

**Water Technology Research Group**

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**ENVIRONMENTAL IMPACT OF ACID MINE DRAINAGE  
ON THE RIVER AVOCA: Metal Fluxes in water and  
sediment. Part II. Metal Contamination of Riverine  
Sediments**

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## EXECUTIVE SUMMARY

The discharge of acid mine drainage (AMD) from sulphur bearing mineral deposits causes iron to precipitate as hydroxides and the formation of ochreous deposits on the substrate of the receiving river system. The sediments were studied during a low flow period to establish the degree of contamination and to identify the major processes affecting sediment metal concentrations. The pH plays a major role in regulating Zinc adsorption and desorption in sediments, showing a significant correlation ( $p < 0.001$ ). The Zinc concentration in the sediment falls below background concentrations obtained from the upstream reference site. However, the metal came out of solution when the pH increased downstream of a fertilizer factory ( $pH > 8.0$ ), some 7 km below the mine. In contrast Cu and Fe concentrations significantly increased ( $p < 0.001$ ) both in the subsurface sediment (0-30 mm depth) and the surface ochre deposit immediately below the mixing zone. Iron concentration decreased with distance from the AMD source, whereas Cu showed a second peak in concentration below the fertilizer factory. Copper removal appears to be primarily by co-precipitation with iron showing a significant relationship. Organic matter content in sediment was highest at the sampling site closest to the mine discharge.

Higher sediment enrichment factors for all metals were obtained in the surface sediment layer (ochre) deposited on larger stones and in floc material collected in sediment traps, compared to the subsurface sediment. Copper showed particularly strong enrichment in the surface layer and floc. Cadmium was not recorded in any of the sediment collected at the detection limit used ( $< 0.01 \mu\text{g g}^{-1}$ ). Metal deposition in the sediments was found to be spatially variable, so sub-sampling is required, although replicates showed less variation. Results indicate that short term variation in metal inputs are identified by sampling the surface layer or by collection of floc material in sediment traps, whereas sampling of the subsurface layer is more suitable for identifying long-term trends in sediment quality.

## INTRODUCTION

Metals are naturally present in aquatic environments due to geochemical weathering. In rivers and lakes, their concentration is variable depending on equilibrium dynamics resulting from two competing processes. The dissolution of minerals from rock, soil, sediments and suspended particles tend to increase the concentration in the dissolved phase, whilst precipitation, co-precipitation and adsorption remove these metals from solution. Local conditions can significantly effect soluble metal concentrations particularly, near the vicinity of ore bodies. Mining effluent is an important source in the overall metal load entering the hydrosphere. The discharge of acidic water containing toxic concentrations of a variety of metals from abandoned mine workings pose a serious and widespread threat to the environment (Kelly, 1988). Sediments contaminated by acid mine drainage (AMD) may represent a significant problem regarding residual contamination.

The mining area in Avoca is principally drained by two major leachate streams. The Deep Adit on the eastern side and the Ballymurtagh Adit on the western side which discharge considerable quantities of AMD directly into the Avoca River resulting in severe contamination by toxic metals, and the elimination of both invertebrates and vertebrates in the river. High concentrations of iron from the AMD precipitate as hydroxides forming ochreous deposits on the substrate of the receiving river system. The scavenging property of these ochreous deposits, and the sorption capacities of sediments and organic matter result in severe toxic metal pollution of the sediments.

The aims of this study are to (i) measure total concentration of Fe, Zn and Cu and organic matter content of the sediment, (ii) determine spatial and temporal variation with regard to metal loading of Fe, Zn and Cu and (iii) to determine metal variability within sites and sub-sites.

## MATERIALS AND METHODS

### Location of sampling sites

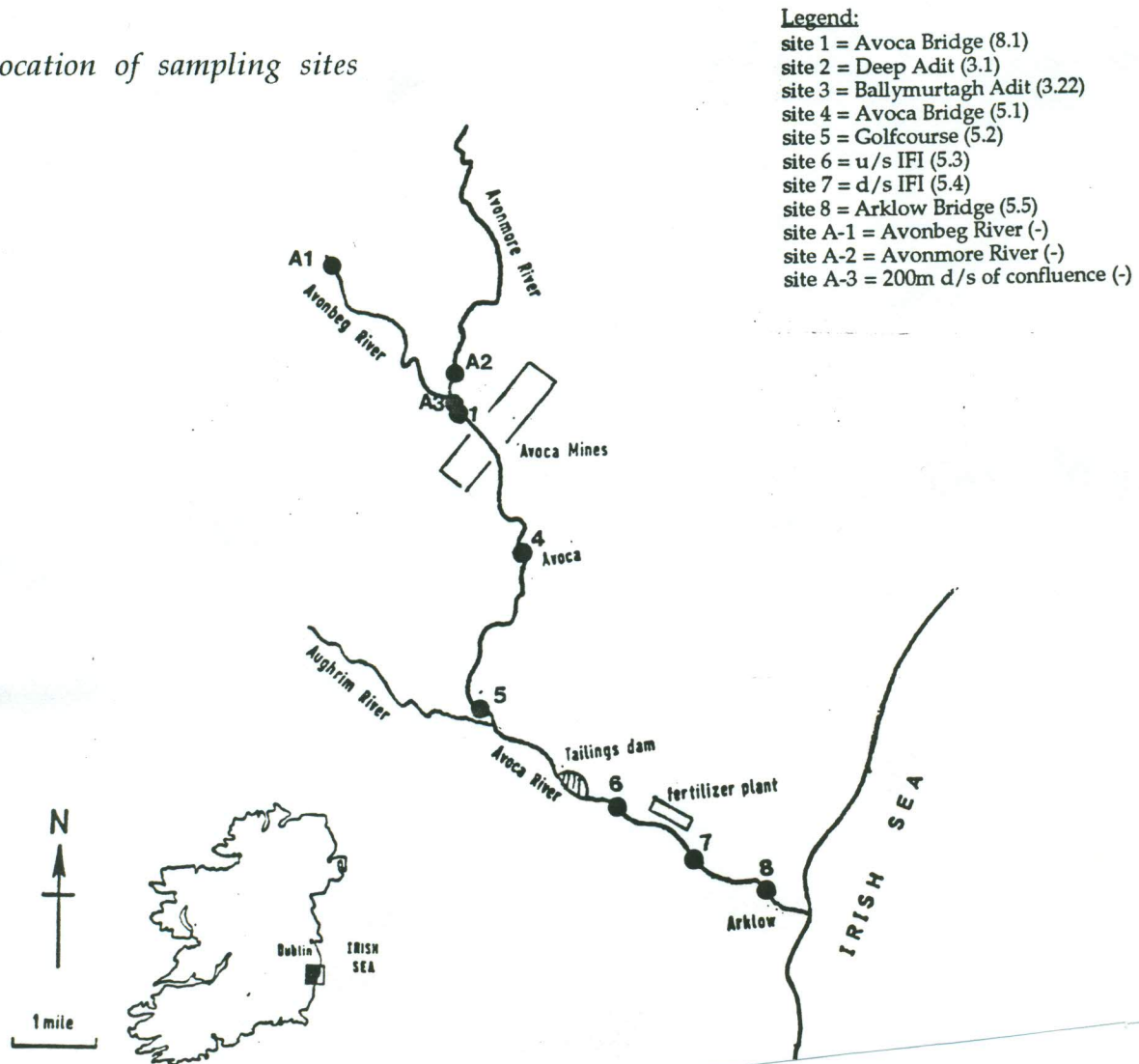


Fig. 1. Map showing location of Avoca Mines and individual sampling sites

### Collection and analysis of subsurface sediment

Samples were taken from both the sediment layer (0-30 mm) and from the deposited ochreous material on the surface of the river bed. The former is defined as the subsurface sample, the latter as surface samples. Approximately 3kg of the subsurface sediment was collected with a plastic scoop at five sites along the river, on the 29.6.94 and 4.8.94 during low flow conditions. All samples were pre-sieved in the field through a 1 mm mesh using river water. The <1mm fraction was retained and stored in 2 l polyethylene bottles. To measure variability of sediment metals within sites three sub-sites were chosen at sampling sites 1, 4 and 6. Sub-site samples

were taken in a cross-transect only when conditions made it possible, otherwise they were taken randomly from the river bank to the furthest reach in the middle of the river. To measure sub-site variation three samples were taken at each sub-site making 9 samples in all for each of the five stations along the river (Appendix I) (Fig. 1). Samples were frozen within eight hours of collection until analysed. Fig. 2 show the sediment analysis procedure diagrammatically.

