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ACID MINE DRAINAGE COMPOSITION AND THE IMPLICATIONS FOR ITS IMPACT ON LOTIC SYSTEMS

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Abstract—Intensive sampling of acid mine drainage from adits draining the abandoned copper and sulphur mines at Avoca, south-east Ireland, has confirmed a seasonal variation in the Zn:Cu ratio observed previously. The variation in the Zn:Cu ratio leads to extreme variations in the toxicity of the drainage, and linked with increased adit flows and surface runoff during wetter months, often results in higher river toxicity, even during high river discharge rates. This seasonal variation in toxicity has important ramifications for the control of AMD to surface waters. Sampling over a three-year period shows that the rate of discharge from the adits follows a seasonal cycle being high in the spring, declining through summer to reach lowest flows in autumn and rising again in the winter. During the intensive sampling study over a 13-month period, the discharge rate in the Deep Adit varied from 8.5 to 37.3 l/s compared to 6.3 to 35.2 l/s in the Ballymurtagh Adit. This represents a total discharge rate for the two adits of between 1265 and 6270 m^3/d. Significant weights of cations were discharged from the two adits, ranging from 169–1279 kg/d for Fe, 69–459 kg/d for Zn, 1.5–34.7 kg/d for Cu, and 0.167–0.875 kg/d for Cd, with the Deep Adit contributing on average 40.4, 70.4, 66.7 and 80.9% of each metal respectively over the sampling period of 13 months. The impact of AMD on the river biota is severe with a major decrease in the number of taxa and faunal abundance. The species deficit at all sites below the mines is in excess of 87%. Dipterans dominate impacted sites with *Chironomidae* abundant. Fish are eliminated except for juvenile eels close to the estuary.

Key words—acid mine drainage, mining waste water, river pollution, sulphate, Zn:Cu ratio

INTRODUCTION

Acid mine drainage (AMD) is a major world-wide environmental problem that adversely affects both surface and ground waters. It is caused by the oxidation and hydrolysis of metal sulphides (in particular pyrite) in water permeable strata, or in mined spoil dumped on the surface. This results in the formation of several soluble hydrous iron sulphates, the production of acidity and the subsequent leaching of metals. It is principally associated with the mining of sulphide ores, the most commonly associated minerals being sulphur, copper, zinc, silver, gold, lead and uranium. Acid mine drainage is a complex pollutant characterised in surface and ground waters by elevated concentrations of iron and sulphate, a low pH, and elevated concentrations of a wide variety of metals depending on the host rock geology. The impact of AMD on rivers and lakes is also complex due to the multi-factor nature of the impacts (Gray, 1997; Kelly, 1988; Parsons, 1977).

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The ores at the abandoned copper and sulphur mines at Avoca, south-east Ireland, are volcanic massive sulphide deposits of Ordovician age. The principal minerals of economic significance in the Avoca region are chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS) and pyrite (FeS_2) (McArdle, 1994). The concentration of lead in sulphate rich waters are low due to the limited solubility of anglesite ($PbSO_4$). So the cations of greatest environmental concern are Cu, Fe and Zn.

The Avoca mining area is transected by the Avoca River into which all the AMD from the site drains. The Avoca mining area is principally drained by two major adits. The Deep Adit drains the eastern side of the disturbed site while the Ballymurtagh Adit drains the western side (Fig. 1) There are also minor secondary inputs of acid mine drainage (AMD) such as small contaminated streams, groundwater discharge and bank infiltration. The Avoca mining area is situated in the lower part of the Avoca-Avonmore catchment (652 km^2), which is of the highest water quality. The catchment is bordered on all sides by EU salmonid designated rivers (European Commission, 1978). However, the AMD discharged from the mines severely damages the normal biota over the

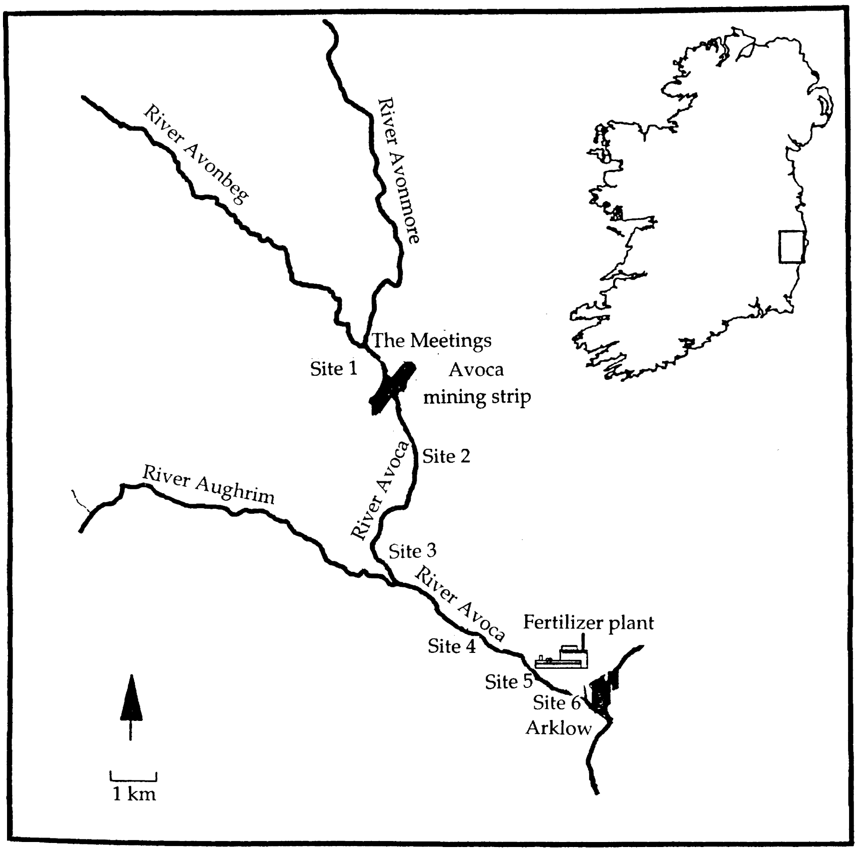

Fig. 1. The location of the Avoca mines and the impacted Avoca River in south-east Ireland.

last 15-km stretch of the river to the sea (Byrne and Gray, 1995a), thus providing an effective barrier for salmonid migration to spawning areas upstream.

Preliminary studies over the period 1992 to 1994 indicated a number of interesting seasonal factors in relation to the AMD discharges into the river. The intensive sampling programme reported in this paper was carried out over a 13-month period from May 1994 to 1995 to confirm and quantify the earlier preliminary findings. A wide range of surface and groundwaters on the mine site were examined, representing 42 separate sampling locations overall. These included springs, leachate streams (adits), surface runoff, temporary and permanent ponds and lakes, as well as the receiving water (River Avoca) into which the mines drained. This report deals with the variability of the main leachate streams and the effect this has on the impact to lotic receiving waters.

