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PROCEDURE FOR THE ESTIMATION OF THE IMPACT OF ACID MINE DRAINAGE TO SURFACE WATERS AND ITS MANAGEMENT

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EXECUTIVE SUMMARY

The rehabilitation of a mine producing acid mine drainage (AMD) involves four discrete steps. These are site characterization, the development of an AMD water quality management protocol, a remediation strategy and finally an implementation strategy. This report presents a water quality management protocol for AMD impacted rivers from which AMD discharge standards can be derived. Prediction of AMD contamination within the Avoca River is also examined.

ABBREVIATIONS

Ω	Toxicity after mixing in the river in TU/l
β^{DA}	Toxicity of discharge from Deep Adit in TU/l
β^{BA}	Toxicity of discharge from Ballymurtagh Adit in TU/l
β^{R}	Toxicity of unpolluted river in TU/l
β^{SR}	Toxicity of surface runoff from mines in TU/l
f^{DA}	Discharge rate from Deep Adit (l/s)
f^{BA}	Discharge rate from Ballymurtagh Adit (l/s)
f^{R}	Discharge rate of the river (l/s)
$\emptyset$	Contribution of two main adits to total AMD discharge to river

INTRODUCTION

The ores at the abandoned copper and sulphur mines at Avoca (Fig. 1), southeast 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 at such sites are Cd, Cu and Zn.

A mine rehabilitation strategy involves four discrete, yet inter-related steps. These are:

Step 1	Site characterization
Step 2	Development of an acid mine drainage (AMD) water quality management protocol which should be integrated into the existing catchment water quality management plan
Step 3	A remediation strategy
Step 4	An implementation strategy

This report looks at the procedures for developing an AMD water quality management protocol, the discharges from the mines, and the procedure used to predict the impact of AMD in the Avoca River.

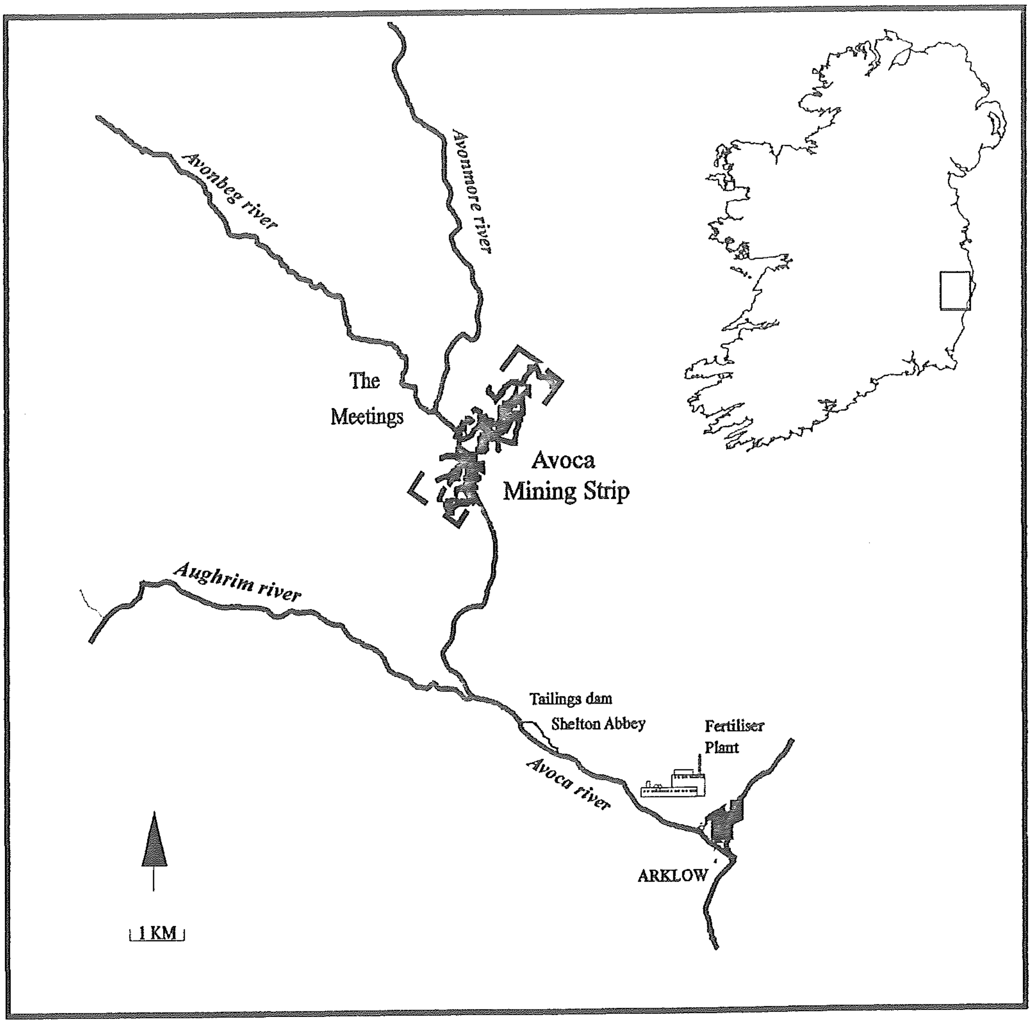


Fig. 1. The Avoca-Avonmore catchment area showing the location of the mining strip.

