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ENVIRONMENTAL IMPACT OF ACID MINE DRAINAGE ON THE AVOCA RIVER: Metal Fluxes in Water and Sediment. Part III. Metals in Water and Suspended Particulate Matter.

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EXECUTIVE SUMMARY

Water and suspended particulate matter (SPM) was collected at weekly intervals during low flow conditions from the Avoca River (May and August, 1994). The total concentration of Zn, Cu, Cd and Fe was measured in both the dissolved and particulate phase. To model metal fluxes, flow measurements of the river and the main leachate streams were also taken. It was shown that the acid mine drainage (AMD) discharged into the Avoca River from the two leachate streams (the Deep and Ballymurtagh Adits) decreased concurrently with a decreasing river flow. Concentrations of dissolved Zn, Cu and Fe generally decreased downstream from the AMD input showing maximum metal concentrations at the site closest to the AMD discharge points. No Cd was detected (<0.001 mg/l) in either the water or particulate matter in river samples.

Zinc adsorption onto suspended particulate matter is clearly influenced by pH, with concentrations of Fe and Cu higher in the particulate phase compared to the dissolved phase, suggesting that the main transport mechanism of metals is through association with the particulate phase. Temporal fluctuation showed that metal concentrations, particularly Fe and Zn, are strongly effected by hydrological factors in the river and leachate streams. Metal fluxes were shown to differ substantially under various flow regimes, with Zn not removed from the dissolved phase during low river flow. Using sulphate as a conservative ion enables quantitative predictions to be made with regard to percentage metal contribution from the main adits. A significant relationship between percentage contribution of sulphate and the ratio of river/AMD discharge was apparent.

INTRODUCTION

Water reacting with sulphide minerals in the presence of oxygen produces acid mine drainage (AMD). The water from the mine drainage at Avoca contains very high concentrations of metals and sulphate. AMD discharging from the mines into the Avoca River has detrimental effects on the water quality of the river downstream of the mines. Gray (1994) identified and documented a series of surface waters on the East and West Avoca mine sites including springs, leachate streams, surface runoff, temporary and permanent ponds and a small lake at the base of the Cronebane Pit, which all have a potential impact on the river system. The main discharge to the river is primarily via three leachate streams i.e. the Deep Adit, the Ballymurtagh Adit and a contaminated stream close to Morans Garage. Continuous monitoring was only carried out on the former two adits, because the metal concentrations in the latter are low, especially during prolonged periods of drought or low rainfall.

The discharge of Fe-rich acid waters into a receiving stream results in the precipitation of 'amorphous ferric hydroxide' (Stumm and Morgan, 1981; Kelly, 1988) which results in increased water turbidity. Iron-hydroxide is also known to have scavenging potential with regard to metals (Chapman *et al.*, 1983; Johnson, 1986) and serves as a transport mode for a wide range of metals.

Large changes in terms of trace element chemistry in the water, particulate matter and sediment composition occur when acid mine drainage enters a river system. Above the acid mine drainage outfall, the Avoca River is of typical upland dilute water with an approximate pH of 6.7, a specific conductivity of just 65 $\mu\text{S}/\text{cm}$, water hardness of 16 mg CaCO_3/l and also low metals content in both dissolved and suspended particulate fractions. Mean concentrations for Fe, Zn and Cu for uncontaminated rivers are given by Salomons (1988) as 0.04, 0.03 and 0.002 mg/l, respectively.

The specific aims of this study were (i) to examine the impact of AMD on the Avoca River in water and suspended particulate matter (SPM), (ii) to evaluate short term variation during the summer months and (iii) to model metal fluxes in the Avoca River.

MATERIALS AND METHODS

Field collection

Individual sampling sites are as shown on the map in Herr and Gray (1995). The sites are located upstream of the mines (site 1; (8.1)), Deep Adit (site 2; (3.1)), Ballymurtagh Adit (site 3; (3.22)), Avoca Bridge (site 4; (5.1)), Golfcourse (site 5; (5.2)), upstream IFI (site 6; (5.3)), downstream IFI (site 7; (5.4)) and Arklow Bridge (site 8; (5.5)).

Collection of water and suspended particular matter (SPM)

Water samples were collected at weekly intervals between 17.5.94 and 7.9.94 and approximately monthly afterwards. Samples were taken in a 3 l square plastic container approximately 10-15 cm below surface. Samples from leachate streams were collected at the vee-notch weirs. To determine suspended particular matter (SPM), 400 ml of river water (2 x 200 ml) was filtered on site through 0.45 μm pore size cellulose nitrate filters. Due to high amount of colloids in suspension no more than 200 ml could be filtered at one time. Filtrate was collected in 250 ml polyethylene bottles which were rinsed several times with filtrate and filled to the top to exclude all air. Filters were rinsed with 5 ml de-ionised water folded carefully into quarters and stored in small (50 x 50 mm) self seal plastic bags. Water samples and filters were kept cool on transport and stored at 4°C until subsequent analysis.

Conductivity and pH measurements were carried out in the laboratory within 24 hours after sampling. Water temperature was recorded on site using a mercury thermometer. The analytical procedure carried out for metal determination in water and suspended solids is shown in Fig. 1.

Because of the large amounts of colloidal matter, filter papers became clogged easily. This may introduce a wide error margin in terms quantification of geochemical information from SPM. However, the method provides a good indication of assessing metals associated with colloidal matter. To measure SPM quantitatively water samples should be filtered through pre-weighed glass fibre filters which allow a larger volume to be filtered. Settling particles were collected in sediment traps (Herr and Gray, 1995). This was an easy and efficient way to collect large amounts of suspended material (floc) that could not be picked up with the ordinary filtration technique. Vernet *et al.* found higher Cu contents in suspended sediment compared to bottom and trap sediment. Because values obtained reflect the situation only at a specific time,

regular sampling over a period of time was carried out to ensure the validity of results.

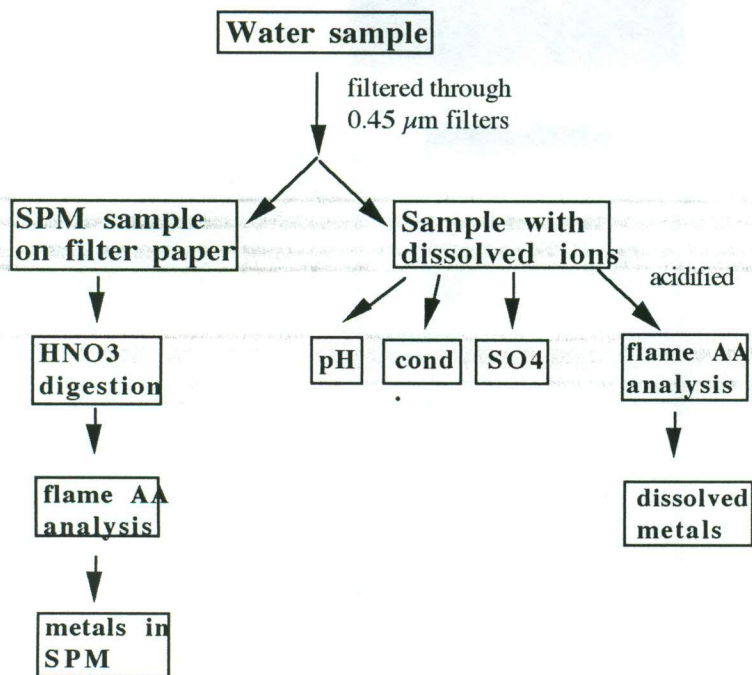


Fig. 1. Flow diagram showing collection and analysis of water samples and suspended particulate matter.

Sample preparation and analysis for water and SPM

Conductivity and pH measurements were carried out within 24 hr after sample collection using a WTW® LF 196 conductivity meter and a Jenaway® 3015 pH meter. Two sub-samples were taken, one being acidified for subsequent metal analysis of Fe, Cu, Cd and Zn and one for sulphate analysis which were stored at 4°C (Fig. 1). Metals were analysed using atomic adsorption spectrophotometry (AAS) and sulphate analysis was carried out by Ion Chromatography using a Dionex® 2020 according to standard methods (APHA, 1989). Filters were dried at 101°C to constant weight (APHA, 1989). They were digested in a MDS® -200 microwave digestion system with 5ml de-ionised water and 5ml nitric acid (70 %) for 70 min. Samples were made up to 10ml in volumetric flasks and stored until analysed for Fe, Zn, Cu and Cd using AAS.

Flow data

The absence of a gauging station on the Avoca River made it necessary to extrapolate flows for specific stations (Gray, 1994). Flow data obtained at the gauging stations 1002 in Rathdrum (Avonmore River) and 1028 in Knocknamohill (Aughrim River) were used to estimate river flow for individual sub-catchments on the Avoca River. Therefore flow had to be corrected to allow for the new catchment area at each of the sampling stations. The catchment area feeding each of the sampling sites was calculated using a Geographical Information System (GIS). The mean daily flow at both permanent gauging stations was obtained from the Environmental Protection Agency (EPA). To obtain an estimated mean daily flow for each sub-catchment, the mean daily flow at the gauging stations was re-calculated using following formula:

$$\frac{\text{new area (km}^2\text{)} \times \text{flow to gauge (m}^3\text{/s)}}{\text{catchment area to gauge (km}^2\text{)}}$$

RESULTS

Flow discharge data for all sampling stations

Calculated flow discharge is given in Table 1 for individual stations on the Avoca River and leachate outfalls. The river flow and the leachate stream discharge generally decreases during the summer months and then recovers in late autumn (Fig. 2). The mean flow discharge of the leachate streams during the study period (site 2 and 3) is 13.2 and 13.3 l/s respectively, showing a standard deviation (SD) of 4.0 and 4.6 respectively. After site 5, the Avoca River meets one of its largest tributaries, the Aughrim River, which exhibits similar flow discharge as the Avoca River which almost doubles the river discharge at site 6. A peak discharge during the summer months occurred on the 24.8.94, whereas the flow in the leachate streams did not change drastically on the same day.