METHODS

Water samples were filtered, as collected, in the field through a Millipore® cellulose nitrate membrane with a pore size of 0.45 μm, and stored in high density plastic bottles. Two subsamples were taken, one being acidified for subsequent metal analysis, the other for sulphate, conductivity and pH analysis. Samples were stored at 4°C in the dark. Conductivity and pH analysis were carried out within 24 h of sample collection using a WTW® LF196 conductivity meter and a Jenway® 3015 pH meter respectively. Representative samples of the mine wasters, adit discharges, surface and groundwaters were analysed by ICP-MS to identify those cations present in significant concentrations. From these results six metals were selected for intensive study. The metals Al, As, Cd, Cu, Fe and Zn were analysed using atomic adsorption spectrophotometry and sulphate analysis was carried out by ion-exchange chromatography using a Dionex® 2020 analyzer. Standard methods were used throughout (APHA, 1989).

There is considerable difficulty in comparing temporal and spatial variation of AMD waste waters, and impacted surface and ground waters, using individual chemical and physical parameters. This is because slight variations in environmental conditions can cause significant differences in individual parameter flux rates (e.g. adsorption, co-precipitation, etc.). An objective index, the acid mine drainage index (AMDI), has been developed and evaluated for assessment of such waters (Gray, 1996a). The AMDI is calculated using a modified arithmetic weighted index using the parameters most indicative of AMD contamination (i.e. low pH, high sulphate and associated cations). Seven parameters were selected and a weighting was used to express the relative indicator value of each (Table 1). This was estimated by consideration of (a) the concentration of parameters in raw and diluted AMD, (b) their sorption properties, (c) the effect of neutralization on concentration, (d) the relevance of concentration to AMD formation, and (e) detection limits of the analytical procedures used. Both pH and sulphate were considered to be of greatest indicator value as they were unaffected by sorption processes, while sulphate was also unaffected by neutralization. The acid mine drainage index (AMDI)

Table 1. Parameters and weightings used in the calculation of the AMDI

Parameter	Unit	Weighting
Sulphate	mg/l	0.25
pH		0.20
Iron	mg/l	0.15
Zinc	mg/l	0.12
Aluminium	mg/l	0.10
Cadmium	μg/l	0.10
Copper	mg/l	0.08
Total weighting		1.00

is used in this study to quantify the degree of contamination of the River Avoca by AMD.

The flow of leachate emanating from the main adits were measured manually using permanent 45° vee-notch weirs. Flows were generally taken on dry days to exclude the effects of surface runoff, as all the adits and streams receive either surface runoff from the mines or from the roads during periods of prolonged rainfall or heavy storms.

The mines discharge into the River Avoca just downstream from the White Bridge. Water and biological samples were taken 0.75 km upstream from the Bridge (control site 1), immediately after complete mixing at 2.5 km (site 2) and then at 6 km below the White Bridge (3). A major tributary with similar discharge rate as the River Avoca enters the river at 7.25 km. The next sample sites (4 and 5) are 10.5 and 12.25 km downstream of the White Bridge, respectively. The final site is located 13.75 km downstream of the White Bridge (site 6), just 1.25 km from where the river finally enters the sea at the port of Arklow (Fig. 1). Site 6 is permanently brackish while site 5 is the only other site subject to the estuary resulting in some salinization at high tides.

Only three discernible habitats could be identified in the river. These were classed as riffle, glide and pool, although the latter was restricted due to the erosional nature of the river. Samples were taken for invertebrate analysis from riffle areas at each site according to the method of Byrne and Gray (1995a). Five replicate pond-net kick samples (20 s duration) were taken as an evenly spaced transect across the river at each site.

RESULTS AND DISCUSSION

Flow rates

There was a wide variation in discharge rate from the adits over the intensive sampling period. The discharge rate from the Deep Adit varied from 8.5 to 37.3 l/s (a range of 28.8 l/s) over the period and from 6.1 to 35.2 l/s (a range of 29.1 l/s) from the Ballymurtagh Adit. This represents a total discharge rate from the two adits of between 1265 and 6270 m^3/d (a range of 5005 m^3/d) giving a mean monthly rate of 2947 m^3/d (S.D. 1412) over the 13 months (Table 2).

The discharge rate from the two main adits were closely correlated ($P < 0.001$), with no significant difference between the discharge rates from the two adits ($P > 0.05$). The discharge rate followed a seasonal cycle declining over the spring, summer and autumn period to reach a minimum rate during October of 1265 m^3/d, increasing over the winter to reach a maximum mean monthly discharge rate in January of 6270 m^3/d then gradually decreasing again. The summer of 1994 was exceptionally dry, with river flows consistently very low until November. During that period the flow in the adits fell steadily, although the rate of decrease slowed during the period of July to August reaching minimum flows during October. The recovery in flow was lower in the Ballymurtagh Adit compared to the Deep Adit, although the rate of increase was similar. This reflects the post-mining hydrological nature of the two sites which is considered later.

Although the discharge rate varied significantly over the sampling period, no significant variation ($P > 0.05$) in flow was found at any time over shorter periods (24–36 h) using hourly samples, or between daily samples. Variation in discharge rates were gradual over prolonged periods. Surface runoff from the mines and roads were diverted into the

Table 2. Monthly mean flow (l/s) and metal discharge rates of iron, zinc, and copper (kg/d) from May 1994 to May 1995

Month	Deep adit				Ballymurtagh adit				Total			
	flow	Fe	Zn	Cu	flow	Fe	Zn	Cu	flow	Fe	Zn	Cu
					Year 1994							
5	23.8	272	143	16.8	23.7	373	68	4.9	47.6	645	211	21.7
6	16.8	160	103	8.0	18.1	197	48	3.4	34.9	357	151	11.3
7	12.1	125	78	3.1	11.7	118	26	1.7	23.8	243	104	4.8
8	10.3	99	65	1.7	10.2	117	24	1.4	20.5	217	89	3.1
9	10.2	101	66	1.2	9.3	112	23	1.1	19.5	212	90	2.4
10	8.5	84	54	0.8	6.1	85	15	0.7	14.6	169	69	1.5
11	12.7	141	76	1.3	9.8	160	27	1.2	22.5	301	103	2.5
12	18.0	161	108	4.5	13.6	245	47	1.9	31.6	406	154	6.4
					Year 1995							
1	21.8	175	130	8.6	19.2	361	61	2.7	41.1	536	191	11.3
2	37.3	244	273	29.0	35.2	1035	186	5.7	72.6	1279	459	34.7
3	24.8	123	277	18.8	29.4	543	89	5.1	54.1	666	366	23.9
4	15.8	165	89	8.3	19.1	215	45	3.0	34.9	380	134	11.3
5	11.7	114	64	2.9	14.1	144	31	1.9	25.8	258	95	4.8
Mean	17.2	151	117	8.1	16.9	285	53	2.7	34.1	436	170	10.8
S.D.	8.05	56	75	8.6	8.5	261	45	1.7	16.3	301	117	10.2
Minimum	8.51	84	54	0.8	6.1	85	15	0.7	14.6	169	69	1.5
Maximum	37.3	272	277	29.0	35.2	1035	186	5.7	72.6	1279	459	34.7
Range	28.8	188	223	28.3	29.1	950	170	5.0	57.9	1110	389	33.2

Table 3. The contribution of the main adits to overall AMD discharge to river (Ø). Values of Ø are given below and are estimated from the discharge rate from the Deep Adit

Flow rate in Deep Adit (l/s)	Value of Ø
0–10	0.9
11–20	0.8
21–30	0.7
31–40	0.6
>41	0.5

adits by the Local Authority during 1990. The surface runoff from the mines had a significant effect on the flow and strength of AMD in the Deep Adit, while surface runoff from the main Arklow–Rathdrum road severely affected the Ballymurtagh Adit and the minor contaminated streams which drain the western side of the mine. For this reason sampling was not carried out during times of heavy or prolonged rainfall, or when surface runoff was found entering either adit.