ACID MINE DRAINAGE WATER QUALITY MANAGEMENT PROTOCOL

The development of the AMD water quality management protocol is outlined in the flow diagram below (Fig. 2), and explained fully in the text. It should be carried out after site characterization (Gray and Doyle, 1994), but closely in conjunction with it. There are five stages:

Stage I establishes water quality criteria and standards for the river:

1. Identify beneficial uses of the river, both present and those required in future, to be protected or facilitated.

2. Compile all existing water quality data on the river including its tributaries.

3. Examine the data collected during step 2, and determine the characteristic elements which are important in relation to AMD (e.g. Alkalinity-acidity, pH, Cu, Zn, Cd, Fe, SO_4 etc.) at selected control sections along main channel and major tributaries.

4. Define required water quality criteria to achieve water quality objectives as defined in step 1.

5. Examine international, national and local factors including socio-economic and political. This will include facilitating international agreements (e.g. Paris Oslo conventions), funding opportunities, cost-benefit analysis of remediation etc.

6. Selection of specific water quality standards for receiving water according to step 4 with due reference to EU, national and other standards. Water quality standards may be different to normal EU standards due to the complexity and interactive nature of the AMD and its resulting impact on the receiving water.

Stage II calculates the natural assimilation capacity of AMD by the river:

7. A hydrometric survey is required of the catchment both upstream and downstream of AMD inputs to calculate river discharge rates.

8. Water quality surveys are required to establish uncontaminated (background) chemical, physical and biological quality. These should consider the water and sediment phases separately. Establishment of the buffering capacity and key AMD parameters, flora and fauna, and sediment characteristics (including metals, particle size, etc.) are required.

9. The theoretical assimilative capacity for AMD at various points in the river should then be calculated using SO_4 (Gray, 1995a).

Stage III assesses the impact of AMD on the river:

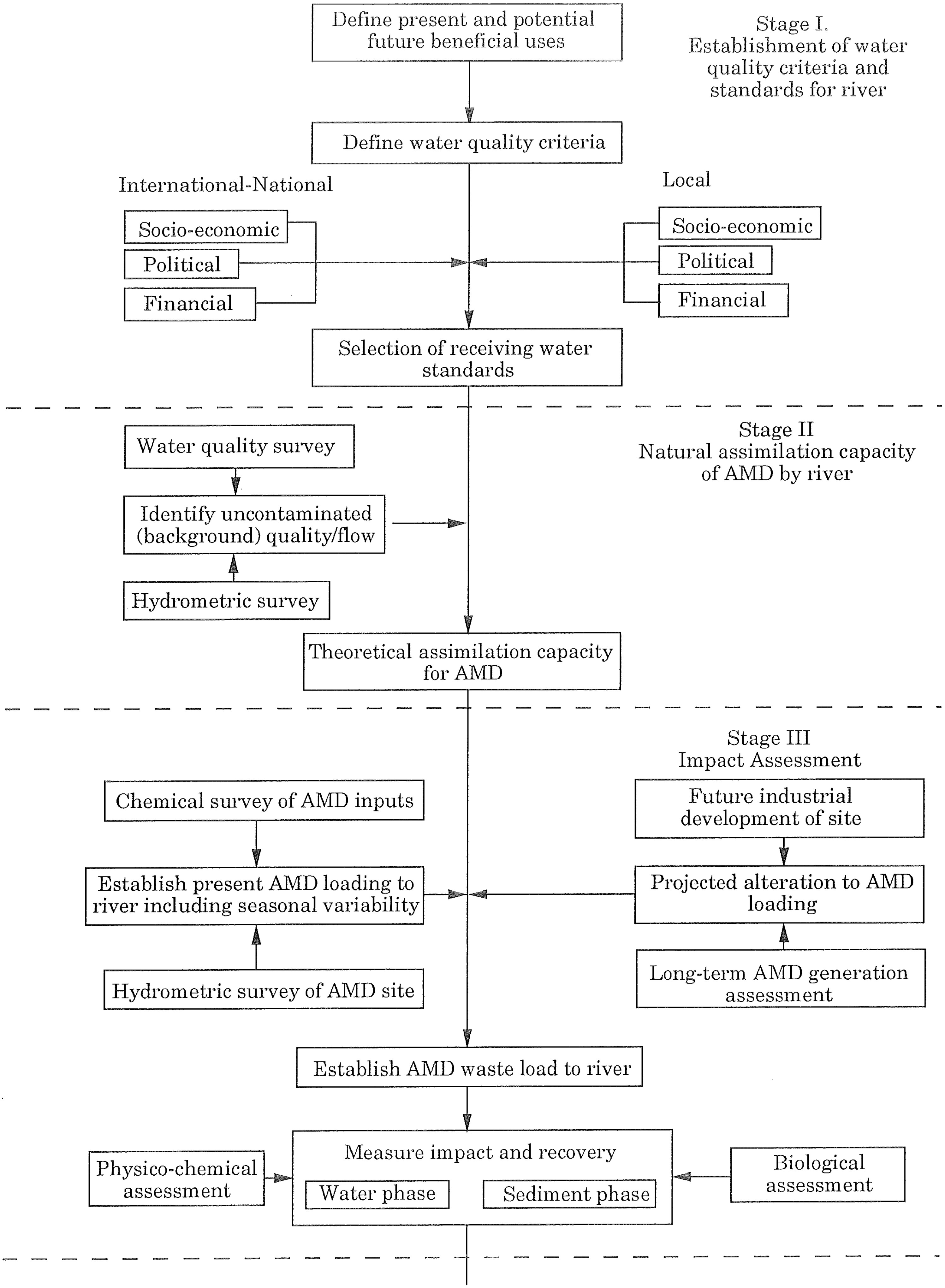
10. The present AMD loading to the river is calculated, including diurnal and seasonal variation, in conjunction with the characterisation study, by
    a) Hydrometric survey of AMD generating sites.
    b) Discharge points and rate of AMD discharges calculated.
    c) Chemical and physical analysis of AMD discharged at each adit.