Water samples and suspended particulate matter (SPM)

Site 1 is situated above the mining area, whereas site 4 and all other consecutive sites are below the mines and impacted by AMD from sites 2 and 3 (Deep and Ballymurtagh adits) as indicated by the arrow in Fig. 3. Summary

Table 1. Flow discharge data (l/s) for the stations at the Avoca River (sites 1 to 8) and leachate streams (sites 2,3)

Date	Leachate Streams		River Sites						
	site 2	site 3	site 1	site 4	site 5	site 6	site 7	site 8	rank*
17/5/94	23.84	23.71	15542	16217	16689	25347	26265	26315	3
2/6/94	18.8	21.2	5128	5352	5508	9600	9600	9986	2
8/6/94	17.03	17.93	5218	5352	5508	9280	9280	9650	2
12/6/94			3720	3892	4005	6807	6807	7077	1
16/6/94	14.91	17.29	3108	3243	3337	5495	5701	5712	1
23/6/94	14.23	13.18	3419	3568	3672	5726	5936	5947	1
29/6/94			3108	3243	3337	5282	5476	5487	1
6/7/94	12.13	12.39	3419	3568	3672	5832	6046	6058	1
14/7/94	12.33	12.01	2798	2919	3004	5159	5355	5366	1
20/7/94	12.95	11.92	2176	2270	2337	3953	4103	4111	1
27/7/94	11.15	11.05	2798	2919	3004	4626	4794	4803	1
4/8/94	10.77	11.3	3108	3243	3337	4963	5141	5.151	1
10/8/94	10.4	10.2	2020	2108	2170	3359	3482	3489	1
17/8/94	10.22	9.07	1710	1784	1836	3661	3806	3814	1
24/8/94	9.69	10.27	6628	6811	7010	10049	10405	10424	2
31/8/94	9.17	9.28	2642	2759	2837	3926	4062	4070	1
7/9/94	10.22	9.3	2487	2595	1670	4077	4224	4232	1
12/10/94	8.51	6.14	3108	3243	3337	5069	5252	5262	1
16/11/94	12.74	9.75	12477	12816	16695	22026	22854	22899	3
14/12/94	18.03	13.58	17251	18001	18525	27305	28281	28334	3
Mean	13.2	12.8	5093.3	5295.2	5574.5	8577.1	8843.5	8652.1	
SD	4	4.5	4529.9	4707.4	5225	7337.8	7603.4	7835.6	
Min	8.5	6.1	1710	1784	1670	3359	3482	5.2	
Max	23.8	23.7	17251	18001	18525	27305	28281	28334	
Median	12.2	11.6	3108	3243	3337	5388.5	5588.5	5599.5	

* ranking only applies to river discharge ((1) < 4000 l/s, (2) > 4000 < 10,000 l/s, and (3) > 10,000 l/s)

statistics for river water quality upstream and all sites downstream the mines are shown in Table 2 and 3 respectively, while the raw data is given in appendices I and II. Mean results of Zn, Cu and Fe in particulate matter and soluble phases, taken on weekly intervals over 11 consecutive weeks (23.6.-31.8.94), are shown in Figs. 5.3(a),(b), and (c) respectively. Soluble Zn concentrations (Figure 3(a)) increased at site 4 (full mixing zone) to 670 µg/l (p<0.001) and slowly decreased downstream. A significant increase of Zn in the particulate fraction occurred only at site 7 to 723 µg/l (p<0.01), whereas Zn concentrations between sites 4 and 6 are low (30 to 68 µg/l). Copper concentrations in the particulate matter, as shown in Figure 3(b), are generally

higher compared to Cu concentrations in the soluble phase after acid mine drainage discharge. Copper and Fe concentrations in the particulate phase increased significantly ($p < 0.001$) at site 4. Particulate Cu concentrations were around 69-71 $\mu\text{g/l}$ between sites 4 and 6 and slightly decreased after that, although not significantly. In contrast particulate Fe (Figure 3(c)) was elevated (1401.9 to 1705.3 $\mu\text{g/l}$) at all sites. Water and SPM was also analysed for Cd, however, no Cd was detected in either phase ($< 1 \mu\text{g/l}$).

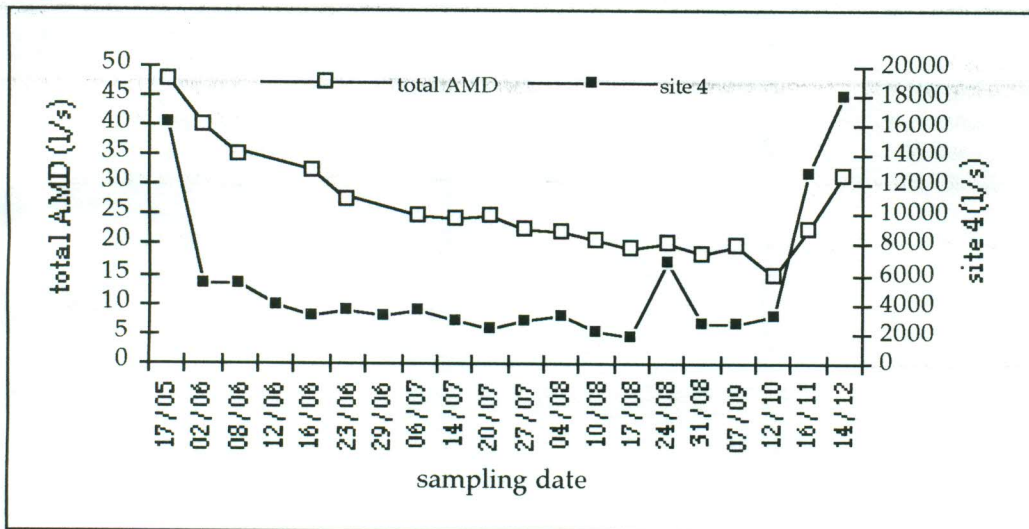


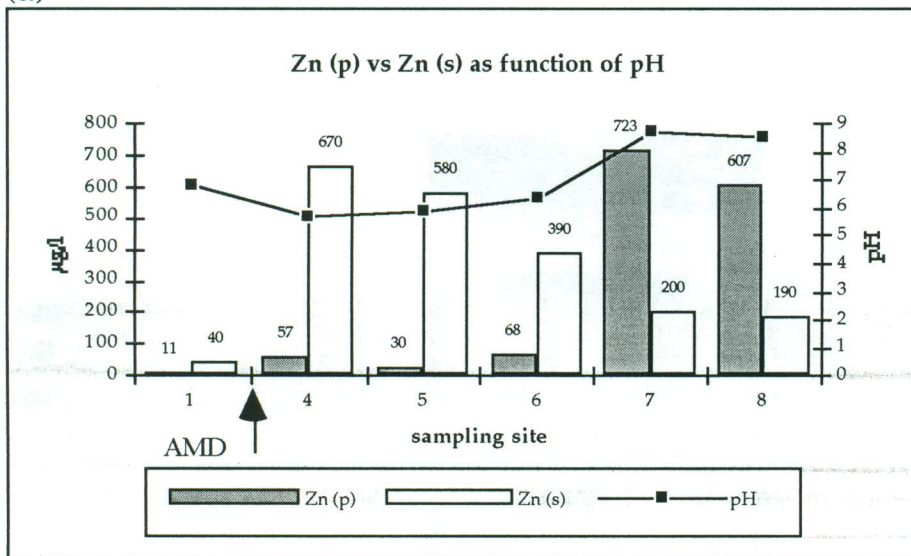
Fig. 2. Discharge relationship between river flow at Avoca Bridge (site 4) and total flow from leachate streams during the sampling period (1994).

Table 2. Summary statistics for river water quality above the mines at site 1

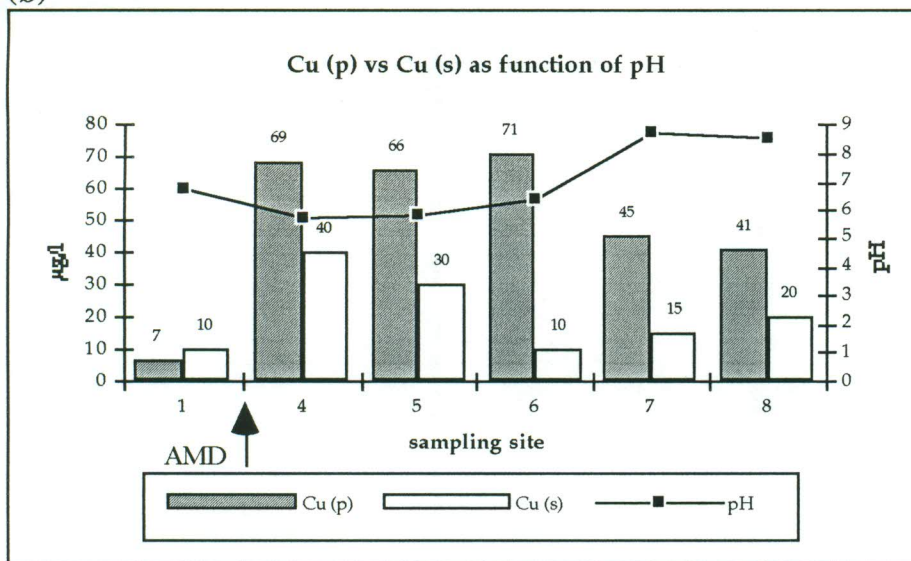
	pH	Cu (p)	Zn (p)	Fe (p)	Fe (s)	Cu (s)	Zn (s)	cond	sulphate
mean	6.82	2.45	11.46	267.33	0.11	0.01	0.06	104.74	4.92
stdev	0.23	1.37	6.22	105.17	0.06	0.07	0.04	10.76	0.90
min	6.38	1.15	1.80	83.00	0.04	0.04	0.01	41.50	3.00
max	7.20	5.00	21.00	446.00	0.23	0.23	0.12	78.90	6.00
median	6.86	2.00	11.50	245.00	0.10	0.10	0.05	70.10	5.00

cond. = conductivity

(a)



(b)



(c)

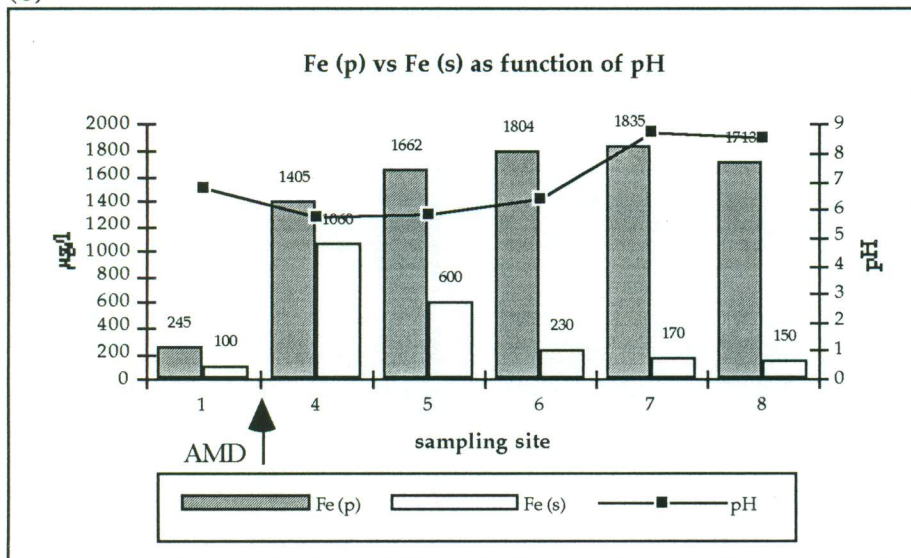


Figure 3. Mean metal concentrations of Zn, Cu and Fe in particulate (p) and soluble (s) phases at all river sampling sites over a sampling period of 11 consecutive weeks (23.6.94-31.8.94)