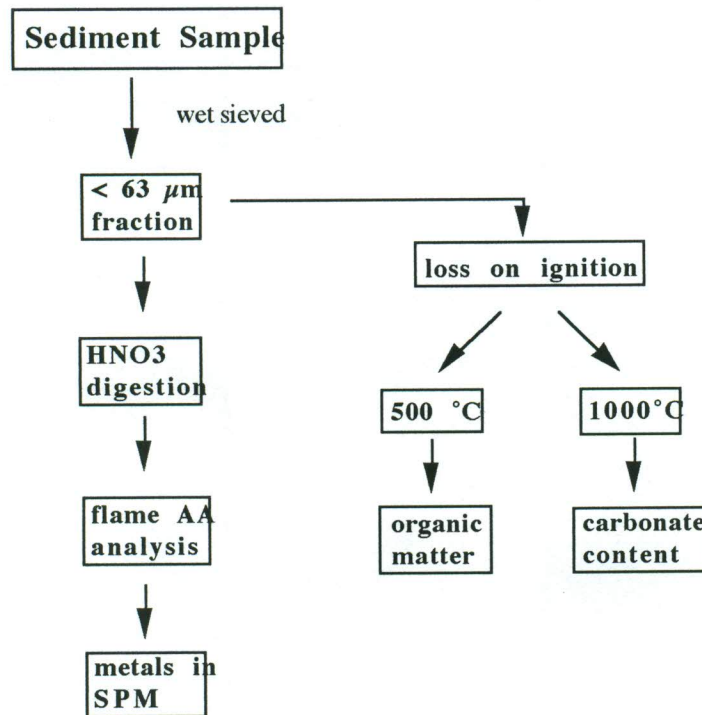


Fig. 2. Flow diagram showing collection and analysis of bottom sediment.

In the laboratory, subsurface sediment samples were wet sieved through a 0.63  $\mu\text{m}$  mesh using river water (Salomon, 1993), and the  $<63 \mu\text{m}$  fraction collected for further metal analysis. Samples were dried at  $101^\circ \text{C}$  to constant weight. Total Zn, Cu, Fe and Cd in sediment samples were determined by nitric acid digestion followed by flame atomic adsorption spectrophotometry (AAS) using a Perkin Elmer<sup>®</sup> 3100. For the acid digestion a sub-sample of between 0.3 to 0.4g dried and ground sample material was weighed into digestion tubes and digested in 10 ml of concentrated nitric acid (70%) for 2 hours on a Tecator<sup>®</sup> digestion block at  $170^\circ \text{C}$ . The tubes were acid rinsed with 20% nitric acid prior to digestion.

When the acid in the tubes had been reduced to 1-2 ml the digested samples were filtered through Whatman No 1 filters, thoroughly rinsed and made up to 50 ml volume in volumetric flasks. Variability within the digestion unit was determined by digesting replicate samples (2 and 3 replicates). Quality control on metal analysis was maintained by digestion of the certified reference material MESS-1 (estuarine sediment) and BCSS-1 (coastal marine sediment), as well as by including method blanks and spiked samples.

Organic carbon and carbonate was determined by loss on ignition (APHA, 1989). Approximately 0.5 g was weighed into pre-dried crucibles and heated to 550°C for 3 hours, cooled in a desiccator and weighed to determine organic matter. After weighing, the samples were further heated to 1000°C for 3 hours and weighed to determine carbonate content.

The erosional characteristics of the river required that the sampling techniques had to be modified. The nature of the top substrate consisted largely of boulders and stones which made it impossible to use sampling devices such as grab samplers (e.g. Eckmann). In order to obtain a sample of fine sediment, the big stones and boulders had to be removed extremely carefully to expose the finer material. Any disturbance caused the iron oxide layer to be washed off, and even with careful collection procedures a significant proportion of the fine material was lost. This was also the case in lowland depositional areas where loosely deposited Fe-floc was washed away during sampling. For this reason surface and subsurface sediment samples had to be sampled separately at the erosional sites and with great care at all depositional sites.

#### *Collection and analysis of floc and surface samples*

Floc samples were collected in several ways: (i) floc samples from pools were taken up using a wide bore syringe and collected in 50 ml bottles; (ii) floc samples were also collected by scraping the surface material from dry or almost dried out pools and stored in plastic bags; (iii) floc samples were collected in 3l plastic sediment traps at sites 4 and 6. Sediment traps were buried in the river bed and collected material removed at weekly intervals, and brought back to the laboratory in 2l polyethylene containers. (iv) Stones of approximately 200 mm diameter were also collected at sites 4 and 6 for the

analysis of surface precipitate composition. Three stones of equivalent size were treated as one replicate sample. Three replicate samples were taken at each site. Floc samples collected by syringe were filtered through 0.45  $\mu\text{m}$  cellulose nitrate filters, dried and digested in the microwave with 5 ml of nitric acid (70 %) and 5 ml de-ionised water for 70 min. Samples were made up to 25 ml in volumetric flasks using distilled deionised water. All other floc samples were dried at 101°C to constant weight and digested on the digestion block as before. Iron precipitate was washed off the stones manually, and dried at 101°C and digested in the digestion block as described above. Samples were analysed for Fe, Zn Cu, and Cd using flame AAS.

## RESULTS

### *Metals in subsurface sediments (<63 $\mu\text{m}$ )*

The sediment analysis carried out provides a measure of the total concentration of specific metal constituents for each site. Results from subsurface sediment analysis for Zn, Cu and Fe in the < 63  $\mu\text{m}$  fraction for sediment samples taken on the 29.6.94 and 4.8.94 and their arithmetic means are shown in Figs. 3 a,b,c respectively, and the raw data is presented in Appendix 2. Mean concentrations including standard deviation of contaminated and uncontaminated sites as well as percentage recovery of metals from reference material is shown in Table 1. Student t-tests were carried out to detect significant differences between sites at a 95 % confidence level (Table 2). Sediment samples were also analysed for Cd, however, no Cd was detected.

It was apparent from the two sampling episodes which were five weeks apart from each other, that the metals measured in the < 63  $\mu\text{m}$  fraction exhibited the same pattern of behaviour at each sampling site on both dates. Numbers of sub-site samples collected were reduced from three to two on the second field survey at all sites to reduce the work load. The change in numbers of samples at each sub-site, however, did not affect the overall pattern for metals found in the sediment fraction. All metal levels in the following text are referred to as mean values.



Figure 3a showed that Zn concentration in the subsurface sediment decreased slightly between site 1 ( $662.2 \mu\text{g g}^{-1}$ ) and the following three sampling sites (4,5 and 6) with values of  $533.5$  ( $p < 0.01$ ),  $433.6$  ( $p < 0.001$ ),  $498.0$  ( $p < 0.01$ )  $\mu\text{g g}^{-1}$ , respectively, after acid mine drainage effluent entered the river system (Table 2). The change in Zn concentration was accompanied with a change in pH. A significant increase ( $p < 0.01$ ) in Zn concentrations ( $2713 \mu\text{g g}^{-1}$ ) was observed at the site 7 where pH also increased significantly ( $p < 0.01$ ) to 8.7.

Table 1. Mean concentrations and standard deviation (in parenthesis) of uncontaminated and contaminated, as well as percent recovery from digestion procedure for certified reference material

	Zn ( $\mu\text{g g}^{-1}$ )	Cu ( $\mu\text{g g}^{-1}$ )	Fe ( $\mu\text{g g}^{-1}$ )
Mean concentration of uncontaminated site	662.2 (146)	84.0 (22)	5.5 (1.4)
Mean concentration for all contaminated sites	834 (741)	593 (173)	7.7 (1.7)
Certified reference material	Percentage recovery		
MESS-1	86.3	76.7	86.4
BCSS-1	78.9	78.4	87.9

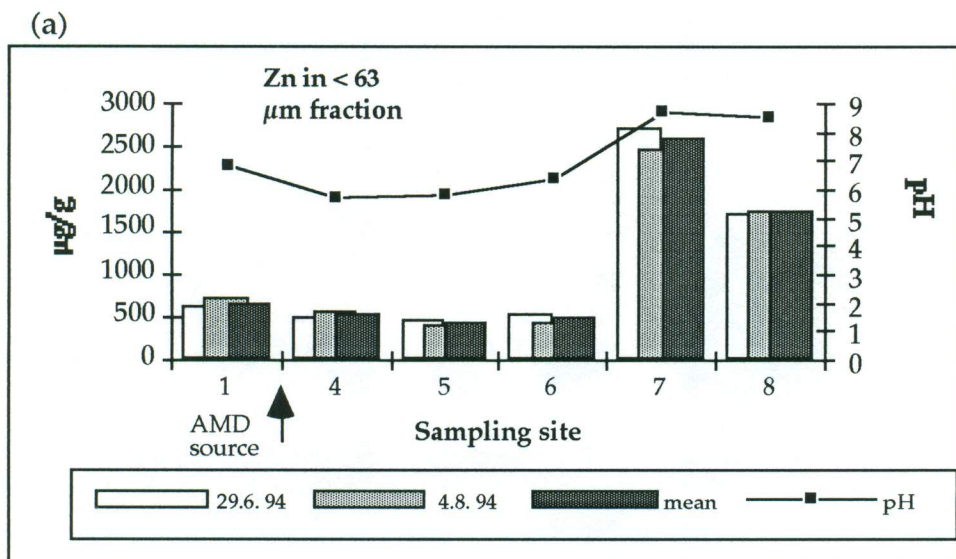
Copper in the sediment, however, behaved somewhat differently (Figure 4b). A significant increase ( $p < 0.001$ ) in Cu concentration between the background levels at site 1 ( $84.0 \mu\text{g g}^{-1}$ ) and site 4 ( $681.3 \mu\text{g g}^{-1}$ ) was observed at site 4 where complete mixing of AMD and river water had taken place. Another significant increase ( $p < 0.05$ ) occurred between the sites 1 and 7 ( $84.0$  and  $891.0 \mu\text{g g}^{-1}$ , respectively) where pH increased to 8.7. At site 8 Cu concentrations ( $430.4 \mu\text{g g}^{-1}$ ) compared to site 7 decreased, although not significantly. The only significant change ( $p < 0.001$ ) for Fe occurred between the background value at the site 1 (5.5 %) and below the mixing zone at site 4 (9.0 %). Iron levels after site 4 gradually decreased downstream, however, no significant changes were detected (Figures 4c). The mean river pH, taken from weekly observations over a 11 week period (29.3.94-31.8.94), dropped from pH 6.8 at the site 1 to pH 5.7 at site 4 Figure 4. The pH slowly recovered

downstream. A significant increase ( $p < 0.01$ ) in pH was observed at site 7 where the river is subjected to a considerable discharge of effluent from the IFI (fertilizer) factory containing large quantities of ammonia.