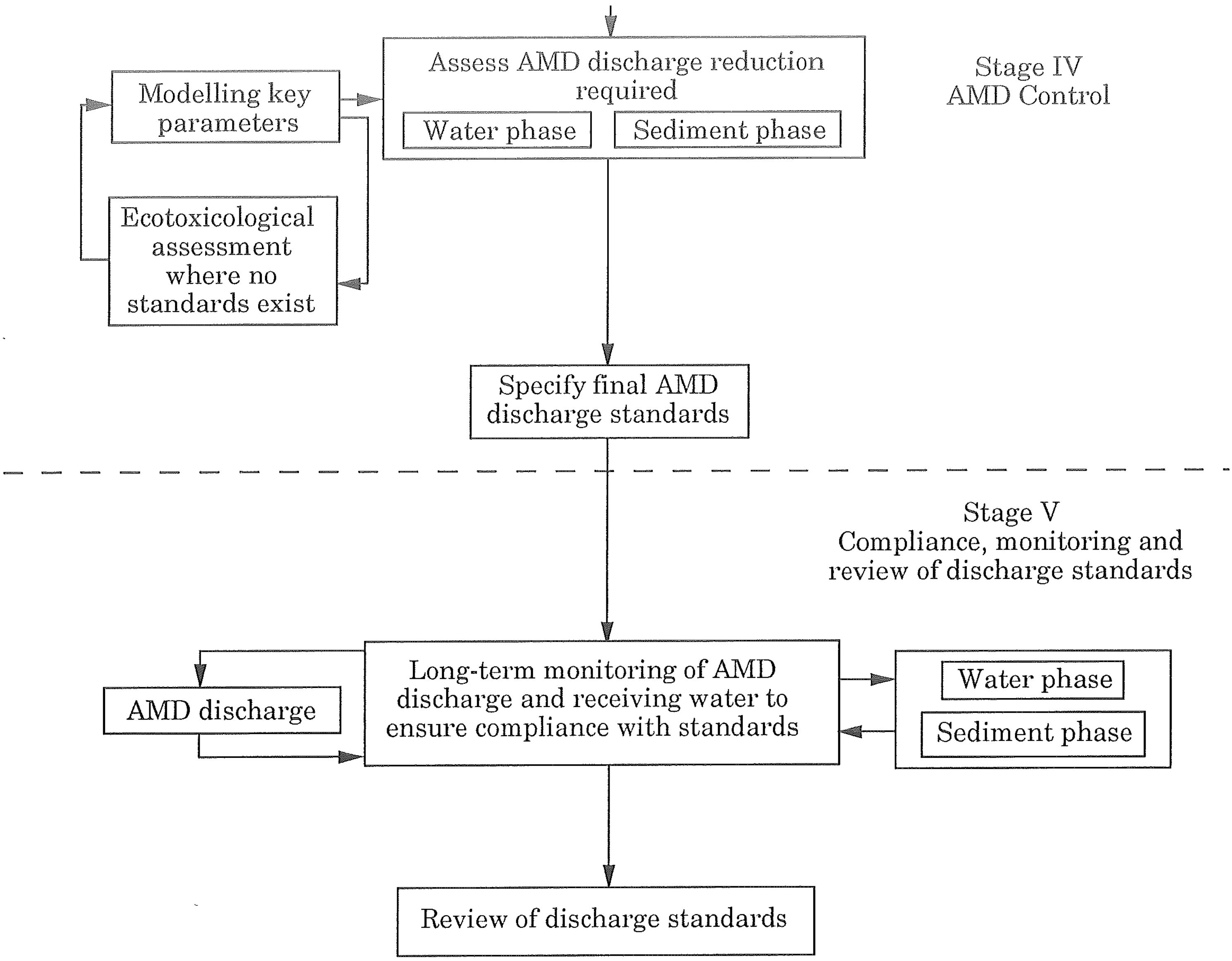
11. The projected AMD loading is estimated for the next 20 years by
    a) Examining future development of the site for mining or other uses that may alter current hydrological characterisation of site.
    b) Examining long term generation of AMD using current models.
    c) Estimation of effects of site remediation activities.