Table 3. Summary statistics for river water quality below the mines for all sites (4, 5, 6, 7 and 8)

	pH	Cu (p)	Zn (p)	Fe (p)	Fe (s)	Cu (s)	Zn (s)	cond	sulphate
mean	6.93	60.05	407.30	1629.81	0.45	0.022	0.40	262.81	24.68
stdev	1.49	25.41	1069.18	421.38	0.36	0.334	0.22	574.16	9.44
min	5.29	4.50	4.00	961.00	0.04	0.040	0.09	58.90	10.00
max	10.08	110.00	6466.00	2735.00	1.34	1.340	0.91	3750.00	59.00
median	6.33	63.50	38.80	1544.00	0.32	0.320	0.37	117.70	23.00

cond. = conductivity

Table 4 shows the pearson-product-moment correlation for the measured parameters using data from all contaminated river sites (excluding site 8). Site 8 was excluded for this analysis because the site is estuarine. The numbers of individual samples (n) in each category varied from 30 to 35. A strong positive correlation with pH is apparent for particulate Zn ($p < 0.001$) and conductivity ($p < 0.001$), and a negative correlation for soluble Fe ($p < 0.001$) and Zn ($p < 0.001$). Flow is positively correlated with particulate Fe ($p < 0.001$), and negatively with soluble Fe ($p < 0.05$), soluble Zn ($p < 0.001$) and sulphate ($p < 0.001$). Particulate Zn is positively correlated with conductivity ($p < 0.001$), and negatively with soluble Zn ($p < 0.01$). Particulate Fe is negatively correlated with soluble Fe ($p < 0.01$), Cu ($p < 0.05$), Zn ($p < 0.001$) and sulphate ($p < 0.05$), soluble Fe is also positively correlated with soluble Cu ($p < 0.01$) and Zn ($p < 0.001$). Soluble Cu is positively correlated to soluble Zn ($p < 0.05$), and soluble Zn to sulphate ($p < 0.05$). There is also a strong positive correlation ($p < 0.001$) between sulphate and conductivity apparent.

Acid mine drainage (AMD) from leachate streams

Table 5 show results chemical characterisation of AMD from the Deep Adit (Tigroney leachate outfall) and Ballymurtagh leachate outfall, respectively. Results show that the main metals entering the river from the Deep Adit and from Ballymurtagh are Fe (mean 118.0 and 123.9 mg/l respectively) and Zn (mean 60.2 and 27.6 mg/l) whereas Cu and Cd levels are relatively low (2.2 and 1.7 mg/l, and 0.21 and 0.07 mg/l, respectively). The pH during weekly sampling intervals varied only slightly in the Deep Adit (SD 0.06), while variation in Ballymurtagh was somewhat higher (SD 0.14). Student t-test analysis between the two mine waters showed significant differences for pH ($p < 0.01$), Zn

($p < 0.01$), Cu ($p < 0.05$), Cd ($p < 0.001$) and for Conductivity ($p < 0.05$) for values obtained during the entire sampling period.

Table 4. Correlation between particulate and soluble metals and other key parameters for contaminated river sites (excluding site 8).

	pH	flow	Cu(p)	Zn(p)	Fe(p)	Fe(s)	Cu(s)	Zn(s)	SO ₄
flow	0.167								
Cu (p)	-0.307	-0.008							
Zn (p)	0.622***	-0.074	0.116						
Fe (p)	0.270	0.568***	0.154	0.050					
Fe (s)	-0.581***	-0.408*	-0.035	-0.312	-0.493**				
Cu (s)	-0.279	-0.139	-0.019	-0.108	-0.391*	0.460**			
Zn (S)	-0.738***	-0.625***	0.143	-0.425**	-0.544***	0.808***	0.383*		
SO₄	0.197	-0.626***	0.094	0.265	-0.372*	0.130	0.098	0.358*	
cond.	0.822***	-0.296	-0.207	0.630***	-0.084	-0.306	0.098	-0.311	0.709***

p = particulate; s = soluble

Levels of significance: $p < 0.05^*$, $p < 0.01^{**}$, $p < 0.001^{***}$

Table 5. Chemical characterisation of the drainage at the Deep and Ballymurtagh Adit

Parameters	n	Deep Adit		Ballymurtagh Adit	
		Mean	SD	Mean	SD
Fe (mg l ⁻¹)	9	118.0	10.5	123.9	17.9
Cu (mg l ⁻¹)	9	2.2	0.7	1.7	0.22
Zn (mg l ⁻¹)	9	60.2	25.1	27.6	19.6
Cd (mg l ⁻¹)	9	0.21	0.06	0.07	0.06
SO ₄ (mg l ⁻¹)	9	1596	23.1	1607	50.9
pH	9	3.70	0.06	3.87	0.14
Conductivity (μS/cm)	9	1970	95.4	2332	385

Mass flux at individual sampling sites

Mass balance studies have been extensively used to assess the relative importance of a specific pollutant input to a watershed to elucidate important catchment processes (Semkin *et al.*, 1994). Therefore the mass flux (i.e.

concentration x flow), rather than chemical concentration, is of primary concern. Mass flux was calculated for each sampling site in tonnes/day (t/d) by multiplying the discharge at each sub-catchment by the concentration of soluble Fe, Cu and Zn, and SO_4^{2-} . Fig. 4 shows the mean mass flow for individual metals at each sampling site for all flow conditions between May and December, 1994. From the graph it is apparent that all metal concentrations decreased downstream, while SO_4^{2-} increased. The slight increase between sites 5 and 6 may be due to naturally higher SO_4^{2-} concentrations from the Aughrim River or to leaching occurring at the tailings pond at Shelton Abbey. However, there is no information with regard to SO_4^{2-} concentration for Aughrim River available. The marked increase at site 8 was mainly due to the saline conditions of the estuary and should not be rated as an increase due to AMD. Copper concentrations were very low compared to Fe and Zn and are therefore illustrated separately in Fig. 5. Increased Cu concentrations were noted after site 6.

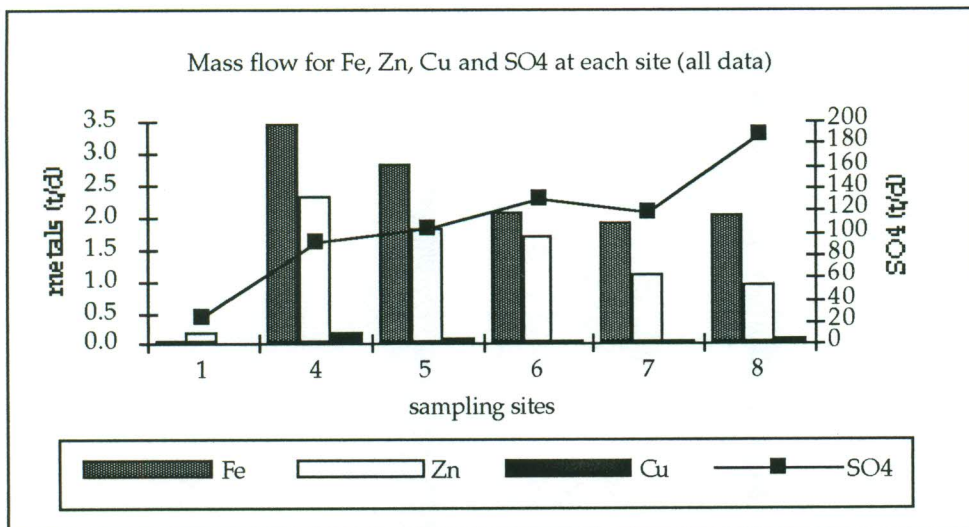


Fig. 4. Mass flow (t/d) of Fe, Zn, Cu and SO_4^{2-} each site (all data)

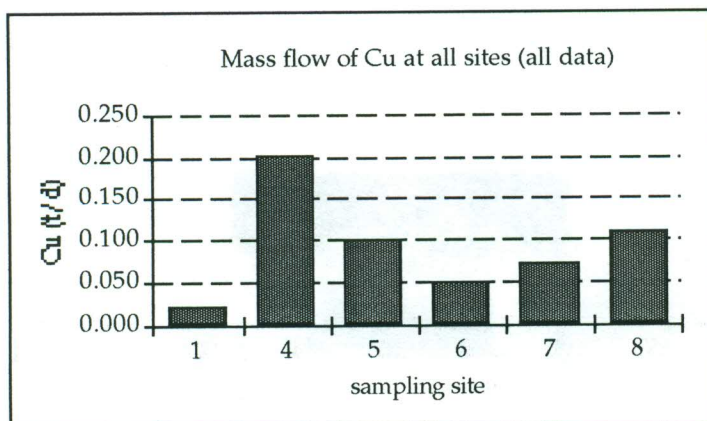


Fig. 5. Mass flow (t/d) for Cu at individual sites at all flow conditions

Figures. 6 to 9 show mean Zn, Cu, Fe and SO_4^{2-} fluxes ranked according to 3 different river flow regimes which were determined as follows: (1) < 4000 l/s; (2) >4000 l/s, <10,000 l/s; (3) >10,000 l/s. In class 2 only one sample was recorded at sites 5 to 8. Student t-tests were carried out to detect significant differences between mass fluxes for the various flow regimes (Table 6). In general, the graphs showed that the mass fluxes for Fe, Cu and Zn were higher in class 3 compared to either 1 or 2. Mass flux was generally greatest at site 4 and gradually decreased downstream. However significant differences among the various flow regimes were not detected (Table 6). All values referred to in the following text are mean values. Zinc mass flux in class 3 was highest at site 4 showing 5.61 t/d and decreasing rapidly thereafter. Zinc fluxes in class 2 ranged between 2.14 and 1.35 t/d at all contaminated sites, while the mass flux at the reference site was 0.36 t/d. In class 1, Zn mass flux between sites 4 and 6 remained at approximately 1.7 t/d and decreased at sites 7 and site 8.