The contribution of the two main adits to the overall discharge of AMD to the receiving water was estimated using sulphate as a conservative tracer of the pollutant and mass balance analysis (Gray, 1996b). The contribution of AMD from the adits was linked to the height of the water table in the mines and therefore to the discharge rates of the adits themselves. During the summer the adits contributed up to a maximum of 94% of all the AMD entering the river; however, as the water table rose in the autumn and winter then the percentage contribution fell with other sources such as groundwater discharge, bank side infiltration and the minor contaminated streams becoming increasingly important. The contribution of AMD entering the river solely from the adits can be calculated with the Deep Adit discharge rate and is given in Table 3 as a reciprocal (Ø).

Chemical composition

The Deep Adit is the main leachate stream discharging into the River Avoca, draining the entire eastern side of the mining area. A summary of the chemical data is given in Table 4. The concentration of Zn, Fe and Cd in the Deep Adit is independent of flow and remained reasonably constant over the year. In contrast the concentration of Cu varied significantly over time and demonstrated a strong second order polynomial relationship with flow $Cu = 5.48 + 0.82x - 1.13e2x^2$ ($r^2 = 0.871$; $P < 0.001$). There are few significant correlations between parameters due to the low variability of the data over time. Aluminium is correlated with Cu ($P < 0.001$) and Cd ($P < 0.05$), and negatively with sulphate ($P < 0.05$) and conductivity ($P < 0.001$). The pH is the only parameter correlated with the AMDI ($P < 0.01$).

The Ballymurtagh Adit is the other main leachate stream discharging into the River Avoca. It drains the western side of the mining area. It is very different in quality to the Deep Adit being only slightly less acidic (median pH 3.8), having a very different chemical composition and being more variable (Table 4). Student *t*-tests between the two adit discharges show that all the parameters measured were significantly different ($P < 0.001$). In the discharge from the Ballymurtagh Adit, Zn, Fe, Al and As are all very highly correlated with each other ($P < 0.001$), and with both sulphate and conductivity ($P < 0.001$). Copper and Cd are independent of all parameters except AMDI. Copper is positively correlated with AMDI ($P < 0.05$) and Cd

Table 4. Comparison of the mean, median, number of samples (No.), standard deviation (S.D.), minimum and maximum for acid mine drainage discharged from the two main adits

Parameter	Mean	Median	No.	S.D.	Min	Max
			Deep Adit			
pH	3.6	3.6	41	0.13	3.3	3.8
As μg/l	7.0	7	28	0.96	5	9
Al mg/l	122	119	28	10	110	143
Cd μg/l	248	240	41	62	190	590
Cu mg/l	4.9	4.7	41	2.7	1.0	10
Fe mg/l	116	112	41	25	85	248
Zn mg/l	71	71	40	7.5	58	103
SO_4 mg/l	1584	1590	38	89	1220	1810
Cond. μS/cm	1946	1960	41	76	1760	2090
AMDI	26.2	26.1	37	1.5	23.9	28.4
			Ballymurtagh Adit			
pH	3.81	3.8	36	0.16	3.4	4.0
As μg/l	20	20	26	2.3	16	25
Al mg/l	76	76	26	8.2	65	91
Cd μg/l	49	60	36	24	0	80
Cu mg/l	1.8	1.7	36	0.29	1.3	2.4
Fe mg/l	165	139	36	67	91	378
Zn mg/l	33	30	36	10	25	72
SO_4 mg/l	1850	1716	36	358	1439	2855
Cond. μS/cm	2605	2415	36	490	2100	4000
AMDI	30.8	30.9	36	3.2	23.9	36

Cond. is conductivity, AMDI the acid mine drainage index, As as ASO_4^{3-} and SO_4 as SO_4^{2-}.

negatively ($P < 0.001$). The pH is only correlated with Cu ($P < 0.001$). The concentrations of all cations were independent of adit flow rate, while the concentration of Zn was independent of flow up to 30 l/s. At flows in excess of this there was a rapid increase in the Zn concentration with increasing adit flow.

The mean quality of the adit drainage, including the Shallow Adit which is an intermediate leachate source on the eastern side which stays on the surface for only a short distance before draining back into the workings via a partially sealed shaft, is compared with contaminated surface runoff and raw acid mine drainage in Table 5. The raw AMD arises from springs emanating from spoil heaps and surface ponds fed by springs. The two main springs studied had mean AMDI (and ranges) of 6.2 (3.6–9.0) and 3.1 (0.6–11.6), while the mean AMDI (and ranges) for two typical ponds were 4.9 (4.0–5.8) and 1.7 (1.2–2.6). Surface runoff ranges from highly contaminated water from spoil heaps (AMDI < 10) to only slightly contaminated water (AMDI > 30). The raw AMD is significantly different from the leachate discharged from the adits for all parameters ($P < 0.001$), the AMD from the adits being highly diluted by uncontaminated groundwater. Surface runoff is, however, more similar to the adit drainage with Zn, sulphate, conductivity and AMDI all similar ($P > 0.05$). Only pH ($P < 0.001$), Fe ($P < 0.05$) and Cu ($P < 0.01$) were significantly different.

Metal discharge rates

The mean monthly discharge rates of Fe, Zn, and Cu from the two main adits are given in Table 2, and for Cd in Table 6. In the Deep Adit Zn showed a seasonal cycle reaching a maximum rate of 227 kg/d during February and March and a minimum discharge rate of 54 kg/d the preceding October. Iron followed a similar cycle to Zn reaching a maximum discharge rate during May 1994 and February 1995 of 272 and 244 kg/d, respectively. Minimum discharge rate was recorded during October 1994 at 84 kg/d. Copper displayed a much wider variation in discharge rate than the other metals falling from 29.0 kg/d in winter to 0.76 kg/d in October. The same seasonal cycle of discharge variability is recorded for Cd with maximum flows in late winter (February) at 0.70 kg/d falling to a minimum in October of 0.14 kg/d.