12. Using the information in steps 10 and 11 the AMD waste load to the river is calculated and projected over the next 20 years.

13. The actual impact on the river is assessed, including any recovery by a full chemical and biological assessment. The water and sediment phases are considered separately.

Fig. 2. AMD Water Quality Management Procedure




Assess AMD discharge reduction required
Water phase
Sediment phase
Stage IV
AMD Control
Modelling key parameters
Ecotoxicological assessment where no standards exist
Specify final AMD discharge standards
Stage V
Compliance, monitoring and review of discharge standards
AMD discharge
Long-term monitoring of AMD discharge and receiving water to ensure compliance with standards
Water phase
Sediment phase
Review of discharge standards

Stage IV sets AMD discharge consents:

14. The key AMD and river parameters are modelled, using assessment where no standards exist, to assess the required reduction of AMD discharge to the river in order to achieve water quality objectives as identified at step 1.

15. Final AMD discharge standards can then be specified to achieve water quality objectives.

Stage V implements a monitoring programme and review procedure of the standards set:

16. A long term monitoring strategy is designed and implemented in order to ensure compliance with AMD discharge standards and to check that receiving water objectives are achieved. This is done for water and sediment phases.

17. Monitoring data is assessed in order to review AMD discharge standards. This may eventually lead to a revision of water quality objectives.

THE AVOCA RIVER

Discharges into river

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. There are secondary inputs of acid mine drainage (AMD) such as small contaminated streams, groundwater discharge and bank infiltration. The rate of discharge from the adits follows a seasonal cycle being high in the winter and spring, declining through summer to reach lowest flows in autumn but rising again in the winter. The discharge rate in the Deep Adit varies from 8.51 to 42.6 l/s compared to 6.1 to 43.4 l/s in the Ballymurtagh Adit. This represents a total discharge rate for the two adits of between 1266 - 7430 m^3/d. The discharge rates from the two main adits are significantly correlated ($p<0.001$), with no significant difference between discharge rates ($p>0.05$), although the discharge rate in the Ballymurtagh Adit recovers more slowly in winter than the Deep Adit. Significant weights of cations were discharged from the two adits, ranging from 169-1738 kg/d for Fe, 69-535 kg/d for Zn, and 1.5-35.5 kg/d for Cu, with the Deep Adit contributing on average 40.4, 70.4 and 66.7% of each metal respectively over the period of May 1994 to May 1995.

During a 13 month sampling period from May 1994 to June 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 results in a predictable fluctuation in the Zn:Cu ratio (Fig. 3). A similar phenomenon, although much less well defined, was also identified in the Ballymurtagh Adit (Fig. 4). However, in the Ballymurtagh Adit there is a more definite variation in Zn concentration (Fig. 5), being closely correlated ($P<0.001$) with Fe (Fig. 6). There is no correlation between Cu and Fe or Zn and Cu in this adit.

The variation in the Zn:Cu ratio in the Deep Adit corresponds closely to the height of the water table within the mine, being correlated to adit flow rate (Fig. 7), which is not the case with the Ballymurtagh Adit (Fig. 8). The ratio is high during low water table periods and *vice versa*. This variation in the Zn:Cu ratio corresponds closely to seasonal variation in expected rainfall, with highest Zn:Cu ratios recorded towards the end of the dry season. The Zn:Cu ratio reaches a maximum by October in the Deep Adit, but some 2 months later in the Ballymurtagh Adit.

The reason for this variation in the Zn:Cu ratio appears to be due to secondary sulphate mineral formation within the mine workings, being 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 many of which were never backfilled. Among the more important secondary sulphate minerals formed are chalcanthite ($CuSO_4.5H_2O$) and melanterite ($(Fe^{II},Zn,Cu)SO_4.7H_2O$). Both minerals may be major contributors to this phenomenon. Melanterite is of

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.