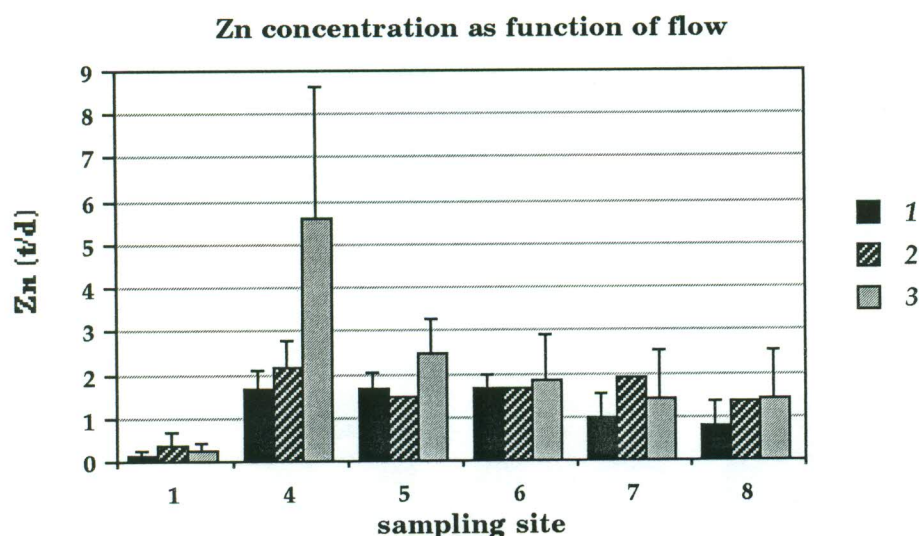


Figure 6. Mass flux of Zn (t/d) at all sites ranked and SD according to discharge ((1)<4000 l/s, (2) 4000 to 10,000 l/s, (3) >10,000 l/s).

The mass flux chart for Cu (Fig. 7) showed significantly higher fluxes in class 3 compared to class 1 ($p < 0.001$) and 2 ($p < 0.05$). Copper mass flux in class 3 at the contaminated sites (4 to 8) ranged from 0.33 to 0.53 t/d while the Cu mass flux at the site 1 was 0.008 t/d. Mass fluxes for class 1 ranged from 0.013 to 0.087 t/d for contaminated sites showing a maximum at site 4 compared to the background flux of 0.007 t/d. In class 2 the Cu mass flux at site 4 was 0.401 t/d compared to a background concentration of 0.018 t/d.

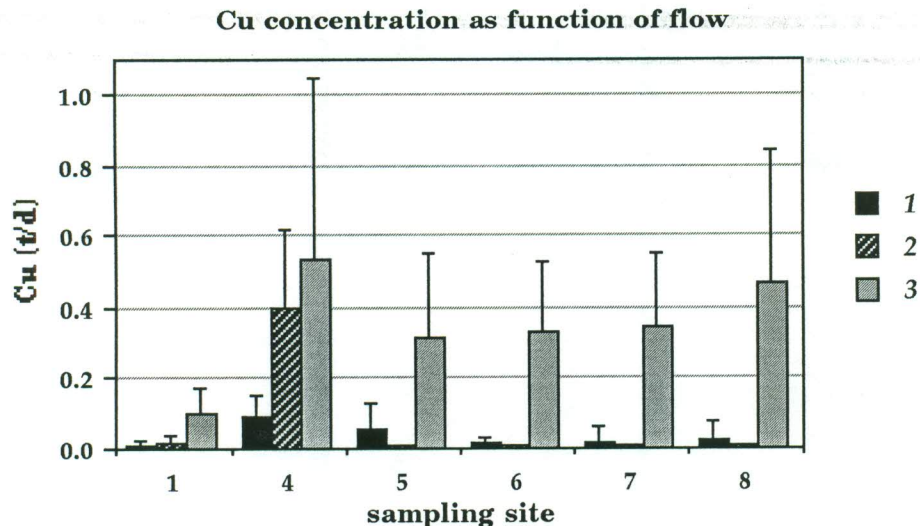


Figure 7. Mass flux of Cu (t/d) at all sites and SD, ranked according to discharge ((1)<4000 l/s, (2) 4000 to 10,000 l/s, (3) >10,000 l/s).

Iron mass flux as shown in Fig. 8 are significantly higher in class 3 compared to 1 ($p < 0.01$) and 2 ($p < 0.05$). The Fe mass flux in class 3 ranged from 6.58 t/d at site 4 to 8.38 t/d at site 8 compared to background of 1.87 t/d. Comparison of metal fluxes between individual classes resulted on average in a 6-fold increase between class 1 and 3, and a 4-fold increase between 2 and 3. In class 1, Fe fluxes decreased downstream, while they slightly increased in class 3.

Figure 9 shows SO_4^{2-} fluxes ranked according to flow classes 1, 2 and 3. As for the cations, SO_4^{2-} concentrations were highest in class 3 ranging from 180.2 to 230.7 t/d for contaminated sites with a maximum at site 6 which occurred after the confluence with the River Aughrim and the tailings pond at Shelton Abbey. Mass flux at site 1 was 82.7 t/d. Significant differences were detected between class 3 ($p < 0.01$) and both class 1 and 2. The fluxes in class 1 ranged from 72.3 to 104.0 t/d for contaminated sites and 13.0 t/d at the reference site (1).

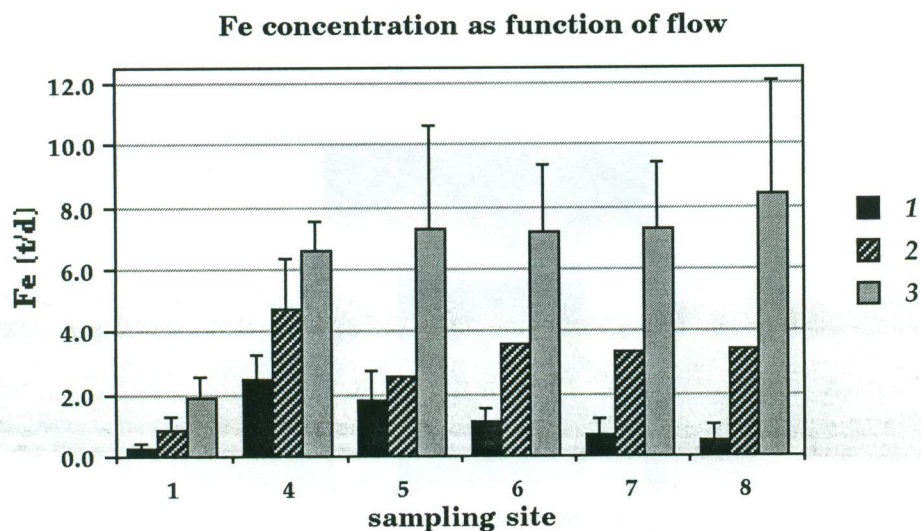


Figure 8. Mass flux of Fe (t/d) at all sites and SD, ranked according to discharge ((1) <4000 l/s, (2) 4000 to 10,000 l/s, (3) >10,000 l/s).

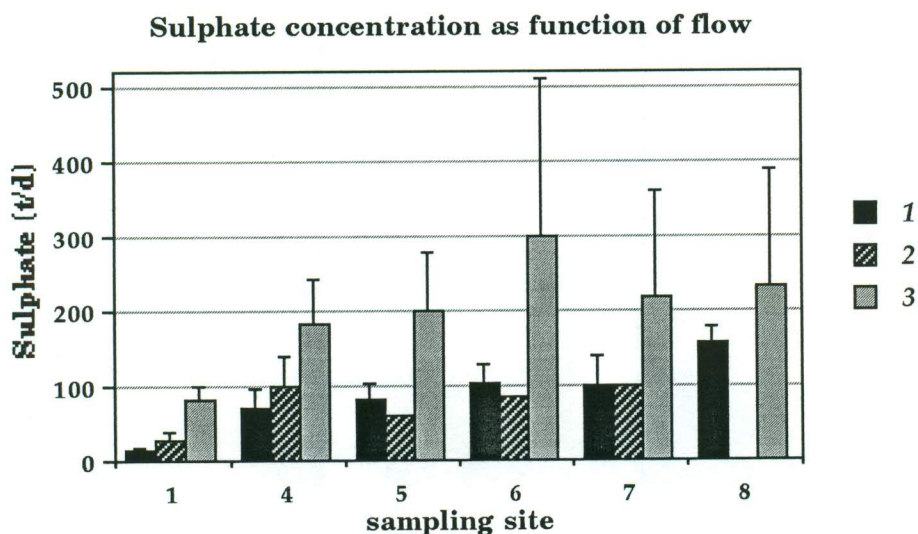


Figure 9. Mass flow of SO_4^{2-} (t/d) at each site and SD, ranked according to discharge ((1) <4000 l/s, (2) 4000 to 10,000 l/s, (3) >10,000 l/s).

Table 6. Significance levels between various flow regimes

rank	Zn	sig.	Cu	sig.	Fe	sig.	SO4	sig.
1 - 2	p=0.39	NS	p=0.55	NS	p=0.011	*	p=0.61	NS
1 - 3	p=0.23	NS	p<0.001	***	p=0.004	**	p=0.009	**
2 - 3	p=0.40	NS	p=0.012	*	p=0.011	*	p=0.007	**

Level of significance p<0.05*, p<0.01**, p<0.001***, NS not significantly different rank: (1) <4000 l/s, (2) 4000 to 10,000 l/s, (3) >10,000 l/s

DISCUSSION

Dissolved metals

The results in Figure 3 (a), (b) and (c) show decreased dissolved metal concentrations of Zn, Cu and Fe (680 to 100 $\mu\text{g/l}$, 69 to 10 $\mu\text{g/l}$ and 1005 to 150 $\mu\text{g/l}$, respectively) downstream. Highest concentrations for all metals were recorded at site 4 and lowest at site 8 for Zn and Fe, and at site 7 for Cu. After site 5 the Aughrim River, a river which has a similar discharge rate to the Avoca River, discharges into the Avoca River, whereby the water of the Avoca River is being diluted by approximately 100 %. A water quality study of the Aughrim River (McGrane, 1993) showed very low concentrations of dissolved metals ($< 0.1 \text{ mg/l}$) and thus the Aughrim River is excluded as an additional source of metals. Metal concentrations after the Avoca-Aughrim River confluence dropped by approximately 50 % at site 6 compared to site 5 (Figure 3 (a), (b), (c)), so that the discharge from the Aughrim River contributed to a faster recovery of the Avoca River in terms of water quality. The slightly more buffered water due to the limestone terrain within its sub-catchment also had a positive effect with regard to the recovery of the Avoca River. Copper concentrations slightly increased at sites 7 and 8, probably due to remobilisation of Cu, as this element is influenced by the formation of soluble $\text{Cu}(\text{OH})_2$ -complexes at pHs above 7 (Salomons and Förstner, 1984).