In the Ballymurtagh Adit Zn had a similar variation in discharge rate to that seen in the Deep Adit having a maximum rate in February of 186 kg/d and a minimum in October of 15.4 kg/d. Iron also followed a similar seasonal pattern to iron in the Deep Adit with discharge rates very similar

Table 5. Comparison of the mean, median, number of samples (No.), standard deviation (S.D.), minimum and maximum for (I) Raw acid mine drainage (springs and seepage from spoil), (II) Surface runoff and (III) Leachate streams from adits

Parameter	Mean	Median	No.	S.D.	Min	Max
			(I) Raw acid mine drainage			
pH	2.67	2.65	58	0.28	2.1	3.3
Al mg/l	774	517	42	732	57	2211
As μg/l	223	66	41	403	0	1641
Cd μg/l	916	840	58	727	30	2480
Cu mg/l	185	147	58	172	4.5	590
Fe mg/l	996	1029	58	780	24	2384
Zn mg/l	229	208	58	191	16	1074
SO_4 mg/l	10203	8720	34	6999	1280	24668
Cond. μS/cm	6874	6580	57	3859	1750	15700
AMDI	9.6	5.4	34	9.0	0.79	28.4
			II. Surface runoff from mines			
pH	2.7	2.7	50	0.36	2.0	3.6
Al mg/l	165	62	38	294	5.5	1429
As μg/l	373	21	38	1237	0	7030
Cd μg/l	134	65	50	171	0	880
Cu mg/l	38	17	50	64	1	383
Fe mg/l	635	182	50	1458	0.75	7520
Zn mg/l	53	16	50	94	0.06	509
SO_4 mg/l	3256	1150	32	6125	159	26050
Cond. μS/cm	3199	2145	50	3452	360	16240
AMDI	27.7	25.6	32	15.5	1.5	57.1
			III. Leachate discharged from adits			
pH	3.5	3.6	94	0.39	2.6	4
Al mg/l	168	114	67	152	65	618
As μg/l	36	19	67	50	5	177
Cd μg/l	247	220	94	237	0	910
Cu mg/l	10.8	2.4	94	17	1.03	70
Fe mg/l	191	130	94	131	85	731
Zn mg/l	71	68	93	46	25	215
SO_4 mg/l	2069	1624	85	1107	1094	6330
Cond. μS/cm	2678	2205	94	1041	1760	5220
AMDI	26.4	27.3	84	6.5	9	36

Cond. is conductivity, AMDI the acid mine drainage index, As as ASO_4^{3-} and SO_4 as SO_4^{2-}.

Table 6. Monthly mean flow (l/s) and metal discharge rates of cadmium (kg/d) from May 1994 to May 1995

	Deep Adit		Ballymurtagh Adit		Total	
Month	flow (l/s)	Cd (kg/d)	flow (l/s)	Cd (kg/d)	flow (l/s)	Cd (kg/d)
			Year 1994			
5	23.8	0.608	23.7	0.061	47.6	0.669
6	16.8	0.353	18.1	0.018	34.9	0.371
7	12.1	0.268	11.7	0.060	23.8	0.328
8	10.3	0.208	10.2	0.053	20.5	0.261
9	10.2	0.212	9.3	0.064	19.5	0.276
10	8.5	0.140	6.1	0.027	14.6	0.167
11	12.7	0.231	9.8	0.059	22.5	0.290
12	18.0	0.312	13.6	0.070	31.6	0.382
			Year 1995			
1	21.8	0.398	19.2	0.106	41.1	0.504
2	37.3	0.703	35.2	0.172	72.6	0.875
3	24.8	0.513	29.4	0.178	54.1	0.691
4	15.8	0.329	19.1	0.116	34.9	0.445
5	11.7	0.223	14.1	0.073	25.8	0.296
Mean	17.2	0.346	16.9	0.081	34.1	0.427
S.D.	8.1	0.169	8.5	0.049	16.3	0.205
Minimum	8.5	0.140	6.1	0.018	14.6	0.167
Maximum	37.3	0.703	35.2	0.178	72.6	0.875
Range	28.8	0.563	29.1	0.160	57.9	0.708

except when peak discharge rates occurred during the winter which were significantly higher than the other adit reaching a maximum during February of 1035 kg/d. The large variation in discharge rate for Cu seen in the Deep Adit was not recorded in the Ballymurtagh Adit, although the same seasonal variation is recorded. Minimum discharge rates occurred in October (0.71 kg/d) and maximum values during February at 5.68 kg/d. This is a range of 4.97 kg/d compared to 28.24 kg/d in the Deep Adit. Cadmium followed a similar seasonal discharge pattern to Cu with minimum rates in June and October (0.018 and 0.027 kg/d, respectively) and maximum rates during February and March (0.172 and 0.178 kg/d, respectively).

Table 7. Percentage contribution of the total metals contributed from the two main adits studied by the Deep Adit

Month	Contribution (%)			
	Fe	Zn	Cu	Cd
		1994		
5	42	68	77	91
6	45	69	70	95
7	51	75	64	82
8	46	73	55	80
9	47	74	52	77
10	50	78	52	84
11	47	74	52	80
12	40	70	71	82
		1995		
1	33	68	76	79
2	19	60	84	80
3	19	76	79	74
4	43	66	74	74
5	44	67	60	75
Mean	40.4	70.4	66.7	80.9
S.D.	11	5	11	6
Minimum	18.5	59.5	51.7	73.9
Maximum	51.4	77.7	83.6	95.1
Range	33.0	18.2	31.9	21.2

Over the sampling period the Deep Adit contributed on average 40.4% of the iron discharged from the two adits, 70.4% of the zinc, 66.7% of the Cu and 80.9% of the Cd. This makes it significantly more polluting in terms of heavy metal toxicity than the Ballymurtagh Adit (Table 7). The percentage contribution of metals by the Deep Adit discharge is affected by flow for two of the metals studied (i.e. Cu and Fe). Copper was positively correlated with discharge rate ranging from 84% during maximum flows to 52% at low flows. Iron behaved in an opposite manner being negatively correlated with discharge rate, with the Deep Adit only contributing 19% at maximum flows from both adits rising to a maximum of 51% during low flows.

The Zn:Cu ratio

During periodic sampling between 1992 and 1993 a discernible variation in the Zn:Cu ratio was observed in both AMD adit discharges. This was studied in detail using weekly samples over the period of May 1994 to May 1995. The concentration of Zn in the Deep Adit varied very little (mean 70 mg/l, sd 0.5), while the Cu concentration fell steadily from 8.2 to 1.0 mg/l up to October and then began to rise again reaching a peak of 9.5 mg/l in February. This demonstrates a predictable fluctuation in the Zn:Cu ratio. A similar phenomenon, although much less well defined, was also identified in the Ballymurtagh Adit. The variation in the Zn:Cu ratio corresponded closely to the height of the water table within the mine, being correlated to adit flow rate. The ratio is high during low water table periods and *vice versa* (Fig. 2). This variation in the Zn:Cu ratio corresponds closely to seasonal variation in expected rainfall (Fig. 3), with highest Zn:Cu ratios recorded towards the end of the dry season.