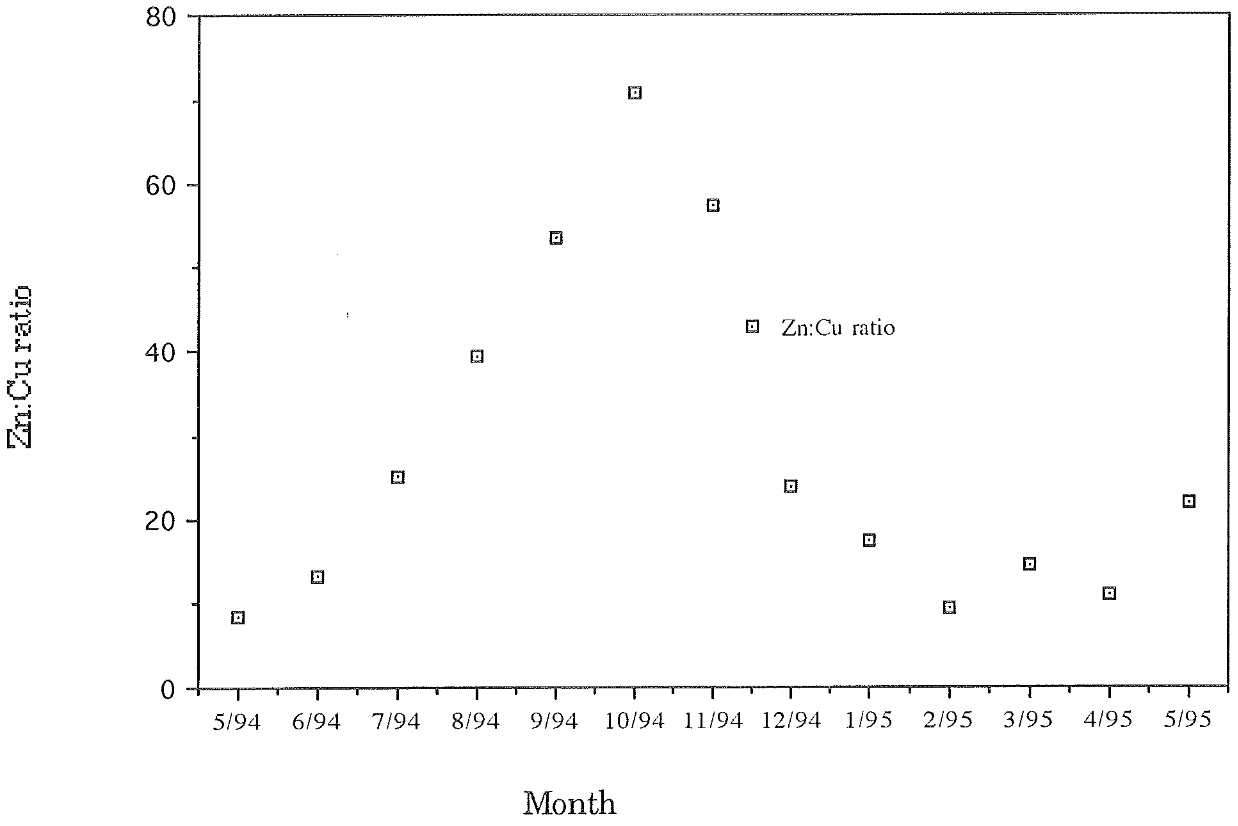


Fig. 4. The variation in the Zn:Cu ratio in the Ballymurtagh Adit showing a similar trend to the Deep Adit, although the ratio is reduced and variations later due to hydrological factors.