Table 2. Significant differences between sites for Zn, Cu and Fe in the subsurface sediment (0-30mm)

	site 1			site 4			site 5			site 6			site 7		
	Zn	Cu	Fe	Zn	Cu	Fe	Zn	Cu	Fe	Zn	Cu	Fe	Zn	Cu	Fe
site 4	**	***	***												
site 5	***	***	***	NS	NS	NS									
site 6	**	***	***	NS	**	**	NS	NS	NS						
site 7	*	**	NS	**	NS	**	**	*	NS	**	*	NS			
site 8	*	**	NS	*	*	**	*	NS	*	*	*	***	NS	NS	NS

Levels of significance is given as  $p < 0.05^*$ ,  $p < 0.01^{**}$ ,  $p < 0.001^{***}$ , N.S. not significant



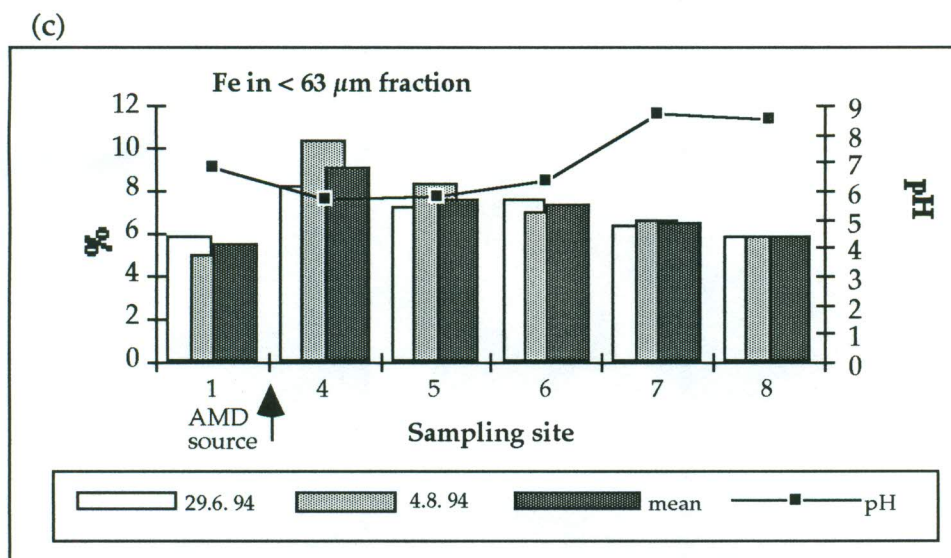
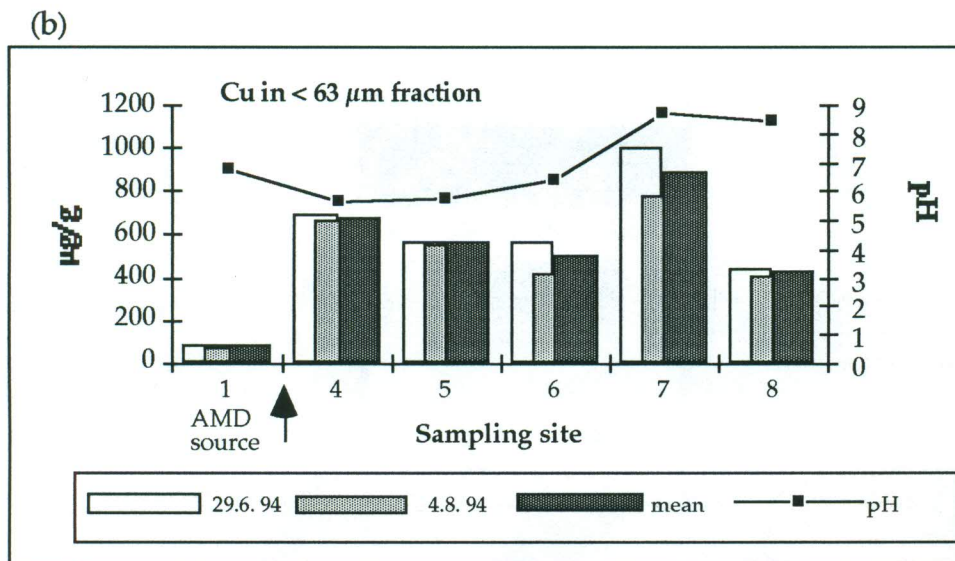


Fig. 3. Mean concentrations of (a) Zn ( $\mu\text{g g}^{-1}$ ), (b) Cu ( $\mu\text{g g}^{-1}$ ) and (c) Fe (%) in the subsurface sediments collected on the 26.6.94 and 4.8.94, including pH

*Additional survey including Avonbeg and Avondale*

Because background concentrations for Zn and Fe were relatively high, an additional sampling survey was carried out further upstream and on the Avonbeg and Avonmore River (sites A-1 and A-2, respectively) on 27.11.94. The results for Zn, Cu and Fe from sampling of the sediment < 63µm fraction are shown in Table 3. Zinc concentrations at site A-3, approximately 400 m upstream of site 1, are significantly ( $p < 0.05$ ) lower than at the site 1 (258.2 and 639.4  $\mu\text{g g}^{-1}$ , respectively). Zinc concentrations at site A-2 and site A-1 were also elevated (754.0  $\mu\text{g g}^{-1}$  and 406.4  $\mu\text{g g}^{-1}$ ), however not

significantly. Copper and Fe concentrations were generally not significantly different at the survey sites. Only Cu concentration between site 1 and A-1 differed significantly ( $p < 0.05$ ). Samples at site A-3 were taken about 2-4 m off the left bank. Complete mixing of the Avonbeg and Avonmore River had not taken place at site A-3 and therefore the sample taken from the left bank is mainly influenced by the Avonbeg River which was not subjected to mining activities. Nineteenth century Pb-Zn mining was extensively carried out in the Avonmore catchment with the exposed riverside spoil heaps still undergoing weathering and erosion.

Table 3. Mean concentrations of Zn ( $\mu\text{g g}^{-1}$ ), Cu ( $\mu\text{g g}^{-1}$ ) and Fe (%) from additional subsurface sediment sampling on 27.11.94.

	N	Mean	Median	SD	Min	Max
<b>Zn (<math>\mu\text{g g}^{-1}</math>)</b>						
site 1	3	639.4	568.3	132.9	557.2	792.7
site A-3	3	258.2	200.3	87.1	158.1	316.3
site A-2	3	754.0	779.0	217.0	526.0	957.0
site A-1	3	406.4	419.2	70.3	330.6	469.5
<b>Cu (<math>\mu\text{g g}^{-1}</math>)</b>						
site 1	3	64.2	62.2	6.1	59.4	71.0
site A-3	3	56.6	40.5	28.1	40.3	89.0
site A-2	3	65.2	62.4	6.3	60.9	72.4
site A-1	3	37.5	36.6	2.5	35.5	40.3
<b>Fe (%)</b>						
site 1	3	5.0	5.1	0.3	4.7	5.3
site A-3	3	4.6	4.5	0.4	4.3	5.0
site A-2	3	5.4	5.3	0.1	5.3	5.5
site A-1	3	5.2	5.2	0.4	4.8	5.6

#### *Organic carbon and carbonate content*

Loss on ignition at 500°C and 1000°C gives an approximate measure of organic content and total carbonate content respectively. Table 4 shows results from organic carbon analysis by loss on ignition in the sediment < 63  $\mu\text{m}$  fraction for samples taken on 29.6.94. The results show that organic carbon levels are highest at site 4. Organic matter level is significantly

reduced after the Avoca-Aughrim river confluence at site 6. Analysis of variance ANOVA also shows significant differences ( $p < 0.001$ ) in % organic matter between sites 1 and 4, and sites 5 and 6.