The mobility of soluble Cu species is a topic of concern, since relatively low concentrations in water proves toxic to biota, especially fish. EU guideline values for freshwater fish are not to exceed concentrations of 0.005 mg/l for Cu, and 0.3 mg/l for Zn at a water hardness of 10 mg/l CaCO_3 (Flanagan, 1992). Both of these values are exceeded during low river flows, particularly at site 4. Dissolved Zn concentrations (Fig. 10) fluctuate at approximately 0.6 mg/l. These concentrations dropped only once below the EU guideline value of 0.3 mg/l at site 4 on the 24.8.94. The decrease was due to a spate discharge of the river, while the total AMD input (Fig. 2) remained constant. Copper analysis of the river water at the sites further downstream may not be precise, as readings fall below the detection limit ($< 0.01 \text{ mg/l}$) of the flame AAS. Therefore furnace AAS for detection of very low Cu concentration is required. Lowest measurable concentrations already exceed the EU guideline level.

The impact of pH

The pH in natural waters is an essential parameter, as most physical and chemical reactions depend upon it. Biological functions and thus aquatic life are sensitive and easily influenced by pH changes. When discussing metal

concentrations in river systems, the pH is a major variable regulating chemical equilibrium among dissolved metal species, adsorption/desorption onto solid surfaces, complexation and other processes in aquatic chemistry. In natural waters the average pH ranges from 6.5-8.0. Rivers with naturally low pH like the Avoca River, are generally of softer water, and of lower productivity and reduced species diversity.

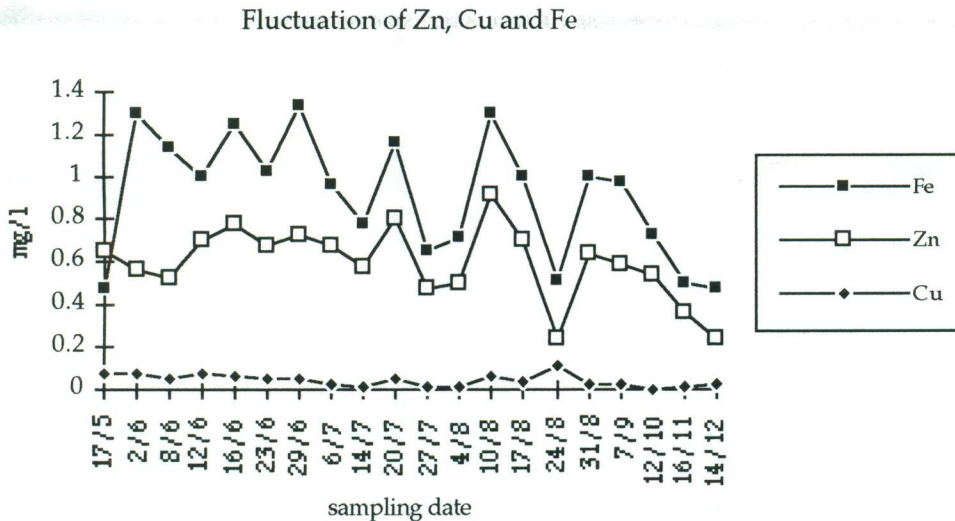


Fig. 10: Weekly variation of Fe, Zn and Cu at site 4 (Avoca Bridge) between 17.5. and 14.12.94

There are obvious differences in the pH of the sites studied. The mean pH of the drainage water from the mines is 3.7 and 3.9 (Table 5), while the mean pH in the Avoca River varies from 5.7 at site 4 to 8.5 at site 8. The pH dropped after mine drainage entered the system from a mean pH of 6.9 to 5.7 and slowly recovered again downstream showing a significant increase in pH below the fertiliser factory due to ammonia discharge. Changing pH also induces change in metal speciation within the river system and thus bioavailability of individual metals. Adsorption studies have shown that at very low pH values there is essentially no adsorption while at high pH values all cations are strongly adsorbed. In the Avoca River it was found that Zn in particular was strongly correlated with pH ($p < 0.001$) which suggests that adsorption of Zn to SPM increases with increasing pH (Fig. 3). The pH at which adsorption became significant was the pH at which it is documented that dissolved cations undergo hydrolysis to hydroxy complexes (Drever, 1982).

Metals in SPM

The forms in which Fe, Cu and Zn are transported, and the ultimate fate in the water, is dependent upon chemical properties of these elements and their interaction with particulate matter (Johnson and Thornton, 1987). Results show that Zn concentrations in particulate matter at sites 4, 5 and 6 are low (54-87 $\mu\text{g/l}$) and increased significantly at site 7 to 601 $\mu\text{g/l}$ when pH also increased to a mean of pH 8.7. This showed that Zn adsorption onto particulate matter is strongly dependent on pH showing a significant correlation ($p < 0.001$). The increase of Zn in particulate matter was due to either precipitation of Zn as an hydroxide or adsorption onto SPM. At site 8, Zn precipitation is not only influenced by pH but also by the saline conditions of the estuary. In contrast, both Cu and Fe increase significantly at site 4 where the dissolved fraction is also highest. Copper concentrations in the particulate phase seemed to decrease after site 6, whereas Fe concentrations seemed to increase downstream as far as the estuary. A correlation between Cu and Fe in the particulate matter has not been found. It is also interesting to note that the dilution after the Aughrim-Avoca confluence downstream of site 5 had no effect on metal concentrations in SPM. High concentrations of Fe at all river sites suggested that Fe is largely present in colloidal form and therefore transported over long distances (Webb and Walling, 1992).

Johnson (1986) observed an increase in concentration in the particulate fraction for both Zn and Cu with increasing pH. In the Avoca River, a close relationship between metal concentration which is expressed as the ratio of particulate/soluble metal and pH (Figs. 11 (a), (b)) was only found for Zn ($p < 0.001$). A less strong relationship was found for Fe ($p < 0.05$), whereas Cu showed no relationship. A possible explanation for the differences in behaviour of soluble Cu in the river investigated by Johnson (1986) and the Avoca River may be found in the differences in concentration of soluble Cu. The mean dissolved Cu concentration in the river investigated by Johnson (1986) was approximately 0.6 mg/l, whereas the mean Cu concentration in the Avoca River during low flow conditions was approximately 0.04 mg/l at site 4. Therefore the differences in adsorption behaviour may be explained by the low Cu concentrations in the Avoca River, as the rate of adsorption is dependent on the metal concentration as well as on pH (Pickering, 1979).

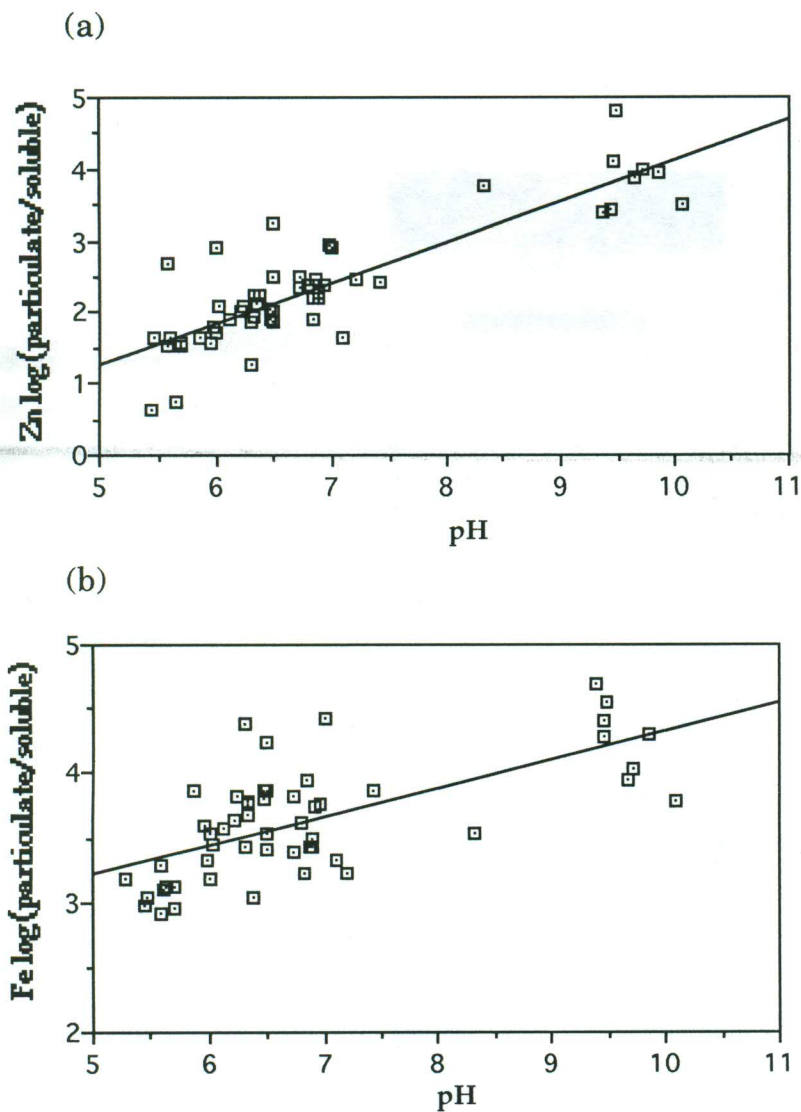


Fig. 11. Ratio of particulate to soluble Zn and Fe concentration as function of pH

Interaction with organic ligands

The concentration of dissolved organic matter in natural waters is typical in the range 1-100 mg C/l. Complexation with organic ligands affects the bioavailability of some metals and therefore reduces toxicity of respective elements. The nature of ligands likely to be present in natural systems is hard to define and poorly characterised. Some plants during growth release hydroxycarboxylic acids, and industrial and home wastes can introduce species such as cyanides, polyphosphates, and nitrilotriacetate (NTA). The role that natural organic compounds play, in complexing metal ions in aquatic systems, provide an ongoing debate. Some experimental evidence supports the argument that some metal ions are largely bound to organic ligands. According

to some estimates, the extent of metal complexation in natural waters can be close to 100 % for reactive metals such as Cu (Morel and Hering, 1993).