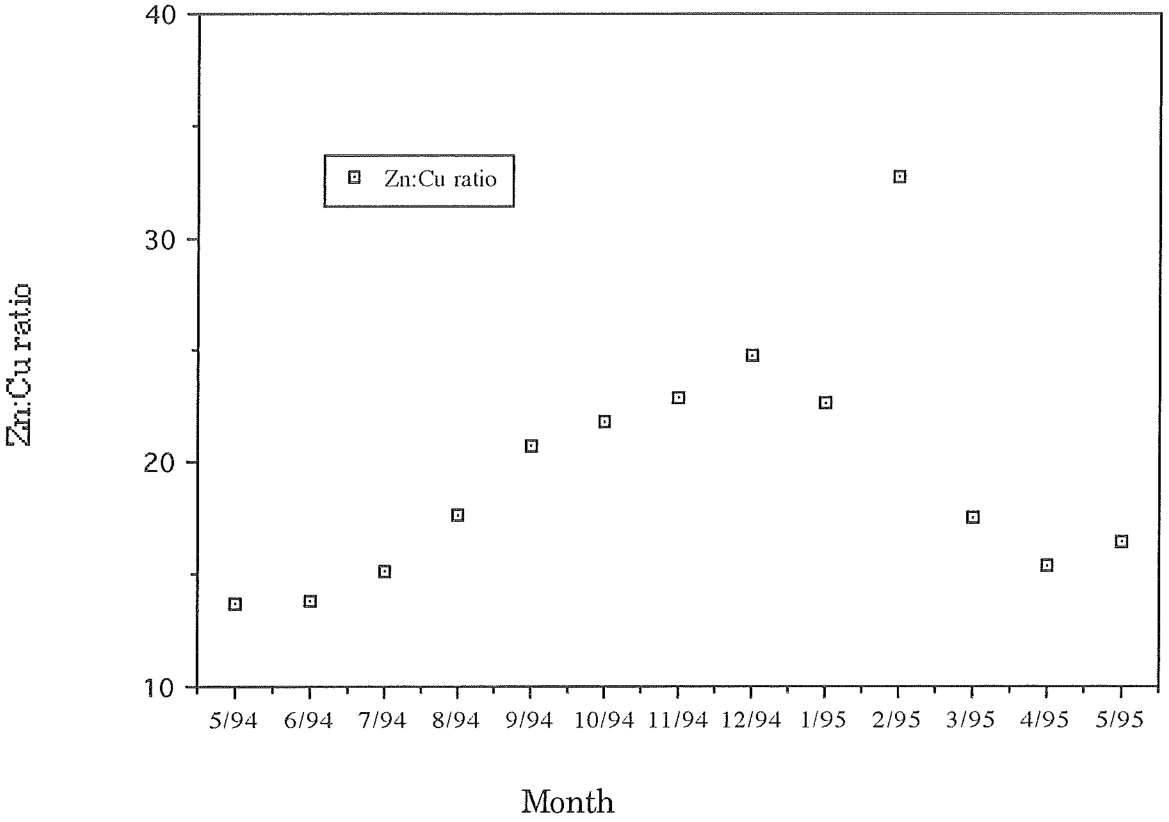


Fig. 5. Total toxicity in Ballymurtagh Adit discharge to river caused by Zn and Cu. Valus are monthly means in toxity units per litre (TU/l)

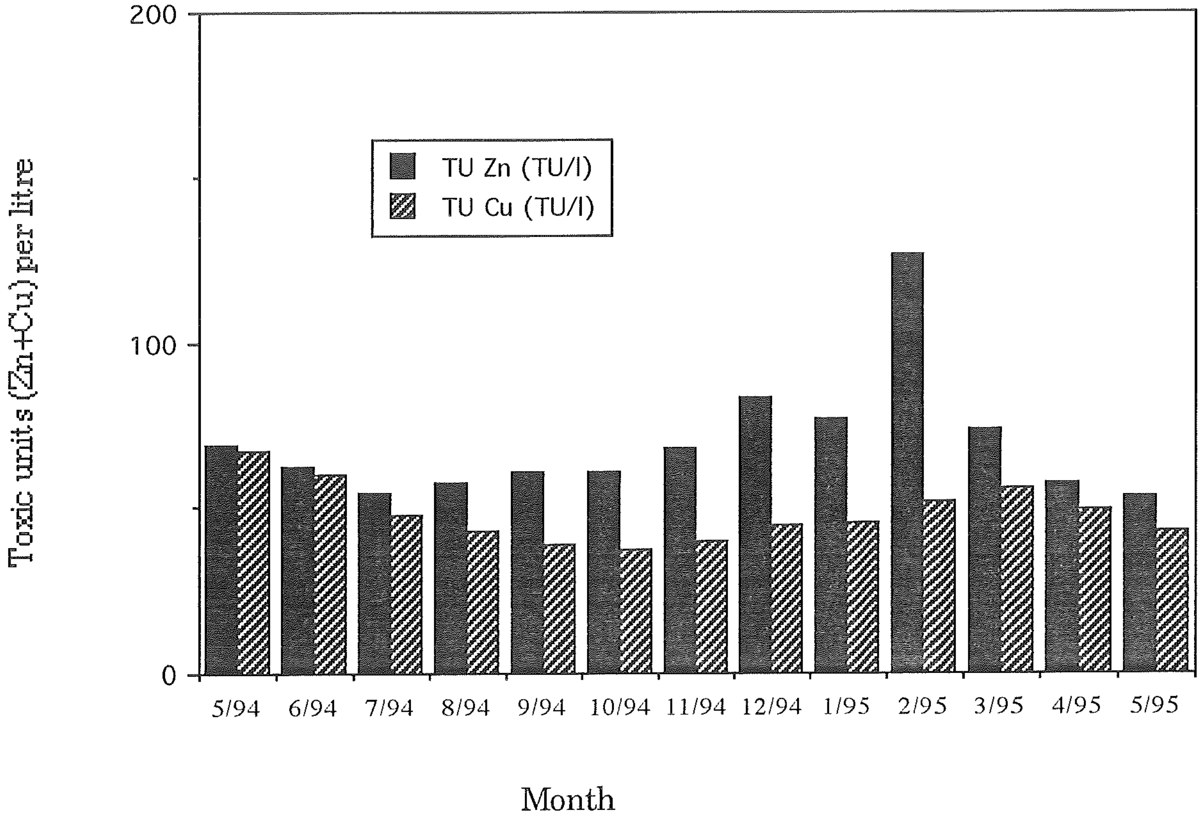


Fig. 6. Iron is closely correlated with zinc in the Ballymurtagh Adit discharge ($p<0.001$).