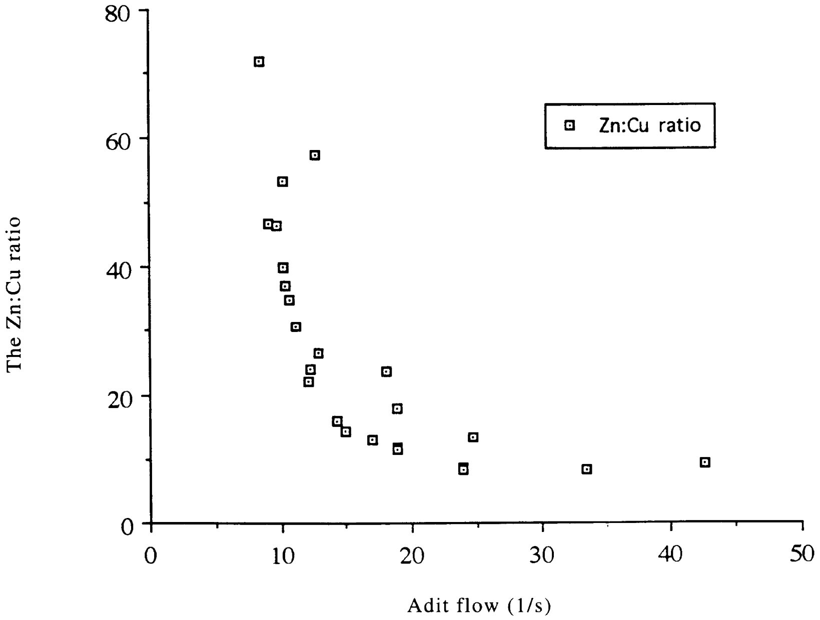

Fig. 2. Variation in the Zn:Cu ratio with adit discharge rate.

The reason for this variation, which was seen annually over a 3-year period is unclear but research by Alpers *et al.* (1994) has shown a similar effect seen at a similar mine in California due to secondary sulphate mineral formation within the mine workings. At Avoca the phenomenon is more pronounced on the east side due to the more complex nature of the workings (shafts and adits) and the highly fractured nature of the bed rock through which mine water freely moves, offering more potential for secondary sulphate formation. In contrast, the western side has been more extensively mined being deeper with fewer shafts and adits with vast underground stoops which were never backfilled. Among the more important secondary sulphate minerals encrusting the underground mine workings in Avoca are chalcanthite ($CuSO_4{\cdot}5H_2O$) and melanterite ((Fe^{II},Zn,Cu)$SO_4.7H_2O$). Both minerals may be major contributors to this phenomenon. Melanterite is of particular interest as it is commonly formed in the iron-rich AMD and has a propensity to incorporate Cu in preference to Zn.

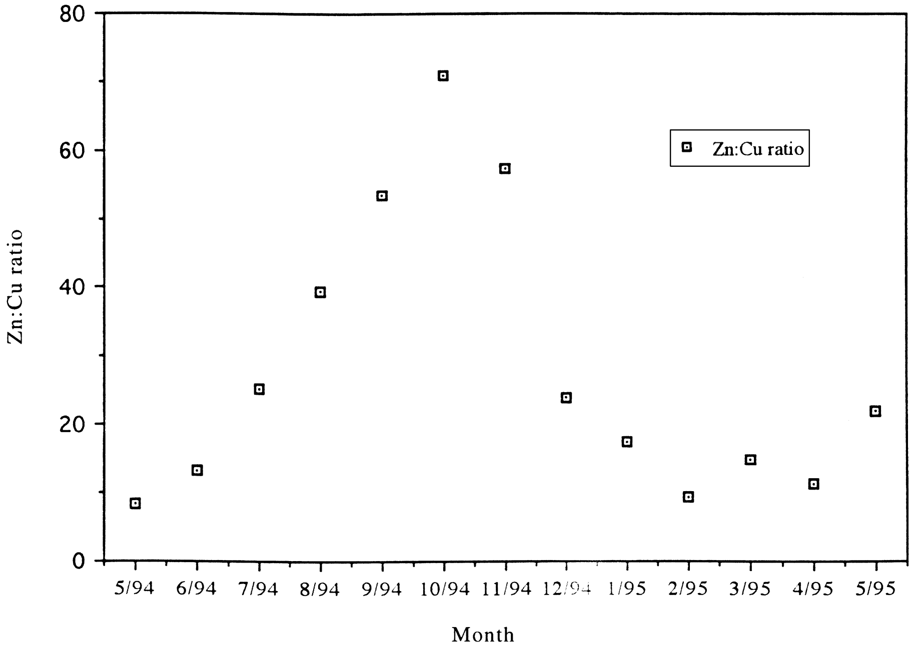

Fig. 3. The variation in the Zn:Cu ratio in the Deep Adit showing the increase during the dry periods and rapid decline once the wet season becomes established. Values are mean monthly ratios.

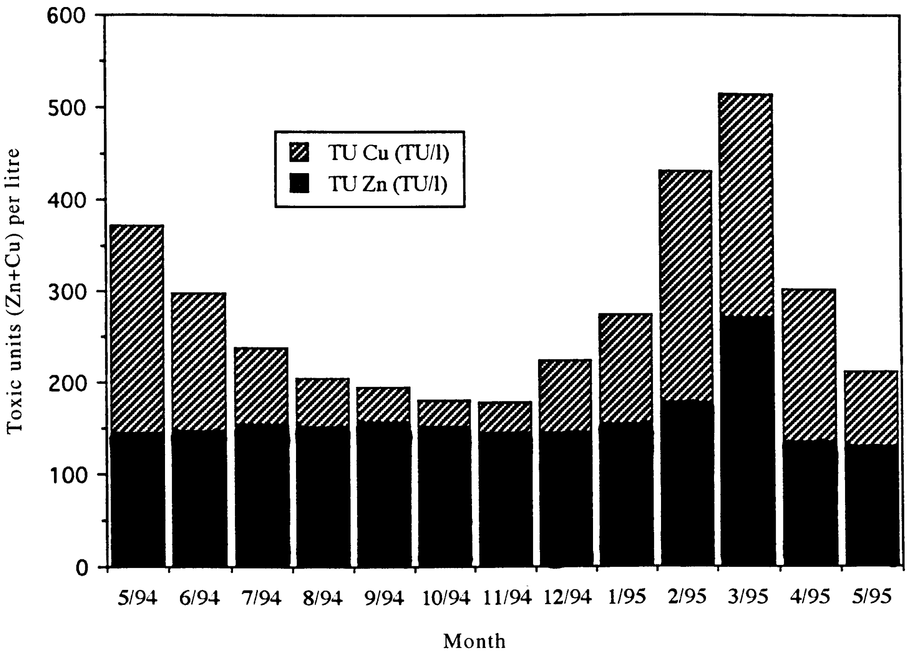

Fig. 4. Total toxicity (as toxicity units per litre) in adit discharge caused by Zn and Cu ions.

The formation and dissolution of these minerals can have a significant effect on the characteristics of AMD discharged from adits, responding to seasonal cycles of wetting and drying. In Avoca the effect appears related to available surface area for sulphate formation.