Table 4. Organic matter (%) in bottom sediment fraction  $< 63 \mu\text{m}$

	n	Mean	Median	SD	Min	Max
site 1	9	13.3	12.1	3.3	8.2	18.8
site 4	9	21.6	19.3	5.4	13.7	30.2
site 5	3	18.2	17.4	6.3	12.2	24.9
site 6	9	10.3	10.8	2.0	6.0	12.3
site 7	3	12.6	12.6	0.7	11.9	13.3
site 8	3	9.7	9.9	1.2	8.5	10.8

The  $\text{CaCO}_3$  provides a measure of the buffering capacity of a sediment. Results for carbonate contents expressed as %  $\text{CaCO}_3$  is shown in Table 5. After the Avoca-Aughrim confluence at site 6, carbonate in the sediment increased to 10.22 %, however, significant differences (ANOVA) were not detected between sites.

Table 5. Carbonate content (%) in  $< 63 \mu\text{m}$  bottom sediment fraction

Location	n	Mean	Median	SD	Min	Max
site 1	9	7.16	7.65	0.95	5.64	8.08
site 4	9	8.18	7.83	1.58	6.10	10.60
site 5	3	8.38	8.42	0.63	7.73	8.98
site 6	9	10.22	8.49	5.45	6.76	24.48
site 7	3	8.43	7.94	1.24	7.52	8.85
site 8	3	6.92	6.93	0.32	6.60	7.23

#### *Metals on surface samples*

To compare metal concentrations of the surface layer with that of the subsurface sediment ( $< 63 \mu\text{m}$  fraction), stones were taken from the river bed, washed and the recovered sediment digested. Results of surface

sampling on 29.6.94 at sites 1, 4 and 6 are shown in Table 6. The surface scraping at site 1 consisted mainly of organic matter, as there was no iron precipitate visible. Analysis of variance (ANOVA) was applied to test for significant differences between sites. Zinc and Cu levels differed significantly from each other ( $p < 0.001$ ), whereas no significant differences could be detected among the sites for Fe levels due to high variance at site 4 (8.3 %).

Table 6. Mean concentrations of Zn ( $\mu\text{g g}^{-1}$ ), Cu ( $\mu\text{g g}^{-1}$ ) and Fe (%) from river surface samples (stones of 20 cm in diameter) taken on 29.6.94.

	N	Mean	Median	SD	Min	Max
<b>Zn (<math>\mu\text{g g}^{-1}</math>) ***</b>						
site 1	3	655.8	634.8	81.9	586.4	746.1
site 4	3	330.0	373.7	102.7	212.6	403.6
site 6	3	966.6	977.8	47.9	914.1	1007.9
<b>Cu (<math>\mu\text{g g}^{-1}</math>) ***</b>						
site 1	3	55.2	35.4	34.3	35.3	94.3
site 4	3	1184.2	1191.1	19.2	1162.5	1199.1
site 6	3	1878.4	1865.6	144.2	1741.0	2028.6
<b>Fe (%) N.S.</b>						
site 1	3	4.5	3.8	1.6	3.3	6.4
site 4	3	17.1	13.1	8.3	11.6	26.7
site 6	3	11.4	11.5	1.3	9.9	12.6

Levels of significance is given:  $p < 0.05^*$ ,  $p < 0.01^{**}$ ,  $p < 0.001^{***}$ , N.S. not significant

Table 7 compares results for metal concentrations obtained from surface sampling with the  $< 63 \mu\text{m}$  fraction. The Student t-test was applied to estimate levels of significance (Table 8) between subsurface and surface sediments. Zinc levels in the  $< 63 \mu\text{m}$  fraction at site 4 are higher ( $509.4 \mu\text{g g}^{-1}$ ) compared to the surface fraction ( $330.0 \mu\text{g g}^{-1}$ ), however not significantly. This observation is reversed at site 6 where the  $< 63 \mu\text{m}$  fraction is significantly ( $p < 0.05$ ) lower ( $542.2 \mu\text{g g}^{-1}$ ) compared to the surface fraction ( $966.6 \mu\text{g g}^{-1}$ ). Both Cu and Fe concentrations are higher at site 4 and site 6 in the surface fraction ( $1184.2$  and  $1878.4 \mu\text{g g}^{-1}$ , and  $17.1$  and  $11.4 \%$ ,

respectively) compared to the <63  $\mu\text{m}$  subsurface sediment fraction (690.5 and 570.9  $\mu\text{g g}^{-1}$ , and 8.3 and 7.5 %, respectively). However only Cu showed significant differences ( $p < 0.001$ ) at site 4, whereas at site 6 Cu and Fe were significantly different ( $p < 0.01$  and  $< 0.05$ , respectively). Metal concentrations at the control site 1 are similar with no significant differences between the two sampling methods.

Table 7. Comparison of mean concentrations of Zn ( $\mu\text{g g}^{-1}$ ), Cu ( $\mu\text{g g}^{-1}$ ) and Fe (%) in the < 63  $\mu\text{m}$  fraction and surface samples collected on the 29.6.94.

	n surface samples		n subsurface			
Zn ( $\mu\text{g g}^{-1}$ )	Mean	SD	Mean	SD		
site 1	3	655.8	81.9	9	624.5	104.0
site 4	3	330.0	103.0	9	509.4	173.9
site 6	3	966.6	47.9	9	542.2	118.1
Cu ( $\mu\text{g g}^{-1}$ )						
site 1	3	55.2	34.2	9	87.2	28.2
site 4	3	1184.2	19.5	9	690.5	177.0
site 6	3	1878.4	144.0	9	570.9	128.2
Fe (%)						
site 1	3	4.5	1.7	9	5.9	1.7
site 4	3	17.1	8.3	9	8.2	0.7
site 6	3	11.4	1.4	9	7.6	0.8

Table 8. Significant levels for Zn, Cu and Fe concentrations between subsurface and surface sediment at individual sites (t-test).

	Zn	Cu	Fe
site 1	N.S.	N.S.	N.S.
site 4	N.S.	$p < 0.05$	N.S.
site 6	$p < 0.05$	$p < 0.01$	$p < 0.001$

Comparison of surface sampling from two sampling intervals at site 4 showed an significant increase of Zn concentration from 330.0 to 919.1  $\mu\text{g g}^{-1}$  ( $p < 0.01$ ), whereas Cu and Fe are not significantly different. However, because of the limited number of sampling surveys these results are not conclusive (Table 9).

Table 9. Comparison of mean concentrations for Zn ( $\mu\text{g g}^{-1}$ ), Cu ( $\mu\text{g g}^{-1}$ ) and Fe (%) from river surface samples taken on the 29.6.94 and 27.11.94.

	n	Mean	Median	SD	Min	Max
<b>Zn (<math>\mu\text{g g}^{-1}</math>) **</b>						
site 4 (29.6.94)	3	330.0	373.7	102.7	212.6	403.6
site 4 (27.11.94)	3	919.1	893.2	133.6	800.4	1063.8
<b>Cu (<math>\mu\text{g g}^{-1}</math>) N.S.</b>						
site 4 (29.6.94)	3	1184.2	1191.1	19.2	1162.5	1199.1
site 4 (27.11.94)	3	1317.7	1303.2	114.7	1211.0	1439.0
<b>Fe (%) N.S.</b>						
site 4 (29.6.94)	3	17.1	13.1	8.0	11.6	26.7
site 4 (27.11.94)	3	24.1	23.4	1.7	23.0	26.1

Levels of significance is given:  $p < 0.05^*$ ,  $p < 0.01^{**}$ ,  $p < 0.001^{***}$ , N.S. not significant (t-test)

#### *Floc samples*

Results of metal analysis from floc material collected in sediment traps at site 4 and site 6 are shown in Table 10. Organic matter content of the floc material was approximately 50%. Zinc concentrations are relatively low ( $592.8$  and  $911.2 \mu\text{g g}^{-1}$ ) compared to Cu ( $808.3$  and  $1879.0 \mu\text{g g}^{-1}$ ). Zinc and Cu concentrations increase significantly ( $p < 0.01$  and  $p < 0.001$ , respectively) from site 4 to 6, whereas Fe concentrations decrease slightly, although, not significantly.

In areas of stagnant water or extremely slow flowing water, floc material accumulates. This floc is easily scoured away when flow increases or when substrate is physically disturbed. Table 11 shows metal concentrations in floc material that accumulates in pools and near the river bank. Zinc concentrations are relatively low at site 4 ( $539 \mu\text{g g}^{-1}$ ) and increase significantly ( $p < 0.01$ ) at site 6 ( $1940 \mu\text{g g}^{-1}$ ) nearly four-fold. Iron and Cu concentrations are approximately the same at the two sites and show no significant increase.