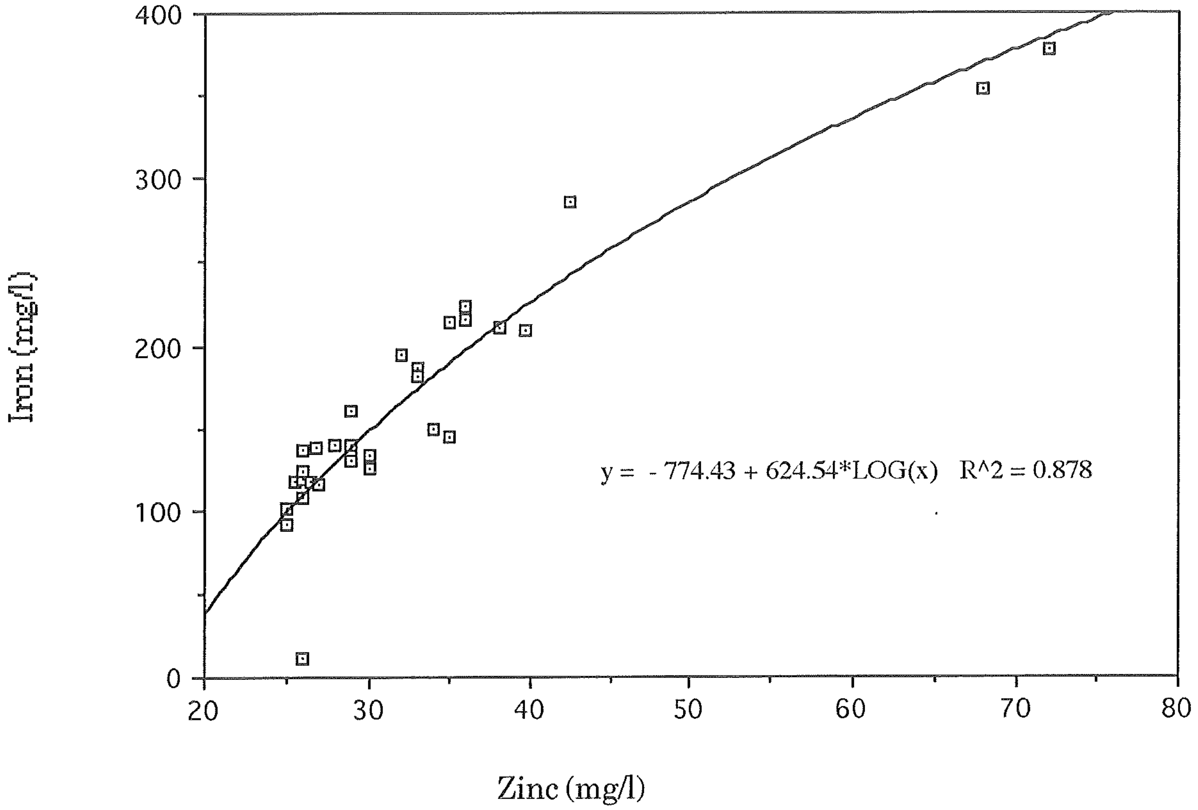


Fig. 7. Variation of the Zn:Cu ratio in the Deep Adit with discharge rate.