Toxicity of AMD

In comparison to the other cations present only Cu and Zn have a significant effect on water toxicity within the receiving water. The variation of the Cu concentration in relation to Zn concentration recorded in the adit discharges has profound effects on the overall toxicity of AMD discharged into the river. The toxicity of the AMD was calculated using Atlantic Salmon (*Salmo salar*), an indigenous fish species to the Avonmore-Avoca catchment, to calculate the 96-h LC_{50} values for each metal. Static renewal bioassays indicated that Cu (96-h LC_{50} of 0.036 mg/l) was 13 times more toxic than Zn (96-h LC_{50} of 0.479 mg/l) (Sullivan and Gray, 1998). The survival time using a mixture of Cu and Zn (in equitoxic proportions) was reduced and produced a 96-h LC_{50} of 0.933 toxic units, indicating that the metals strongly effect each other's lethal action in the restricted sense of the rapidity of death of the fish. The River Avoca is extremely soft (hardness 15 mg $CaCO_3$/l) and so the calculated toxicity threshold concentrations for Cu and Zn are low. It can be seen from Fig. 4 that while the toxicity exerted by the Zn remains constant at about 150 toxicity units per litre (TU/l), the toxicity exerted by the copper varies from <50 to >250 TU/l. The variation in total toxicity can be related to the Zn:Cu ratio (Fig. 5). When earlier, less intensively sampled, data is re-examined then a similar seasonal pattern of toxicity emerges. Using just zinc and copper for toxicity assessment purposes, as for most sites all other metals were at normal back ground concentrations and so were considered unimportant in effluent management terms, then the total toxicity of the leachate varied from 177 toxicity units per litre (TU/l) in the late summer to 431 TU/l in late winter due to the variation in Cu concentration alone.

The overall adit flow increased by up to 500% over the same period, while total toxicity (Cu + Zn) discharged from the two adits varied from 2.86×10^8 to 2.10×10^9 TU/d; so that during high flow periods the impact of the adits is 7.4 times greater than at low flow periods. This does not include the effect of surface runoff which is significantly more acidic and contains higher concentrations of most metals than the leachate discharged from the adits, as well as a high solids content comprising of fines from the spoil heaps. This results in higher toxicity concentrations being frequently recorded in the river during the winter period even though maximum dilution is available.

The toxicity of each discharge can be calculated using the simple models developed from the Figs 6 and 7. To calculate the toxicity emanating from the Deep Adit (β^{DA}) then

$$\beta^{DA} = -228.6 + 424.3 \log f^{\,DA} \text{ TU/l},$$

where f^{DA} is the discharge rate from the Deep Adit (l/s).The toxicity emanating from the Ballymurtagh Adit (β^{BA}) is

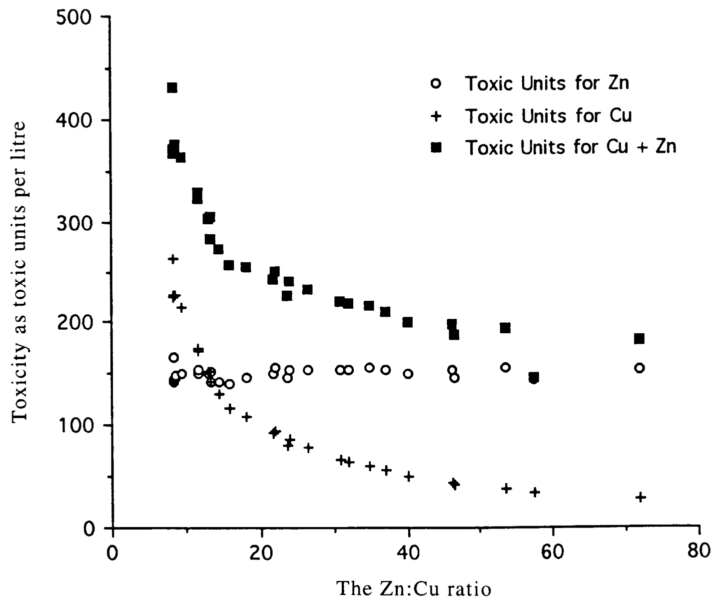

Fig. 5. Variation in toxicity (as toxicity units per litre) with the Zn:Cu ratio.

$$\beta^{BA} = (32.9 + 2.11 f^{\,BA}) + (16.4 + 3.23 f^{\,BA} - 6.26e - 2 f^{\,BA^2})\ \mathrm{TU/l},$$

where f^{BA} is the discharge rate from the Ballymurtagh Adit (l/s).

The total toxicity from the two main adits is ($\beta^{DA} + \beta^{BA}$), while the total toxicity of AMD discharged into the river is $((\beta^{DA} + \beta^{BA})/\text{Ø})$. Where Ø is the contribution of two main adits to total AMD discharge to river (Table 3).

Field measurements have shown that the rate of storm water is approximately equal to the adit discharge rate and so can be taken as ($f^{DA} + f^{BA}$). The annual mean total toxicity (Cu + Zn) of the surface runoff (β^{SR}) has been measured as 525 TU/l, which should be taken for modelling purposes. During a typical prolonged period of heavy rain resulting in

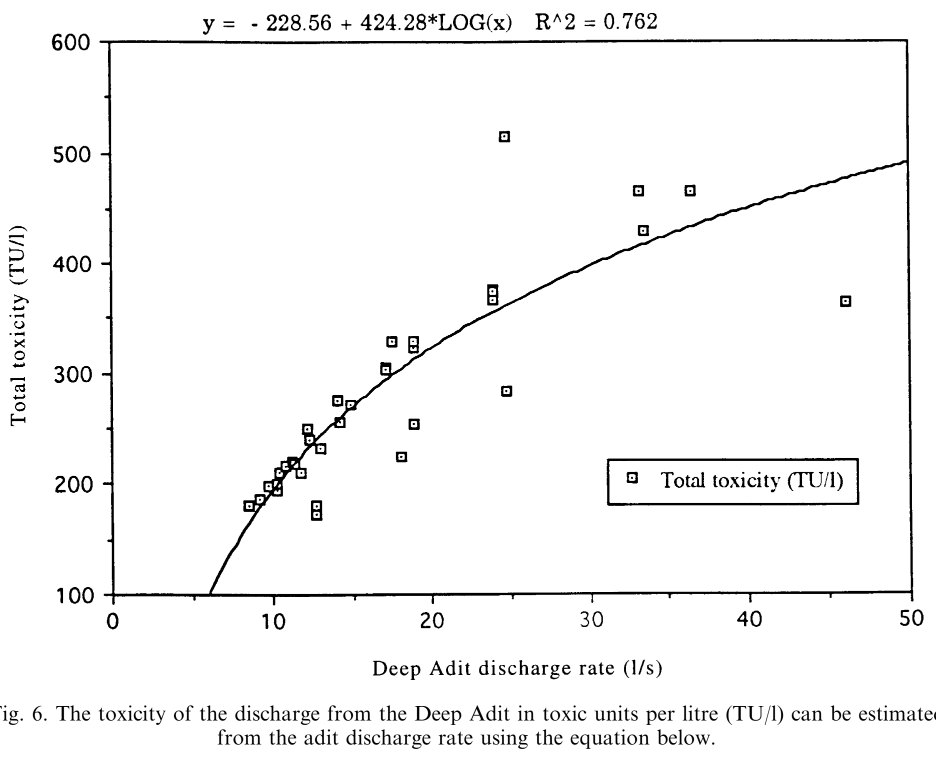

Fig. 6. The toxicity of the discharge from the Deep Adit in toxic units per litre (TU/l) can be estimated from the adit discharge rate using the equation below.