Table 10. Mean concentrations of Zn ( $\mu\text{g g}^{-1}$ ), Cu ( $\mu\text{g g}^{-1}$ ) and Fe (%) from floc samples collected in sediment traps.

	n	Mean	Median	SD	Min	Max
<b>Zn (<math>\mu\text{g g}^{-1}</math>) **</b>						
site 4	4	592.8	602.4	94.7	486.4	680.2
site 6	10	911.2	875.8	63.6	832.8	1007.3
<b>Cu (<math>\mu\text{g g}^{-1}</math>) ***</b>						
site 4	4	808.3	777.1	86.8	742.7	936.1
site 6	10	1879.0	2074.0	474.0	1331.0	2410.0
<b>Fe (%) NS</b>						
site 4	4	9.8	9.1	1.7	8.7	12.3
site 6	10	7.7	7.5	1.0	6.5	9.4

Levels of significance is given:  $p < 0.05^*$ ,  $p < 0.01^{**}$ ,  $p < 0.001^{***}$ , N.S. not significant (t-test)

Table 11. Mean concentrations of Zn ( $\mu\text{g g}^{-1}$ ), Cu ( $\mu\text{g g}^{-1}$ ) and Fe (%) of floc samples collected from pools using a wide bore syringe.

	n	Mean	Min	Max	SD
<b>Zn (<math>\mu\text{g g}^{-1}</math>) **</b>					
site 4	12	539	168	1903	513
site 6	3	1940	364	4325	1213
<b>Cu (<math>\mu\text{g g}^{-1}</math>) NS</b>					
site 4	11	1818	1067	4314	971
site 6	3	2099	1529	2560	524
<b>Fe (%) NS</b>					
site 4	12	5.6	2.0	11.5	3.0
site 6	3	4.6	2.4	6.3	2.0

level of significance:  $p < 0.05^*$ ,  $p < 0.01^{**}$ ,  $p < 0.001^{***}$ , NS not significant (t-test)

Table 12 shows results of the floc material that was collected from dry and semi-dry pool areas. Zinc concentration at site 4 are relatively low ( $227 \mu\text{g g}^{-1}$ ) and increase five fold ( $p < 0.001$ ) at site 6 ( $1165 \mu\text{g g}^{-1}$ ), whereas Fe concentrations decrease significantly ( $p < 0.05$ ) and Cu shows no significant changes.

Table 12. Mean concentrations of Zn ( $\mu\text{g g}^{-1}$ ), Cu ( $\mu\text{g g}^{-1}$ ) and Fe (%) from dry and semi-dry pool areas.

	n	Mean	Min	Max	SD
Zn ( $\mu\text{g g}^{-1}$ ) ***					
site 4	5	227	200	251	20
site 6	5	1165	251	1764	700
Cu ( $\mu\text{g g}^{-1}$ ) NS					
site 4	5	1116	531	1291	329
site 6	5	1253	455	1947	630
Fe (%)*					
site 4	5	7.6	7.1	8.3	0.56
site 6	5	5.8	4.0	7.7	1.4

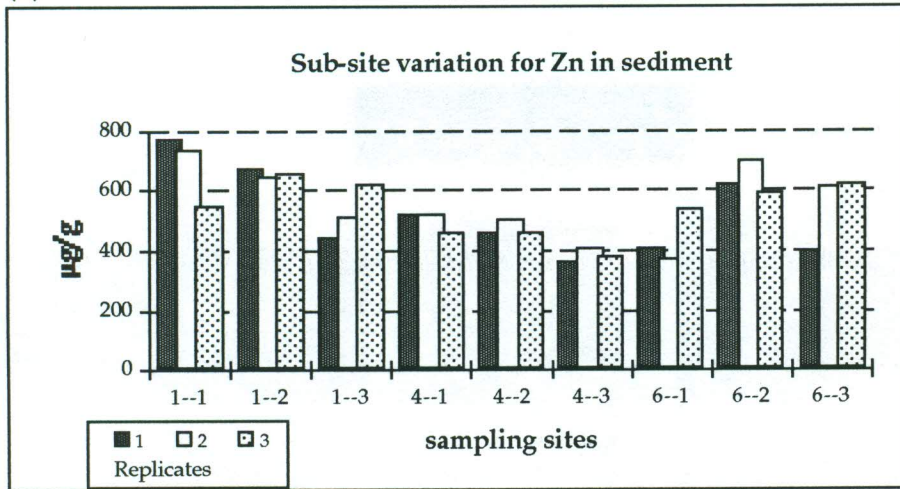
level of significance:  $p < 0.05^*$ ,  $p < 0.01^{**}$ ,  $p < 0.001^{***}$ , NS not significant

#### *Metal variability in bottom sediment*

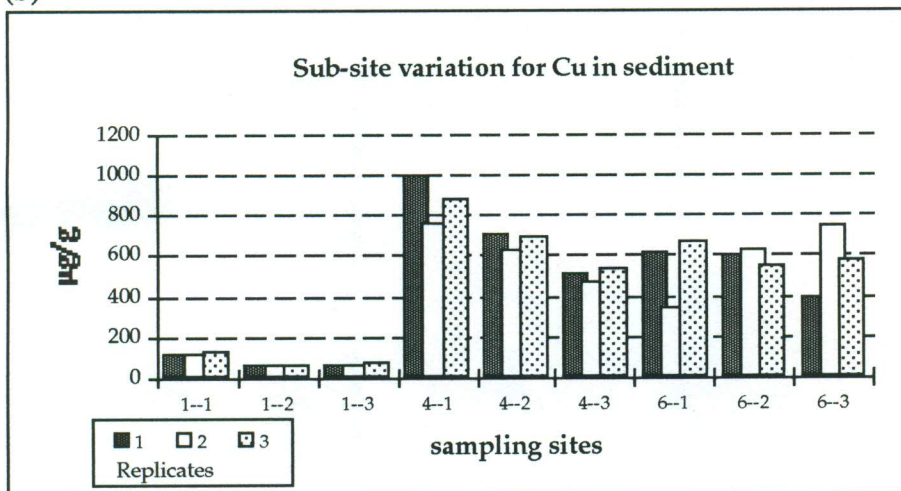
Sub-sites variation studies were carried out at three individual sampling sites (sites 1, 4 and 6) on 29.6.94 and the results are shown in Figs 4a,b,c and raw data is presented in Appendix 3. Due to the depth of the river, sediment samples could only be taken from a straight cross-transect at site 6 (Appendix 1c). At sites 1 and 4 samples were collected from the middle of the river bed and from approximately 2-3m from the river bank (Appendix 1 a, b).

Analysis of variance (ANOVA) was applied to detect significant differences in metal concentrations between sub-sites replicates, sub-sites, and sites (Figs. 54a,b,c). Significant differences for Zn ( $p < 0.05$ ), Cu ( $p < 0.01$ ) and Fe ( $p < 0.001$ ) at sub-site and also significant differences ( $p < 0.01$ ) in metal concentration for sites were detected. Analysis of variance was also used to test machine variability of digested replicate samples on the digestion block. There was no significant difference ( $p > 0.05$ ) for Fe, Cu and Zn between replicates, whether two ( $p = 0.983$ ,  $p = 0.966$ ,  $p = 0.814$ , respectively) or three ( $p = 0.854$ ,  $p = 0.996$ ,  $p = 0.996$ ) replicate samples were digested.

(a)



(b)



(c)

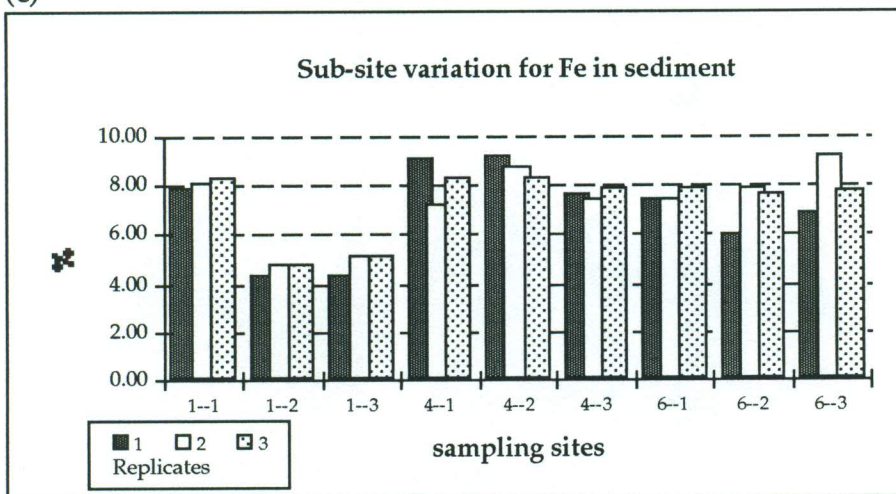


Fig. 4. Metal concentration in subsurface sediment showing sub-site and replicate variation for Zn ( $\mu\text{g g}^{-1}$ ), Cu ( $\mu\text{g g}^{-1}$ ) and Fe (%) at sites 1, 4 and 6.

## DISCUSSION

### *Spatial variation of Zn, Cu and Fe*

The main discharge of dissolved Cu and Zn occurs via the two main adits (Ballymurtagh and Deep Adit). The mean monthly discharge for Fe, Zn and Cu, over the period of May to October 1994, was 312, 117 and 7.2 kg d<sup>-1</sup> respectively. There was a maximum discharge in May of 645, 210 and 21.7 kg d<sup>-1</sup> and a minimum discharge in October of 169, 69 and 1.5 kg d<sup>-1</sup> respectively. The mass input of Fe, Zn and Cu in both Adits decreased over the sampling period (Gray, 1995).