It is predicted that Zn complexes to a smaller extent than Cu in freshwater. The dominant species up to pH 8 is the free ion. At pH values below 7 virtually all the dissolved Zn is predicted to be in this form (French and Hunt, 1986). Zinc adsorption may also be affected by masking from natural occurring complexing agents in the river system. It has been found in adsorption studies using EDTA as complexing agents that Zn was virtually not adsorbed onto clay minerals. Only at higher pH the masking efficiency begins to decline and some loss occurs by precipitation (Pickering, 1980).

Due to the acidic nature of the soils in the Avoca Catchment (Sullivan and Gray, 1992) natural organic ligands may be introduced during decomposition processes of organic matter. Because total organic carbon was not measured, the only evidence of the presence of organic ligands is based on the observation of brown or yellow-brown coloration of river water after rainfall events which is often associated with humic acids. These complex brown or yellow acidic polymers play an important role in the metallic geochemistry of sediments. For example, a major proportion of the total Zn, Cu and Mo content of sediments is found in the humic acid fraction (Nissenbaum and Swaine, 1976).

Metal flux calculations

Determination of input and output budgets for a catchment or lake is an acceptable research tool in environmental studies (Dillon *et al.*, 1982). It provides insight into various geochemical and biological processes which may take place in a watershed or stream catchment. As already mentioned metal input into the River Avoca is primarily via two main leachate streams during the summer months. Acid mine effluent is being discharged in East Avoca via the Deep Adit (Tigroney) and in West Avoca via Ballymurtagh leachate stream. Flow data from River and Leachate streams, as well as chemical data collected between May and December 1994 was used for metal flux calculations (Appendix I).

Since SO_4^{2-} is naturally present at only small concentrations (e.g. 5 mg/l at uncontaminated site (1)) it provides a good tracer for mine waters. Therefore it can be assumed that elevated concentrations measured in the river water originate from the oxidation of sulphide ores. It is also thought that SO_4^{2-} is a relatively stable compound in an oxic environment as S has assumed its highest oxidation stage. This, and the fact that it is generally not adsorbed onto

solid surfaces allows the use of SO_4^{2-} as a conservative ion in mass flux calculations.

In order to determine spatial and temporal variation in the investigation of trace metal contamination, hydrological factors need also to be taken into account (Bouldt *et al.*, 1994; Bird, 1987; Grimshaw *et al.*, 1976). Uneven distribution of rainfall in the catchment is likely to affect metal variability (Grimshaw *et al.*, 1976). Rainfall in the upland area of the Avoca-Avonmore catchment would result in lower metal concentrations, whereas rainfall in the vicinity of the mines would most likely include surface runoff from spoil heaps and erosional material and thus increase total input of metals into the Avoca River. Although metal flow (t/d) generally decreased (Fig. 4) the consideration of various hydrodynamic conditions revealed substantial variation in mass flow with increased discharge. Zinc only showed one noticeable peak at site 4 (Fig. 6) and showed no significant differences between various flow conditions at all other sites while the mass flow of Cu, Fe and SO_4^{2-} seemed to be higher at increased discharge (Figs. 7-9). The increased Fe and Cu concentration at higher flow may be reflecting increased erosion and metal resuspension (Bird, 1987; Boulton *et al.*, 1994) while Zn may be precipitated from solution. It was also interesting to note that the mass flux for Zn at low flow conditions (< 4000 l/s) did not seem to decrease despite the expected dilution from the Aughrim River that was noticed for Cu and Fe. This may indicate that Zn is liberated from the sediment at site 6 possibly due to microbial activity. The increase in SO_4^{2-} concentrations at site 6 may be due to natural elevated sulphate concentration in the Aughrim River which leads to a wide flux in SO_4^{2-} . However, this has not yet been investigated. It also may be an indication of leaching of metal sulphides from the Tailings pond at Shelton Abbey situated upstream of site 6 has occurred.

Predicted metal input of Fe, Cu and Zn, SO_4 was calculated and compared to the measured concentration at site 4 using equation (1). Summary results are shown in Table 7. The results were expressed as the difference (%) between predicted and measured concentration. Therefore a value exceeding 100 % means that the predicted concentration was higher than the measured concentration.

$$T = (FC + f_1c_1 + f_2c_2) / (F + f_1 + f_2) \quad (1)$$

where

- T = metal concentration at site 4
- F = discharge rate of river at site 1
- C = metal concentration at site 1
- f1 = discharge rate at Deep Adit
- c1 = metal concentration at Deep Adit
- f2 = discharge rate at Ballymurtagh Adit
- c2 = metal concentration at Ballymurtagh Adit

Table 7. Percentage difference between predicted and observed concentrations of Fe, Cu, Zn and SO₄²⁻ derived Deep Adit and Ballymurtagh Adit as measured in the Avoca River at site 4.

	% SO ₄	% Fe	% Zn	% Cu
Mean	72.4	108.0	72.5	71.7
SD	7.7	28.0	18.4	54.7
Min	59.4	77.1	31.4	4.98
Max	90.8	169.6	110.8	212.1
Median	72.5	96.6	71.74	54.4

Results in Table 5.11 suggest that on average 72.4 % of the SO₄²⁻ in the Avoca River at site 4 are derived from the two leachate streams (Deep Adit and Ballymurtagh Adit). Therefore if metals are not being precipitated or solubilised approximately 72 % of the metals would also be derived from AMD discharged by the two adits. A mean of 72.5 % for Zn would suggest that all the Zn that enters the river via the leachate streams is still in the dissolved phase at site 4 and thus not lost from the system. This is also shown by the low concentrations in SPM (Fig. 3) and also the low Zn concentrations in the sediment (Herr and Gray, 1995) which indicates that Zn stays in solution at site 4. In contrast for Fe a value of 108.0 % was obtained. This suggests that approximately 36 % of the Fe was lost from the river system at site 4. The mean percentage contribution for Cu was calculated as 71.1 %. However, because of large variation among individual calculations it is not possible to make any prediction. Whereas values for SO₄²⁻ and Zn are relatively constant throughout the entire sampling period (SD 7.7 and 18.4 respectively), Fe and Cu, however, are much more variable (SD 28.0 and 54.7, respectively). The loss of Fe from the dissolved phase was visible with the river water constantly turbid and large amounts of Fe were measured in SPM (Fig. 3(c)). Iron concentrations of approximately 8 % in the < 63 μm sediment fraction led also to the conclusion that Fe is lost from the river system. Copper was found to

have accumulated in the ochre (mean 1800 $\mu\text{g/g}$) and in the $< 63 \mu\text{m}$ sediment fraction (mean 600 $\mu\text{g/g}$) (Herr and Gray, 1995).

There was a relationship found between percentage SO_4^{2-} and river flow at site 4 ($p < 0.05$) and also a significant relationship ($p < 0.05$) was found between the ratio of the river discharge at site 4 and total AMD discharge from the two adits, and the percentage sulphate contribution (Appendix III). A trend seems to be apparent showing that with increasing river/AMD discharge ratio the sulphate concentration also increased (Fig. 12). However, for all other cations analysed no such relationship could be elucidated. It also seemed that the minimum percentage contribution for Zn and Cu (Table 7) are both attributable to changes in hydrological conditions in the river and to some extent in the leachate streams. However there is not enough data for high flow conditions to draw any conclusions and therefore a larger data base should be used to make more precise predictions.

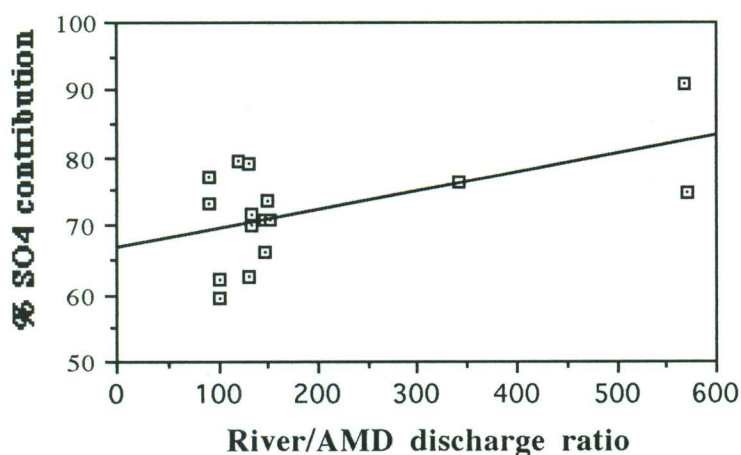


Fig. 12. Regression relationship between river/AMD discharge and percent sulphate derived from the two leachate streams

Water toxicity assessment

There is only little information available with regard to toxicity of the Avoca River. Experiments carried out in August 1994 indicated that sites only in the proximity of leachate inputs proved to be toxic. At the site below the mixing zone (site 4) almost 90 % survival of *Gammarus duebeni* was recorded which indicated no acute toxicity of the water (Byrne and Gray, 1994). However, monitoring of macro-invertebrate communities (Reynolds, 1986; Byrne and

Gray, 1994) indicated a decrease in the number of taxa and abundance. An increase in percentage of *chironomidae* was evident in response to AMD. Copper is extremely toxic to aquatic organisms, however, effects vary greatly among species. For example, Cu concentrations were found to be toxic to *Chironomus* species using the LC₅₀ (96 h) test at 30 µg/l, whereas for *Gammarus* species an LC₅₀ (96 h) was found to be 910 µg/l. Copper concentrations in the Avoca River are low, generally < 0.05 mg/l and therefore are not likely to affect *Gammarus* species. Zinc is less toxic to invertebrates than Cu. Threshold concentration LC₅₀ (96 h) for Zn was established for *Chironomus* species at 21.5 mg/l at a water hardness of 50 mg/l as CaCO₃. While for very soft water (hardness = 5.8 mg/l as CaCO₃) the LC₅₀ (24 and 96 h) was found to be 14.9 and 7.4 mg/l respectively using ZnSO₄. *Gammarus* species seem to have a lower threshold level for Zn. The LC₅₀ (24 and 96 h) was found to be 10.2 and 8.1 mg/l respectively at a water hardness of 50 mg/l (Jørgensen *et al.*, 1991). Zinc and Cu concentrations in the Avoca River are generally below these threshold concentrations found in acute toxicity studies. However, during rainfall events and high surface run-off from unvegetated spoil heaps in the vicinity of the mines, threshold levels for Cu may be exceeded causing short-term acute toxicity to some invertebrates. Therefore acute Cu toxicity may only be of significance during some periods of heavy rainfall throughout the year whereas chronic or indirect toxicity may have a stronger long-term effect. However, direct effect on invertebrate growth and reproduction caused by long-term exposure to low levels of toxic substances may have a stronger impact. There are also many other metals associated with AMD which are likely to influence toxicity and therefore induce a change in community structure. Single species acute toxicity tests, although they are the most frequently used toxicity tests (Rosenberg and Resh, 1993), may not give an accurate assessment when compared to the field trials. A mesocosm test, which reflects the field situation may better to provide more accurate information in ecological risk assessments (Rosenberg and Resh, 1993).

