon selective extraction procedures as does AAS, but provides a measure of total surface metal concentration on samples.

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