The study showed that Zn concentrations in the subsurface sediment at site 4 decreased slightly (Fig. 3(a)) which would suggest that Zn is leached from the sediment rather than accumulated. Zinc only increased significantly at site 7 ( $p < 0.01$ ) which was due to a significant increase ( $p < 0.01$ ) in pH in the surface water. This suggested that Zn may have come out of solution at this site and adsorbed to the sediment. This trend was also observed in a study carried out by Fitzpatrick (1982) using the larger sediment fraction of  $< 2$ mm. However, because of the large difference in grain size of the analysed sediment fraction, results are not comparable. It was also found that Zn in the surface layer was lower at site 4 compared to site 1 and 6 (Table 6). The pH at site 4 was generally below 6 and increased slowly downstream. The Zn in the sediment was strongly correlated with pH ( $p < 0.001$ ) so that Zn concentrations can be estimated using the regression equation  $Zn = \log 1.04 + 0.27 \text{ pH}$ . Thus it was concluded that pH is a key variable in regulating Zn adsorption and desorption in a river contaminated by AMD.

Sorption behaviour of metals onto sediments is strongly influenced by pH and is also dependent on clay type. For example, Zn is less adsorbed onto the clay mineral kaolinite than to montmorillonite and illite (Farray and Pickering, 1977). Florence and Bately (1980) found that Zn concentrations are chiefly controlled by adsorption rather than precipitation which is strongly affected by pH, with virtually no adsorption at pH 6 and increasing adsorption at higher pH values. Acid water prevents the formation of Zn(OH)<sub>2</sub> and thus precipitation. It was suggested by Maes and Cremers (1975) that adsorption of Zn onto the clay mineral Na-montmorillonite is nearly perfectly reversible with low pH (approximately 98 % recovery at pH

< 6) where site occupancy is low or intermediate. The pH region where most of the metal ion is precipitated and sorbed is between 6.9 and 7.9 (Pickering, 1980; Salomons and Förstner, 1984; Kelly 1988).

At site 4 Cu and Fe concentration were significantly increased ( $p < 0.001$ ) in the subsurface sediment compared to background levels at site 1 which suggested that these metals were deposited at this site (Figs. 3 b,c). Iron concentration decreased gradually downstream showing no significant changes between sites. The slow gradual decrease of Fe in the sediment may indicate that Fe is transported over long distances in the solute phase. Iron concentrations in sediments of contaminated sites were correlated with pH ( $p < 0.05$ ). The concentration can be estimated using the regression equation  $Fe = 11.46 - 0.63 \text{ pH}$ . Another significant increase ( $p < 0.05$ ) in Cu concentration occurred at site 7. Although Stumm and Morgan (1981) found that Cu adsorption is regulated by pH, regression analysis showed no relationship between pH and Cu in the sediment of the Avoca River. Any trends associated with pH may be hidden by other removal mechanisms affecting Cu in the river. However, a significant correlation ( $p < 0.001$ ) was found between Fe and Cu which indicates co-precipitation of Cu with iron hydroxides.

The influence of hydrological factors with respect to Cu and Zn precipitation is also important. Lui *et al.* (1992) reported of large amounts of Cu and Zn in sediments collected during the dry season. It was suggested that Cu and Zn concentration increase in the sediment as a result of deposition of Cu and Zn associated with particulate suspended matter. However, this was found to be the reverse in the Avoca River where the Cu and Zn concentration increased in the winter during high river discharge. Comparison between two sampling events of the top surface at site 4 showed large increases of Zn and Fe (Table 8). However, because of the small numbers of samples it can not be concluded whether this is due to variation in sampling or because of different hydrological and chemical regimes in the river.

Examination of organic matter content in the sediment (Table 4) showed highest levels at sites 4 and 5 (21.6 and 18.2 %, respectively). An increased growth of periphyton was noticed from visual examination at sites 4, 5 and 6 on the substrate during sampling in July and August. Although organic

contents in the sediment is lower at site 6, almost 100 % of the substrate was covered by periphyton. However periphyton consists to 95-98 % of water and therefore increased organic matter due to periphyton is strongly dependent on the amount collected in relation to the sediment volume. Small amounts of periphyton do not contribute significantly to an increase in organic matter. Microscopic examination of the substrate showed among other organisms filamentous bacteria, presumably *Thiobacillus* species. This suggests that the microbial activity in the sediment may affect Zn adsorption at sites 4, 5 and 6 (Fig. 3a). Bacterial oxidation of pyrite and consequently the acid production in sediments may cause a decrease in pore water pH and metals may be mobilised from residual material. Because of increased solubility of Zn at lower pH this metal may be more readily leached from the sediment.

The extent to which individual sediments can concentrate metals varies considerably. Thus it is expected that with respect to metal reactivity the varies types of sediments will have a different impact on the environment. The porewater provides a link between exchanges of surface water and sediment. It was found from examination of pore water profiles of lakes and estuaries that metal concentrations increased with decreased sediment depth and highest concentrations were recorded in the oxidised surface layer (Salomons, 1988). This evidence is not as well documented for rivers. Kemble *et al.* (1994) found Zn, Cu and Fe concentrations in filtered pore water in the Clark Fork River, Montana, to be as high as 2630, 79 and 3.5  $\mu\text{g l}^{-1}$  respectively. However these concentrations were not linked to pore water pH. The decrease of Zn concentration in the sediment from site 1 to 4 and the low concentrations at site 5 and 6 suggests mobilisation of Zn from the sediment. However, it is not very likely that the pore water pH at the erosional sites (1,4 and 5) would differ substantially from the surface water pH. Therefore it is assumed that if Zn mobilisation processes occur in the sediment at erosional sites, this is preliminary influenced by the surface water pH. Only at depositional sites (6 and 7) will pore water pH possibly differ from the surface water. Nienke *et al.* (1982) observed in Lake Michigan that Zn in the sediment was not highly mineralised, as the Zn occurred as  $\text{Zn}(\text{OH})_2$  or  $\text{ZnCO}_3$ , but that it was rather loosely bound to organic matter and so was leached from the sediment when the pH was lowered.

The low carbonate content of the sediment indicates that the acid inputs from mine drainage or the production of acids from microbial activity are effectively not neutralised by the sediment. The surface water of the Avoca River is classified as soft (Hardness  $<20\text{mg CaCO}_3$ ) which suggests low buffering capacity of water and sediment. Highest level of carbonate content was detected at site 6 (Table 5) which may be due to the input of the slightly harder water from the Aughrim River.

Comparison of reference site 1 with average geochemical background levels for shales and clays as shown in Table 12 indicated that Zn concentrations were relatively high at the reference site. The second survey (Table 3) that was conducted showed lower Zn concentrations at site A-3 which are approximately the same as the levels in Table 9 for river sediments. The sample was taken from a site which upstream of the complete mixing zone of the two rivers and therefore results may be biased towards the influence of the Avonbeg river which has not been subjected to historical mining activities. Because the sediment sample in the Avonbeg river was taken approximately 300 m downstream of Ballinaclash, it may be possible that sewage discharge contributed to elevated Zn concentrations in sediments. The Avonmore was subjected to nineteenth century Zn-Pb mining resulting in spoil tips close to the river and elevated Zn concentrations in the sediment. Metals associated with the sediment phase, especially the  $<63\ \mu\text{m}$  fraction, are likely to be scoured during high flow conditions. Therefore Zn from the Avonbeg may be an additional source for elevated metal levels at site 1 if assumed that the discharge from the Avonmore river constitutes 75-80 % to the total flow in the Avoca River at site 1. Dissolved Zn concentrations were found to be below detection limit of the instrument ( $0.01\ \text{mg}^{-1}$ ) used for analysis and therefore dissolved Zn is not likely to have an impact at site 1. Copper concentrations at sites A-1 to A-3 and site 1 conformed with the values suggested for river sediments in Table 13. Iron seemed to differ by approximately 2% from the results obtained in this study.

Table 13. Average background concentrations of some trace metals in shales and clays, river sediments and recent lakes. River sediment values are the average of 29 unpolluted surface river sediments from the Detroit river and western Lake Erie (Canada). Avoca River values are the average of nine subsurface samples (<63 $\mu$ m fraction).

	Shales and Clays	Recent Lakes)	River sediments	Avoca River
	Turekian and Wedepohl (1961)	Förstner and Wittmann (1983)	Chester (1988)	current study (upstream of mines)
Iron (%)	4.7	5.9	3.4	5.9
Copper ( $\mu$ g g <sup>-1</sup> )	45	35	70	87
Zinc ( $\mu$ g g <sup>-1</sup> )	95	70	263	625
Cadmium ( $\mu$ g g <sup>-1</sup> )	0.3	-	4	-

Comparison of Avoca River sediments with sediments from the Lo An River (China) (Table 14), which are affected by the Dexing Copper Mine, showed stronger Fe and Zn sediment enrichment in the Avoca River, whereas the Lo An river sediments showed higher Cu enrichment. This reflects the nature and quality of the ores mined at each site.