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Appendix I

Raw data from chemical analysis of Avoca River and leachate stream

No.	coll.	date	site	pH	Zn mg/l	Fe mg/l	Cu mg/l	SO4mg/l	Cond μ S
1	CH	94.06.16	8.1	7.4	0.02	0.00	0.00	6	85.6
2	CH	94.06.16	8.1	7.4	0.01	0.00	0.00	19	85.3
3	CH	94.06.16	8.1	7.4	0.00	0.00	0.00	6	-
4	CH	94.06.16	5.1	5.5	0.78	0.00	0.05	-	131.9
5	CH	94.06.16	5.1	5.5	0.78	1.2	0.06	34	130.9
6	CH	94.06.16	5.1	5.5	0.78	1.3	0.07	33	-
7	CH	94.06.23	8.1	6.5	0.01	0.00	0.00	5	74.2
8	CH	94.06.23	8.1	6.5	0.00	0.00	0.00	5	73.7
9	CH	94.06.23	8.1	6.5	0.01	0.00	0.00	5	75
10	CH	94.06.23	5.1	5.6	0.68	1.0	0.05	27	113.8
11	CH	94.06.23	5.1	6.6	0.67	1.0	0.06	27	114.3
12	CH	94.06.23	5.1	5.6	0.68	1.0	0.05	23	113.4
13	CH	94.06.23	5.3	6.6	0.38	0.10	0.00	23	117.9
14	CH	94.06.23	5.3	6.5	0.38	0.11	0.01	21	117.7
15	CH	94.06.23	5.3	6.5	0.38	0.12	0.00	21	117.5
16	CH	94.06.29	8.1	7.2	0.00	0.00	0.00	6	79.2
17	CH	94.06.29	8.1	7.1	0.02	0.00	0.00	5	77.5
18	CH	94.06.29	5.1	5.7	0.73	1.4	0.05	30	129.8
19	CH	94.06.29	5.1	5.7	0.73	1.3	0.05	31	128.7
20	CH	94.06.29	5.3	6.2	0.43	0.09	0.02	29	148.8
21	CH	94.06.29	5.3	6.3	0.42	0.11	0.00	24	127.7
22	CH	94.06.29	5.3	6.2	0.42	0.08	0.00	24	-
23	CH	94.06.29	5.2	5.7	0.68	0.90	0.05	29	127.7
24	CH	94.06.29	5.2	7.7	0.68	0.90	0.04	30	127.7
25	CH	94.06.29	5.5	6.9	0.25	0.00	0.00	-	831
26	CH	94.06.29	5.5	7.1	0.32	0.00	0.05	-	801
32	CH	94.07.06	8.1	7.1	0.04	0.10	0.00	5	75
33	CH	94.07.06	8.1	7.1	0.05	0.09	0.00	5	74
34	CH	94.07.06	8.1	7.1	0.04	0.08	0.00	5	71
35	CH	94.07.06	5.1	6.0	0.68	0.98	0.02	22	121
36	CH	94.07.06	5.1	6.0	0.68	0.96	0.02	22	121
37	CH	94.07.06	5.1	6.0	0.66	0.95	0.02	22	120
38	CH	94.07.06	5.3	6.5	0.41	0.35	0.00	28	117
39	CH	94.07.06	5.3	6.5	0.41	0.37	0.00	28	116
40	CH	94.07.06	5.3	6.5	0.40	0.37	0.00	28	116
41	CH	94.07.06	3.1	3.7	72	106	3.3	1589	1910
42	CH	94.07.06	3.22	3.9	25	101	1.7	1550	2100
43	CH	94.07.14	8.1	6.9	0.06	0.16	0.01	5	62
44	CH	94.07.14	3.1	3.8	-	119	3.1	1636	1971
45	CH	94.07.14	3.22	4.0	26	159	1.8	1591	2130
46	CH	94.07.14	5.1	5.6	0.57	0.77	0.01	23	94
47	CH	94.07.14	5.2	5.9	0.52	0.22	0.00	21	95
48	CH	94.07.14	5.3	6.3	0.34	0.30	0.00	19	102
49	CH	94.07.14	5.4	6.7	0.31	0.24	0.00	19	109
50	CH	94.07.14	5.5	7.0	0.27	0.26	0.00	-	145
51	CH	94.07.20	8.1	6.9	0.04	0.08	0.00	5.5	75
52	CH	94.07.20	5.1	5.6	0.80	1.2	0.05	32	128
53	CH	94.07.20	5.3	6.3	0.46	0.26	0.00	26	130
54	CH	94.07.20	5.4	9.5	0.10	0.05	0.00	28	236
55	CH	94.07.20	3.22	4.0	26	123	1.7	1630	2190
56	CH	94.07.20	3.1	3.7	74	129	2.8	1598	1936
57	CH	94.07.27	8.1	6.8	0.06	0.11	0.00	5	69
58	CH	94.07.27	5.1	6.1	0.48	0.65	0.00	21	100
59	CH	94.07.27	5.2	6.0	0.60	0.54	0.02	26	106
60	CH	94.07.27	5.3	6.5	0.33	0.26	0.00	20	102
61	CH	94.07.27	5.4	6.8	0.27	0.15	0.00	19	111
62	CH	94.07.27	5.5	9.4	0.09	0.04	0.00	-	353
63	CH	94.07.27	3.22	3.8	26	108	1.6	1540	3310
64	CH	94.07.27	3.1	3.7	74	117	2.4	1570	1925
65	CH	94.08.04	8.1	6.7	0.05	0.14	0.00	6	60
66	CH	94.08.04	5.1	6.0	0.50	0.71	0.01	22	96
67	CH	94.08.04	5.2	6.2	0.45	0.29	0.00	23	100
68	CH	94.08.04	5.3	6.5	0.31	0.29	0.00	21	104
69	CH	94.08.04	5.4	10.1	0.17	0.29	0.00	21	200
70	CH	94.08.04	5.5	8.3	0.19	0.32	0.00	-	352
71	CH	94.08.04	3.1	3.5	75.25	114	2.16	1560	1950
72	CH	94.08.04	3.22	3.8	26.9	138	1.56	1590	2220
73	CH	94.08.10	8.1	6.9	0.04	0.04	0.00	6	79
74	CH	94.08.10	5.1	5.5	0.91	1.3	0.06	36	136
75	CH	94.08.10	5.3	6.3	0.55	0.43	0.01	31	132

Appendix I

Raw data from chemical analysis of Avoca River and leachate stream

No.	coll.	date	site	pH	Zn mg/l	Fe mg/l	Cu mg/l	SO4mg/l	Cond μ S
76	CH	94.08.10	5.4	9.9	0.19	0.09	0.00	59	311
77	CH	94.08.10	3.1	3.7	74	109	2	1590	1958
78	CH	94.08.10	3.22	3.9	26	136	1.6	1610	2260
79	CH	94.08.10	5.2	5.3	0.87	0.76	0.07	42	136
80	CH	94.08.17	8.1	6.9	0.07	0.08	0.00	5	70
81	CH	94.08.17	5.1	5.6	0.70	1	0.04	29	115
82	CH	94.08.17	3.1	3.7	72	109	1.8	1610	1948
83	CH	94.08.17	3.22	3.8	26	111	1.5	1650	2280
84	CH	94.08.17	5.3	6.5	0.37	0.28	0.00	27	116
85	CH	94.08.17	5.5	9.5	0.12	0.05	0.00	-	3750
86	CH	94.08.17	5.4	9.7	0.18	0.18	0.04	24	241
87	CH	94.08.24	8.1	6.4	0.12	0.23	0.00	3	42
88	CH	94.08.24	5.1	6.0	0.24	0.51	0.11	10	59
89	CH	94.08.24	5.2	6.2	0.24	0.43	0.00	10	62
90	CH	94.08.24	5.3	6.3	0.19	0.39	0.00	10	67
91	CH	94.08.24	5.4	7.4	0.21	0.37	0.00	11	75
92	CH	94.08.24	5.5	9.2	0.15	0.38	0.00	-	262
93	CH	94.08.24	3.22	4.0	29	130	1.5	1660	2310
94	CH	94.08.24	3.1	3.7	74	113	1.6	1560	1930
95	CH	94.08.31	8.1	6.8	0.11	0.17	0.00	4	65
96	CH	94.08.31	5.1	5.5	0.64	1	0.03	20	110
97	CH	94.08.31	3.22	3.9	29	133	1.5	1680	2340
98	CH	94.08.31	5.3	6.0	0.44	0.41	0.00	30	114
99	CH	94.08.31	5.4	9.7	0.14	0.16	0.00	10	245
100	CH	94.08.31	5.5	9.5	0.13	0.10	0.00	40	1030
101	CH	94.08.31	3.1	3.7	70	112	1.5	1570	1933
22	NG	94.05.17	3.1	3.4	68	127	8.1	1616.47	1800
23	NG	94.05.17	3.1	3.4	69	130	8.2	1585.12	1810
24	NG	94.05.17	3.1	3.5	71	131	8.2	1711.54	1780
25	NG	94.05.17	3.1	3.5	70	140	8.2	1738.12	1760
28	NG	94.05.17	3.22	3.9	33	182	2.4	1822.32	2250
29	NG	94.05.17	3.22	3.8	33	182	2.4	1804	2180
36	NG	94.05.17	5.1	6.1	0.20	0.52	0.05	19.65	70
38	NG	94.05.17	8.1	6.7	0.00	0.00	0.00	7.05	60
39	NG	94.05.17	8.1	6.6	0.00	0.00	0.00	6.42	60
40	NG	94.06.02	5.1	6.8	0.56	1.3	0.07	28	120
41	NG	94.06.02	5.1	6.7	0.56	1.3	0.07	27	120
42	NG	94.06.02	3.22	4.0	34	149	2.2	1720	2480
43	NG	94.06.02	3.22	4.0	35	145	2.2	1790	2560
44	NG	94.06.02	3.1	3.6	74	110	6.3	1560	2080
45	NG	94.06.02	3.1	3.5	72	135	6.2	1220	2090
46	NG	94.06.02	8.1	7.2	0.08	0.42	0.02	7	90
47	NG	94.06.02	8.1	7.2	0.05	0.16	0.00	8	90
48	NG	94.06.08	5.1	6.8	0.52	1.16	0.28	24	110
49	NG	94.06.08	5.1	6.9	0.52	1.09	0.05	26	110
52	NG	94.06.08	3.22	3.9	30	125	2.2	1730	2420
53	NG	94.06.08	3.22	3.8	30	133	2.1	1720	2420
55	NG	94.06.08	3.1	3.6	72	104	5.5	1590	2020
56	NG	94.06.08	3.1	3.5	73	108	5.5	1620	2010
57	NG	94.06.08	8.1	6.4	0.05	0.14	0.30	7	80
58	NG	94.06.08	8.1	6.4	0.02	0.12	0.00	6	80
63	NG	94.06.12	8.1	7.4	0.07	0.00	0.02	7	85
64	NG	94.06.12	5.1	5.8	0.70	1.1	0.07	28	120
65	NG	94.06.12	5.5	8.8	0.01	0.00	0.00	25	235
66	NG	94.06.12	5.2	6.5	0.68	0.9	0.05	28	125
67	NG	94.06.12	5.3	7.0	0.40	0.16	0.01	23	132
68	NG	94.06.12	5.4	7.1	0.38	0.00	0.00	23	144
70	NG	94.06.16	8.1	6.8	0.00	0.00	0.00	10.94	220
72	NG	94.06.16	3.1	3.5	68	99	4.7	1582.13	1990
73	NG	94.06.16	3.22	3.8	25	92	2.2	1512.22	2150
74	NG	94.06.16	5.1	4.9	2.3	7.2	0.21	46.61	140
75	NG	94.06.16	5.2	5.4	0.74	1.0	0.06	44.31	140
76	NG	94.06.16	5.3	6.2	0.40	0.05	0.00	30.86	130
77	NG	94.06.16	5.4	9.3	0.07	0.00	0.00	28.99	210
78	NG	94.06.16	5.5	6.2	0.34	0.00	0.00	28.71	160
79	NG	94.06.22	5.1	7.2	0.42	0.48	0.00	18.33	90
80	NG	94.06.22	3.22	3.8	25	91	2.0	1438.54	2140
81	NG	94.06.22	3.1	3.4	67	101	4.2	1552.6	1980
82	NG	94.06.22	8.1	6.8	0.04	0.00	0.00	4.83	60
83	NG	94.06.22	5.2	6.6	0.39	0.29	0.00	18.89	120