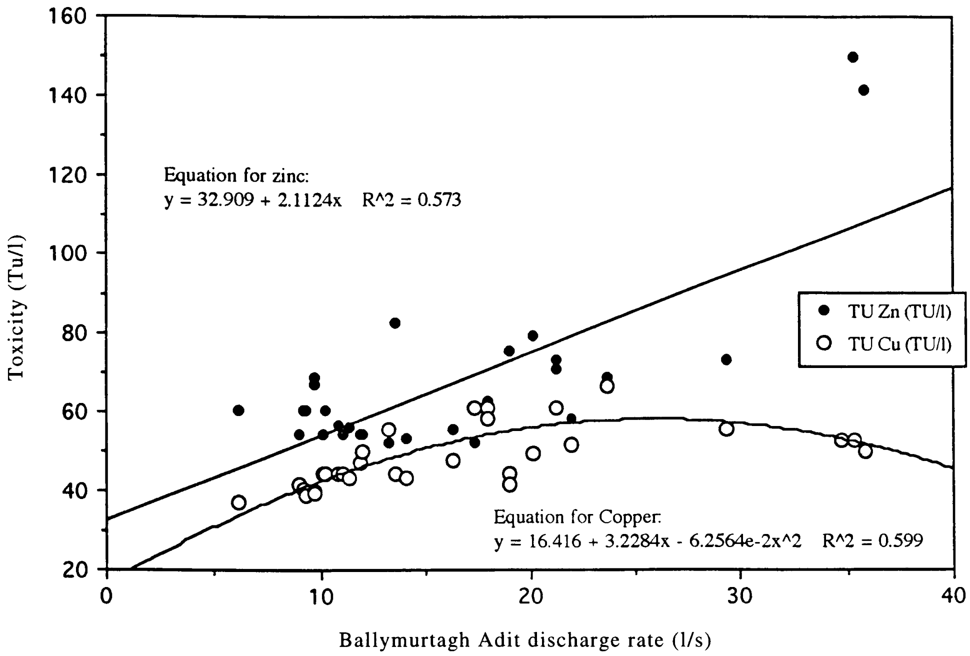

Fig. 7. The toxicity of Cu and Zn must be calculated separately for the Ballymurtagh Adit as the Zn:Cu ratio is not directly related to discharge rate due to the different hydrological nature of the western mining zone.

surface runoff the toxicity will vary from 86 to 1748 TU/l, the variation due to dilution and flushing of stored acidity from spoil. Despite continuous dilution by clean water from upstream, the first post-mine sampling site (site 2) has a mean toxicity of 3 toxicity units, with the mean Cu and Zn concentrations 12.0 and 21.3 times higher than that permitted by the Freshwater Fish Directive (European Commission, 1978). Ten km downstream, the toxicity imposed by the mine on the river is reduced to less than one toxic unit (Table 8).

In the River Avoca, dilution is often poor and ephemeral due to the discharge characteristics of the catchment, making the river extremely spatey. However, from the current study it is apparent that even at higher flow rates it is unlikely that toxicity levels will be low enough for sufficient periods to permit migration of fish. Salmon tend to mass off shore and attempt to swim up river during a spate. During the early period of these spates there is a very high sediment load in the river, so it is probable that the salmon only attempt their migration

Table 8. Summary of the river water quality upstream and downstream of Avoca mines

Site	1		2		3		4		5		6	
Parameter	mean	S.D.	mean	S.D.	mean	S.D.	mean	S.D.	mean	S.D.	mean	S.D.
n	49	49	31	31	31	31						
pH	6.8	0.50	5.8	0.6	6.0	0.6	6.4	0.31	8.4	1.24	8.23	0.96
Al mg/l	0.25	0.33	0.83	1.18	0.2	0.1	0.15	0.09	0.30	0.15	0.33	0.21
As μg/l	0	0	0.03	0.18	0	0	0	0	0	0	0	0
Cd μg/l	0	0	0.61	4.3	0.45	2.1	0	0	0	0	0	0
Cu mg/l	0.001	0.005	0.06	0.07	0.02	0.02	0.004	0.006	0.003	0.009	0.005	0.01
Fe mg/l	0.15	0.20	1.4	1.7	0.63	0.30	0.32	0.16	0.25	0.13	0.23	0.17
Zn mg/l	0.06	0.06	0.64	0.40	0.44	0.22	0.33	0.12	0.17	0.11	0.17	0.11
SO_4 mg/l	6.5	3.2	28	47	25	16	21	6.9	19	10	23	12
Cond. μS/cm	78	24	107	24	111	28	114	16	163	55	513	829
AMDI	96.0	4.6	81.7	6.3	85.9	6.2	90.3	2.7	92.3	2.2	92.0	2.9
Toxicity (Zn only) TU/l	0.13	0.13	1.34	0.84	0.92	0.46	0.69	0.25	0.36	0.23	0.36	0.23
Toxicity (Cu only) TU/l	0.03	0.14	1.67	1.94	0.56	0.56	0.11	0.17	0.08	0.25	0.14	0.28
Toxicity (Zn and Cu) TU/l	0.16	0.27	3.01	2.78	1.48	1.02	0.80	0.42	0.44	0.48	0.50	0.51

Table 9. Mean number of taxa (S), individual invertebrates (N) and "species deficit" (spd) recorded in the Avoca River annually from 1990 to 1993

Site	1	2		4		5	
Year	S (N)	S (N)	spd (%)	S (N)	spd (%)	S (N)	spd (%)
1990	34 (120)	1 (54)	97.0	0 (0)	100	2 (25)	94.1
1991	30 (131)	1 (23)	96.7	0 (0)	100	1 (30)	96.7
1992	31 (103)	1 (39)	96.7	2 (5)	93.5	4 (69)	87.1

once the water begins to clarify (post-advance) and the river discharge rate is stabilised or on the decline. Maximum toxicity in the river occurs prior to the peak of the spate due to surface runoff and the period when the river discharge rate is rapidly declining and returned to a lower stabilised rate. It is during these critical periods for fish migration that the river is at its most toxic, leaving fish with a very small opportunity during the spate-time interval to successfully pass the mining area up into the unpolluted catchment.

Impact on the biota

Acid mine drainage and the discharge of ammonia from a fertiliser factory in the lower reaches are the two major pollutants of the Avoca River.