Table 14. Average concentrations of river and lake sediments contaminated by acid mine drainage compared to the Avoca River.

	Avoca River (Ireland)	Lo An River (China)	Poyang Lake (China)
	current study (impacted sites)	Ramezani (1994)	Ramezani (1994)
Iron (%)	7.1	6.3	5.1
Copper ( $\mu$ g g <sup>-1</sup> )	655	1191	122
Zinc ( $\mu$ g g <sup>-1</sup> )	1187	509	250
Cadmium ( $\mu$ g g <sup>-1</sup> )	-	1.2	

*Metal accumulation in surface and subsurface sediment*

Iron concentrations in the subsurface sediment (< 63  $\mu$ m fraction) increased significantly (p<0.05) at site 4 (Table 6). The increase in Fe concentration is due to the formation of Fe(OH)<sub>3</sub> which precipitates from solution and which also has a large sorption capacity for heavy metals (Chapman *et al.*,



1983). However, from visual examination of the site it was expected that the Fe concentration would have been higher.

Analysis of the orange surface layer (ochre) from stones and comparison with metal concentrations in the subsurface sediment showed that Fe and Cu concentrations increased approximately 2-fold at site 4, while Zn concentrations decreased (Table 6). This decrease in Zn confirms the earlier assumption that Zn is not deposited at site 4. Copper was enriched in the 'ochre' by a factor of 26.3 compared to a factor of 15.3 in the subsurface sediment (Table 15). This suggests that this element may be preferentially co-precipitated with Fe-hydroxide (Chapman *et al.*, 1983; Kondos *et al.*, 1991) rather than adsorbed onto the subsurface sediment. Fuge *et al.* (1994) reported Fe concentrations of variable ochreous sediments ranging from 13.3 % to 40 %. It was also found that Cu was highly concentrated in the ochre and increased with increasing pH. The Fe content in ochreous sediments in the Avoca River ranged between 12 % and 27 %. It has been proposed by Bigham *et al.* (1990) that the degree of adsorption of Zn, Cu and Cd is controlled by the nature and structure of the ochreous precipitate as this varies with pH.

The current study showed that Fe is largely concentrated in the surface sediment showing a sediment enrichment factor (SEF) of 4.0 at site 4 (Table 15) and less concentrated in the subsurface sediment (<63  $\mu\text{m}$  fraction) with an SEF of 1.9. Highest Fe accumulation in the Lo An River (China) was found to occur in the coarser sediment fraction consisting of 1 % clay, 45 % silt and 54 % sand. It was assumed that most of the Fe accumulated in the silt and sand fraction (Ramezani, 1994) and therefore was not primarily dependent on grain size. Table 15 shows a high enrichment of Cu in all contaminated subsurface sediments with the SEF ranging from 15.3 to 22.2, with a maximum enrichment at site 7. Enrichment of Zn in sediment occurred at sites 7 and 8 only, giving an SEF of 23.0 and 14.7 respectively. Comparison of subsurface samples with surface samples showed that the SEF for Cu is almost 2-fold higher in surface sediments. The SEF for Zn at site 4 is lower in surface sediments compared to subsurface sediments, whereas Zn was almost 2-fold higher at site 6.

Table 15. Calculated sediment enrichment factor (SEF) for Zn, Cu and Fe based on recent lake sediments (Table 12).

site No	subsurface sediment (< 63 $\mu\text{m}$ fraction)			surface sediment ('ochre')			sediment traps (floc material)		
	Zn	Cu	Fe	Zn	Cu	Fe	Zn	Cu	Fe
1	5.3	1.9	1.4	5.6	1.2	1	-	-	-
4	4.3	15.3	1.9	2.8	26.3	4.0	5.0	18.0	2.3
5	3.8	12.6	1.7	-	-	-	-	-	-
6	4.6	12.7	1.8	8.4	41.7	2.6	7.7	41.8	1.8
7	23.0	22.2	1.5	-	-	-	-	-	-
8	14.7	9.9	1.4	-	-	-	-	-	-

Metal concentration in floc material was close to levels obtained in ochreous sediments (Tables 6 and 10). The colour of the floc material was dark brown to greenish compared to the orange to rusty colour of the 'ochre'. It consisted to a large portion of Fe (6.5 and 12.3 %) and up to 50 % of organic matter. Floc material collected from pools (Table 11) showed increased Cu concentrations at site 4 and lower Fe concentrations at sites 4 and 6. Floc material was collected from the sediment traps at weekly intervals and so was of recent origin, whereas the floc collected from pools may have been there for a longer period of time. This may explain the higher Zn and Cu concentration in pools (Table 11) compared to sediment traps (Table 10). Decrease in Fe concentrations between the two floc types may be due to decomposition of organic matter resulting in Fe becoming associated with the sediment. It is also interesting to note that Zn levels in floc material are relatively low at site 4 compared to site 6. This appears to be due to the same reason as for surface sediment where the pH strongly influences adsorption.

Comparison between metal concentrations from sediment traps and the ochreous surface samples showed that Zn and Cu concentrations for site 4 and 6 are very similar, while Fe levels show large differences. This suggests that sediment traps may be a useful method for monitoring short-term variation of metals deposition and transport. Metal in sediment traps (Table 10) also showed less variation (as standard deviation) between individual samples compared to floc samples taken from pools (Table 11). Metal

concentrations in floc collected from dry and semi-dry areas (Table 12) showed generally lower concentrations compared to floc collected from pools (Table 11). This may be due to weathering and leaching processes where Zn and Cu are liberated from the floc.

#### *Metal variability in sediment*

Collection of representative samples and selection of appropriate sample location is of great importance in sediment analysis. Förstner and Salomon (1980) recommended the particle size fraction  $< 63 \mu\text{m}$  to be of most benefit because most metal is associated with this fraction. Although variability of the bed material cannot be eliminated entirely due to the heterogeneous nature of the river, it can be reduced by analysing the clay-silt fraction.

Ramezani (1994), working on river sediments from the Lo An River (China), showed that the concentration of Cu in the various grain size fractions  $< 63 \mu\text{m}$  (20-63  $\mu\text{m}$ , 6.3-20  $\mu\text{m}$ , 2-6.3  $\mu\text{m}$  and  $< 2\mu\text{m}$ ) are reasonably consistent ranging from 687-817  $\mu\text{g g}^{-1}$ . A decrease was detected in the particle size fraction  $> 63 \mu\text{m}$ . In contrast the maximum concentration of Zn (497  $\mu\text{g g}^{-1}$ ) was found in the  $< 20 \mu\text{m}$  fractions, while concentrations in the fraction 20-63  $\mu\text{m}$  were significantly lower (92  $\mu\text{g g}^{-1}$ ).

Studies were carried out to test variation of sampling sites (1, 4 and 6) to test the metal variability between sites, sub-sites and replicates (Fig. 4). Comparison with typical geochemical background concentrations of some trace metals in rocks (Table 13) suggested that metal concentrations for Zn are elevated at all upstream sites. Copper and Fe concentrations (124.3  $\mu\text{g g}^{-1}$  and 8.1 % respectively) at site 1 (sub-site 1) were approximately twice as high as levels at sub-sites 2 (67.9  $\mu\text{g g}^{-1}$  and 4.4 % respectively) and 3 (61.5  $\mu\text{g g}^{-1}$  and 4.4 % respectively). The sample at sub-site 1 was taken from the middle of the river, whereas samples 2 and 3 were taken close to the left river bank. This particular site is downstream of a wide area of raised substrate, and is exposed to the air at low flows and dries out. This may influence the metal accumulation in the subsurface sediment at this sub-site. Therefore sub-site 1 would not represent average background levels at the upstream site and is not suitable for further sediment sampling.

Analysis of variance showed significant differences between the mean of the sub-site and the mean of the replicates for Zn ( $p < 0.05$ ), Cu ( $p < 0.01$ ) and Fe ( $p < 0.05$ ). This suggests that the collection of replicate samples at sub-sites is not necessary as significant difference among replicates were not detected. However, it is important to take several sub-site samples to obtain a reasonably accurate estimate of metal concentrations within a site. Metals deposition seemed to be uneven and varies considerably within a sampling site as shown in Figs. 4.