Appendix I

Raw data from chemical analysis of Avoca River and leachate stream

No.	coll.	date	site	pH	Zn mg/l	Fe mg/l	Cu mg/l	SO ₄ mg/l	Cond μ S
109	NG	94.08.03	3.22	3.7	27	116	1.6	1670	2230
110	NG	94.08.03	5.1	4.6	1.8	7.1	0.17	16.7	80
111	NG	94.09.07	5.1	5.2	0.59	0.97	0.02	24	107
112	NG	94.09.07	3.22	3.7	29	139	1.4	1610	2330
113	NG	94.09.07	3.1	3.6	75	114	1.4	1600	1960
114	NG	94.09.07	8.1	5.9	0.12	0.26	0.00	5	62
121	NG	94.10.12	8.1	6.5	0.12	0.24	0.00	9	69
123	NG	94.10.12	3.1	3.4	24	114	1.03	1810	2010
124	NG	94.10.12	3.22	3.5	29	160	1.33	2050	2620
130	NG	94.10.12	5.1	5.8	0.54	0.72	0.00	50	99
131	NG	94.10.12	5.2	6.0	0.56	0.50	0.00	40	104
132	NG	94.10.12	5.3	6.5	0.37	0.34	0.00	30	108
133	NG	94.10.12	5.4	9.0	0.24	0.32	0.00	25	183
134	NG	94.10.12	5.5	7.8	0.34	0.34	0.00	40	475
146	NG	94.11.16	8.1	7.1	0.00	0.18	0.00	4	74
147	NG	94.11.16	8.1	6.6	0.04	0.22	0.01	7	79
148	NG	94.11.16	3.1	3.4	71	129	1.2	1617	2010
149	NG	94.11.16	3.1	3.3	67	127	1.2	1617	2020
152	NG	94.11.16	3.22	3.4	33	186	1.43	2014	2780
153	NG	94.11.16	3.22	3.4	32	194	1.42	2022	2750
154	NG	94.11.16	5.1	6.2	0.22	0.50	0.01	14	80
155	NG	94.11.16	5.1	6.7	0.49	2.0	0.02	10	80
156	NG	94.11.16	5.2	6.9	0.13	0.36	0.01	9	84
157	NG	94.11.16	5.2	6.2	0.13	0.32	0.01	10	88
158	NG	94.11.16	5.3	6.7	0.06	0.30	0.01	9	98
159	NG	94.11.16	5.3	6.9	0.05	0.30	0.01	6	95
160	NG	94.11.16	5.4	8.4	0.03	0.29	0.01	6	127
161	NG	94.11.16	5.4	8.5	0.03	0.28	0.01	6	128
162	NG	94.11.16	5.5	8.8	0.02	0.28	0.01	6	140
163	NG	94.11.16	5.5	8.8	0.05	0.30	0.01	5	138
186	NG	94.12.14	5.5	7.6	0.09	0.45	0.03	14	120
187	NG	94.12.14	5.2	4.9	0.19	0.6	0.03	16	180
188	NG	94.12.14	5.4	7.2	0.09	0.36	0.02	13	110
189	NG	94.12.14	5.3	6.8	0.11	0.37	0.02	19	89
190	NG	94.12.14	8.1	7.0	0.03	0.16	0.01	6	68
191	NG	94.12.14	3.1	3.6	103	103	2.9	1640	2020
192	NG	94.12.14	5.1	6.4	0.23	0.48	0.02	10	76
193	NG	94.12.14	3.22	3.8	39.6	209	1.6	2230	2940
207	NG	95.01.18	3.22	3.9	-	211	1.77	-	2860

APPENDIX II

pH and Cu ($\mu\text{g/l}$), Zn ($\mu\text{g/l}$) and Fe ($\mu\text{g/l}$) in suspended particulate matter

date	site	pH	Cu (p) ($\mu\text{g/l}$)	Zn (p) ($\mu\text{g/l}$)	Fe (p) ($\mu\text{g/l}$)
23/6/94	1	6.5	3.5	18	256.6
29/6/94	1	7.2	1.5	3	83
6/7/94	1	7.1	1.15	1.8	188.5
14/7/94	1	6.86	2.5	17.8	430.5
20/7/94	1	6.88	1.5	6.5	213.5
27/7/94	1	6.79	2	14.5	446
4/8/94	1	6.73	5	11.5	338
10/8/94	1	6.92	-	9.5	216
17/8/94	1	6.88	-	13.5	243.5
24/8/94	1	6.38	-	21	245
31/8/94	1	6.83	-	9	280
23/6/94	4	5.6	65.4	30.7	1293
29/6/94	4	5.7	70	27.5	1227
6/7/94	4	6	10.5	35.4	1467
14/7/94	4	5.59	82.5	18.8	1492
20/7/94	4	5.59	62.5	383.8	961
27/7/94	4	6.12	75	37.5	2416
4/8/94	4	5.98	110	30	1526
10/8/94	4	5.45	87.5	4	1217
17/8/94	4	5.64	35	4	1315
24/8/94	4	6.03	-	30	1428
31/8/94	4	5.46	-	29	1079
29/6/94	5	5.7	80	22.5	1175
14/7/94	5	5.87	83.8	23.8	1577
27/7/94	5	5.95	85	22.5	2104
4/8/94	5	6.24	70	55	1907
10/8/94	5	5.29	63.5	-	1132
24/8/94	5	6.21	-	25	1814
23/6/94	6	6.5	85.7	40	1912
29/6/94	6	6.3	85.8	30	2122
6/7/94	6	6.5	84.6	29	1255
14/7/94	6	6.34	56.3	45	1452
20/7/94	6	6.32	90	38.8	1512
27/7/94	6	6.46	75	37.5	1919
4/8/94	6	6.5	53	95	2089
10/8/94	6	6.31	50	10	1132
17/8/94	6	6.46	38.5	28.5	1822
24/8/94	6	6.33	-	32.8	2277
31/8/94	6	6	38.5	363.5	1407
14/7/94	7	6.72	52.5	96.3	1574
20/7/94	7	9.48	95	-	1761
27/7/94	7	6.84	45	45	1324
4/8/94	7	10.08	9	531	1760
10/8/94	7	9.85	70	1650	1800
17/8/94	7	9.66	25.5	1335	1562
24/8/94	7	7.43	-	54.8	2735
31/8/94	7	9.72	38.5	1348	1675
29/6/94	8	7	43.8	228	2607
14/7/94	8	6.97	42.5	227.5	1467
27/7/94	8	9.38	4.5	226	1909
4/8/94	8	8.32	45	1090	1118
17/8/94	8	9.46	41.5	1525	1247
24/8/94	8	9.19	-	-	-
31/8/94	8	9.45	71	347	1884

Appendix III

% difference between predicted and observed concentration of metals and sulphate derived from the main Adit as measured at site 4, and ratio of river flow (site 4) to AMD discharge

Date	River/AMD flow ratio	% SO4 contribution	% Fe contribution	% Zn contribution	% Cu contribution
2/6/94	134	71.77	89.82	80.46	57.75
8/6/94	153	70.84	79.31	69.32	51.69
16/6/94	101	62.01	79.49	65.63	57.16
23/6/94	130	62.69	77.14	54.29	50.19
6/7/94	146	70.8	83.06	55.11	90.58
14/7/94	120	79.34	169.62	82.21	212.09
20/7/94	91	73.21	125.73	74.16	51.58
27/7/94	131	79.14	147.88	90.98	163.34
4/8/94	147	66.13	139.39	77.72	135.67
10/8/94	102	59.4	94.94	58.05	30.54
17/8/94	92	77.26	126.54	87.45	48.05
24/8/94	341	76.42	113.84	110.81	4.98
31/8/94	150	73.5	98.24	67.79	35.85
7/9/94	133	70.26	123.33	87.17	57.45
16/11/94	570	74.87	93.3	31.44	21.7
14/12/94	569	90.75	86.29	67.41	68.48