An electro-fishing survey indicated that the indigenous brown trout (*Salmo trutta*) of the upper catchment were generally small, slow-growing fish, in good condition with stock densities ranging from $0.16/m^2$ to $0.54/m^2$. The fish were totally eliminated from the lower reaches of the Avoca River below the mines (Sullivan and Gray, 1992). Juvenile eels (*Anguilla anguilla*) have since been recorded at sites 4 and 6 during 1996 and 1997.

As the river flows through the mining area, there is a distinct decrease in water quality (Table 8) and a significant deterioration of the fauna composition of the river (Table 9). Routine biological monitoring of the River Avoca downstream of the input of acid mine drainage (AMD) consistently shows a significant impact on both diversity and productivity (Reynolds, 1986; Byrne and Gray, 1995a). Major habitat loss occurs as ferric precipitate blankets the substrate, destroying the natural habitat and clogging the interstices (Gray, 1996a,b). At all habitat types there was a clear decrease in the number of taxa and faunal abundance, with low levels in the mixing zone, and a slow improvement downstream but not full recovery. In general, there was no taxa unique to sites impacted by AMD, however, the percentage representation of *Chironomidae* showed an increase in response to AMD rising to almost 100% at site 2 and then decreased. As noted above the response of the faunal community to AMD was a significant drop in the number of taxa accompanied by a sharp drop in the abundance of taxa remaining (Byrne and Gray, 1995a). The Shannon–Wiener diversity index (H') showed a mean annual reduction from 1.385 upstream from the mines at site 1 to just 0.052 below the mixing zone at site 2. The effects of AMD were still evident 10 km downstream at site 4 with $<10\%$ of the species above the mines represented, even after 100% dilution by an unpolluted tributary (Aughrim River) (Table 9). At this site the benthic community is maintained primarily by dipteran (78.5%) and uncased trichopteran (11.3%) larvae. Artificial media (stone and plastic) were used to examine the recolonization potential by invertebrates downstream from the mines. They proved to be equally as efficient as the natural substrate in discriminating between the extent and impact of the contamination at the stations located downstream from the mines. Chandlers Biotic Index dropped from 587 at site 1 to 17 at site 2 using plastic media while a similar reduction was recorded (724 to 71) using stone media (Sullivan, 1995).

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 (Table 8). The mean pH of the river fell from site 1 (6.8) to 5.8 at site 2. It recovers slowly to site 3 but the higher natural buffering capacity of the Aughrim river raises the mean pH to 6.4. The fertilizer factory through the discharge of ammonia contaminated process and surface waters raises the pH to 8.4 which causes a slight increase in aluminium but a decrease in zinc concentrations due to their relative solubilities. Apart from Cu, Fe and Zn, concentrations of metals have returned to background levels by site 3, although Cd was still measurable (detection limit 0.001 mg/l) at site 3. The overall impact and recovery of the river is summarized by the AMDI (Table 8). The toxicity of the river arising from Zn and Cu show that the background toxicity of 0.16 TU/l rises to a mean of 3.01 at site 2 and remains above 1.0 TU/l until dilution by the Aughrim River. The effect of the ammonia discharge is to significantly reduce the metal toxicity from a mean of 0.80 TU/l to 0.44 TU/l by reducing the solubility of Zn in particular. The effect of ammonia at such a high pH has a significant toxicity of its own. Mean concentrations of total free ammonia were 19.0 mg/l, some 25 times greater than the mandatory (I) value in the EU Freshwater Fish Directive (European Commission, 1978). A clearly defined incipient LC_{50} of 0.019 mg unionised ammonia/l was obtained after only a short exposure period. The combined effect of Zn, Cu and ammonia in equitoxic proportions was found to be 0.952

toxic units, i.e. just slightly more than additive. At this point, however, a fertiliser factory discharging ammonia waste water increases the overall river toxicity. Below the factory at site 5 the toxicity caused by the metals is only 0.5 TU/l while the toxicity of the ammonia is in excess of 130 toxic units. The use of toxicity assessments allows direct comparison of various pollutional inputs into the river, allowing pollution control strategies to be prioritised in terms of impact. This is discussed elsewhere (Sullivan and Gray, 1998).

Field toxicity tests carried out in the river by Byrne and Gray (1995b) indicated that only the water in the mixing zone was toxic to the test organisms used (*Gammarus duebeni*, *Ephemerella ignita* and *Baetis rhodani*). The routine biological surveillance has shown the impact to be on a more extensive scale with the entire river below the mines severely damaged. Byrne and Gray (1995b) have suggested that factors other than direct water toxicity are responsible for the elimination of species in the lower Avoca, although the water quality may result in long term chronic toxicity.

CONCLUSIONS

During the 12-month period from May 1994, some 62.2 tonnes (t) of Zn, 159.1 t of Fe, 3.9 t of Cu and 0.16 t of Cd were discharged from the two main adits draining the mines at Avoca. Mass balance studies using sulphate indicates that the adits represent approximately 70% of the discharge from the mines overall, the remainder coming from the other sources including minor contaminated streams, bank infiltration, and as groundwater discharge. The annual discharge of metals as AMD is estimated as 90 t of Zn, 230 t of Fe, 5 t of Cu, and 0.25 t of Cd. The Deep Adit is the main source of Zn, Cu and Cd, while the Ballymurtagh Adit is the major source of Fe. During the year it is estimated that a further 20% contamination (excluding the particulate material) comes from storm water bringing the total annual metal burden entering the river from the mines at Avoca to 108 t of Zn, 276 t of Fe, 6 t of Cu and 0.3 t of Cd.

Intensive sampling of acid mine drainage from adits draining the abandoned copper and sulphur mines at Avoca, has revealed a seasonal variation in the Zn:Cu ratio. The most likely explanation for this is secondary sulphate mineral formation due to wetting and drying cycles within the mine workings and surface spoil heaps, leading to an annual cycle of formation and dissolution causing a predictable fluctuation in the Cu concentration only. In order to confirm this hypothesis a detailed analysis of the minerals formed within the mines is required. Unfortunately, due to the instability of the underground workings this is currently not possible. The variation in the Zn:Cu ratio leads to extreme variations in the toxicity of drainage, and linked with increased adit flows during wetter months, can result in higher river toxicity, even at high river discharge rates.

The biota of the river is severely damaged by AMD. With the exception of small eels caught 10 km downstream of the mines (site 4) and in the estuary (site 6), all fish are absent from the impacted river in what is an otherwise salmonid catchment with excellent water quality. Estimates of toxicity derived from AMD show that there is a significant increase ($P < 0.001$) above background levels for its entire 15.4 km length, with mean toxicity > 1 TU/l at all impacted sites upstream of the confluence with the River Aughrim. Macro-invertebrates are able to survive outside the mixing zone for short periods, and tolerant species are found at some downstream sites. The loss of the riffle, glide and pool habitats by orche formation and the elimination of macrophytes severely reduces habitat diversity. This, linked to chronic toxicity leading to physiological and behavioural problems, may be the major factor in the reduction of species diversity and faunal abundance.

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