#### *Environmental impact assessment*

The conditions and processes within riverine sediments contaminated by AMD vary considerably between the surface deposited layer and the subsurface sediment (0-30mm), as well as spatially. The use of the  $< 63 \mu\text{m}$  fraction provides a base for normalizing data from different types of sediments. However, every attempt must be made to sample similar substrate types, and in riverine systems these should be gravely type sediments only. The sedimentation processes seen in AMD contaminated rivers not only result in direct metal toxicity, but also the destruction of the most important habitat in such systems, i.e. gravely substrates. The substrate provides a variety of niches for freshwater organisms (e.g. invertebrates, periphyton) and is important for fish spawning. Hydrous iron oxides will co-precipitate heavy metals to form a thick ochre layer over the substrate. In the most impacted areas this tends to be so excessive that the substrate becomes *welded* together by a compacted iron panning. Further downstream, only the larger stones become coated with ochre, with the smaller gravely material discoloured, but with a variable burden of associated floc and fines which is constantly being scoured away by the river flow inducing water movement through and across the substrate. Therefore sampling should examine both the surface of stones which provides an important niche for periphyton which is a major food resource for riverine invertebrates, and the smaller gravely type substrate (subsurface sediment) in which up to 80% of the invertebrate fauna of fast flowing rivers are found. Ponds and still areas of river water close to the banks are often highly contaminated with floc material which, as shown by the sediment trap data, is constantly moving downstream affecting all sites. These flocs are often highly contaminated with metals and can become compacted causing localised areas of substrate panning, especially when some areas dry

out. The flocs should also be collected using a sediment trap and analysed. Stony substrates such as those found in fast flowing rivers like the Avoca River are rarely anoxic, with oxygen penetrating deeply into the sediment allowing invertebrates to live far below the sediment-water interface (Bretscho, 1991).

It is difficult to assess the environmental impact of AMD on sediments as there is little threshold toxicity data available for freshwater animals or communities in metal contaminated sediments. Therefore physico-chemical sediment analysis should be carried out in conjunction with biological assessment in the field at the time of sediment collection, as well as subsequent toxicity assessment using collected material in the laboratory (Nebeker *et al.*, 1984). Metals are constantly being deposited on to the sediment via a number of different processes. However, the majority of these are ephemeral, their deposition and contribution to the long term toxicity of river sediments is governed by hydraulic conditions within the river. The metals associated with the deeper sediments (0-30mm) provide a long term monitor for the contamination from which seasonal and annual trends can be derived.

## CONCLUSION

Zinc concentration in sediments of the Avoca River are found to be the key factor regulating pH, with less Zn accumulation at lower pH. Copper seemed to have been concentrated in surface sediments (ochre) and also showed a tendency to be more highly concentrated in sediments with increased organic matter content. However, removal of Cu from solution was primarily by co-precipitation with iron. Cadmium was not found in any of the sediments at the detection limit ( $<0.01 \mu\text{g g}^{-1}$ ). Short term variation in metal inputs are identified by sampling the surface (ochre) layer only, whereas sampling of the subsurface sediment (0-30 mm) ( $<63 \mu\text{m}$  fraction) is important for monitoring long-term trends in sediment quality. It is important to take several sub-site samples to obtain a reasonably accurate estimate of metal concentration within a site as metal deposition is variable within riverine sediments.

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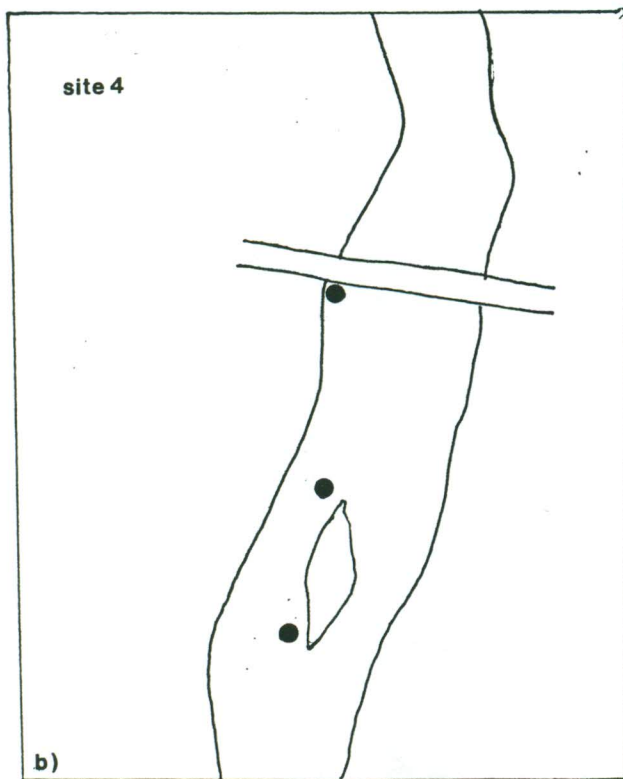
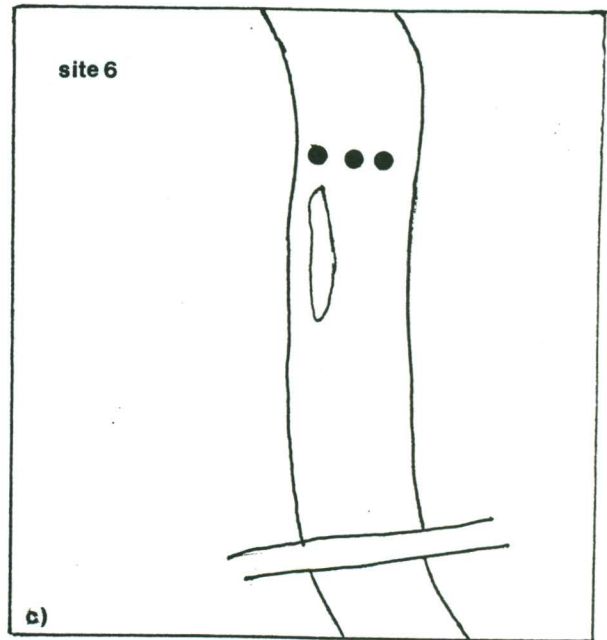
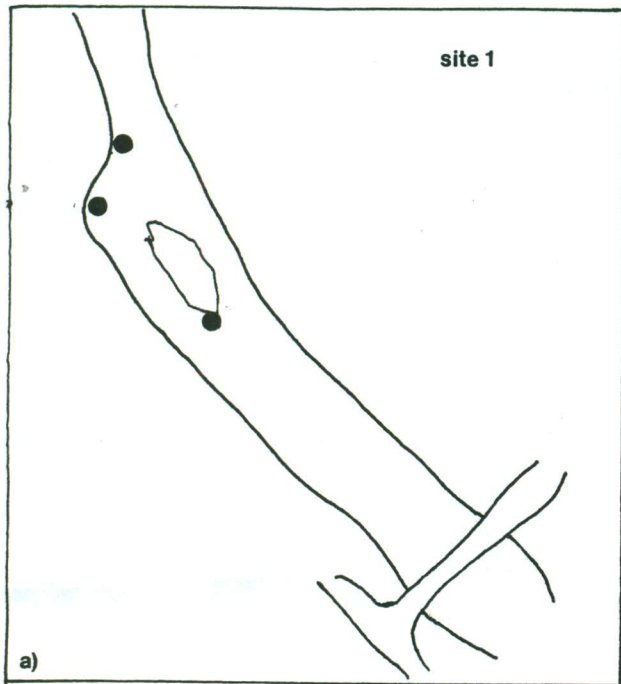
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Appendix 1. Maps showing individual sub-sites at main sampling locations on the Avoca River (sites 1, 4 and 6)



● sub-sites

Appendix 2. Mean concentrations and standard deviation (SD) of Zn ( $\mu\text{g g}^{-1}$ ), Cu ( $\mu\text{g g}^{-1}$ ) and Fe (%)

Site	N	pH	Zn ( $\mu\text{g g}^{-1}$ )		Cu ( $\mu\text{g g}^{-1}$ )		Fe (%)	
			Mean	SD	Mean	SD	Mean	SD
1	9	6.9	624.5	104.0	87.2	28.2	5.9	1.7
4	9	5.7	509.4	173.9	690.5	177.0	8.2	0.7
5	3	5.9	449.4	75.0	566.4	149.8	7.2	0.6
6	9	6.4	542.2	118.1	570.9	128.2	7.6	0.8
7	2	8.7	2713.0	230.0	1000.2	36.4	6.4	0.1
8	3	8.5	1729.0	881.0	446.2	161.6	5.9	0.5

Appendix 3. Concentrations of Zn ( $\mu\text{g/g}$ ), Cu ( $\mu\text{g/g}$ ) and Fe (%) in subsurface sediment (< 63  $\mu\text{m}$  fraction) including sub-sites and replicates (Zn, Cu in  $\mu\text{g/g}$ , Fe in %)

location	Zn - 1	Zn - 2	Zn - 3	Cu - 1	Cu - 2	Cu - 3	Fe - 1	Fe - 2	Fe - 3
1--1	772	732	553	125.8	118.9	128.1	7.91	8.10	8.35
1--2	671	648.9	660	67.9	66.4	70.4	4.39	4.85	4.85
1--3	445	518	619	61.5	71.7	73.9	4.42	5.12	5.12
4--1	519	521	463	1004	765	884.9	9.10	7.26	8.28
4--2	465	507	463	714.4	634	695	9.24	8.75	8.34
4--3	368	411	382	513.9	468	534	7.72	7.46	7.89
6--1	407	376	544	616.7	347	671	7.48	7.42	7.89
6--2	619	700	595	599.6	627.6	557.2	6.07	7.91	7.73
6--3	401	614	625	389.6	750.3	578.3	6.95	9.22	7.78