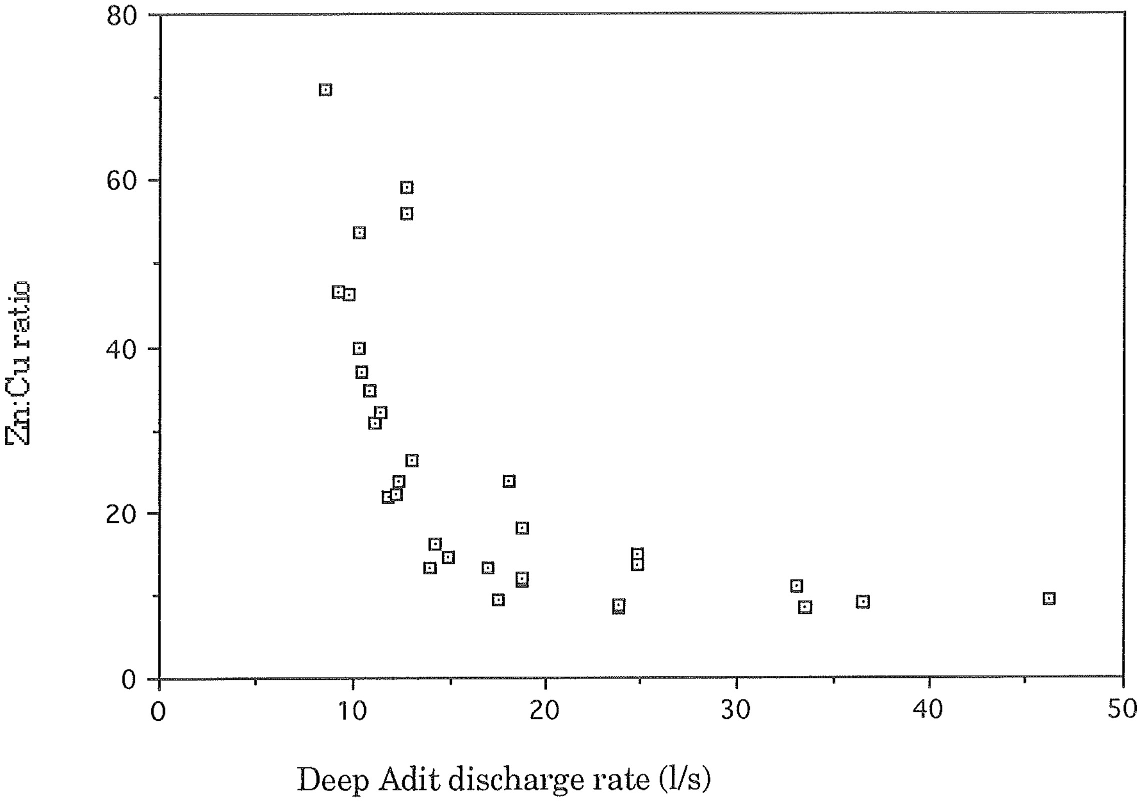
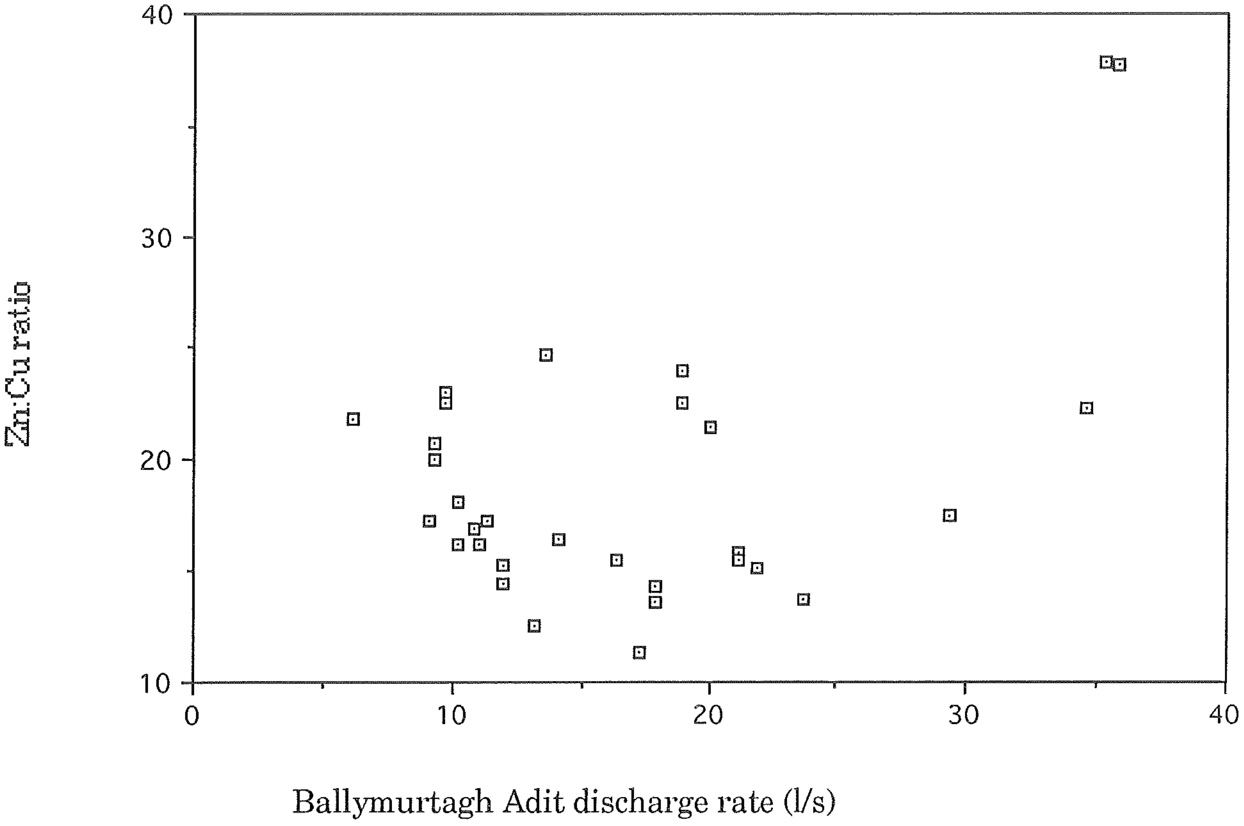


Fig. 8. Variation in Zn:Cu ratio in the Ballymurtagh Adit with discharge rate.



particular interest as it is commonly formed in iron rich AMD and has a propensity to incorporate Cu in preference to Zn. 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. The effect appears related to available surface area for sulphate formation.

Toxicity of discharges

The variation of Cu in relation to Zn in AMD at Avoca has profound effects on the toxicity of AMD discharged in to the river. The toxicity of the AMD can be calculated using the 96h LC_{50} values for each metal calculated using Atlantic Salmon. The River Avoca is extremely soft (hardness 15 mg $CaCO_3$/l) and so the calculated toxicity threshold concentrations for Cu and Zn are 0.036 and 0.479 mg/l respectively (Sullivan and Gray, 1995). While the toxicity exerted by Zn in the Deep Adit discharge remains constant over the period at about 150 toxicity units per litre (TU/l), the toxicity exerted by the copper varies from <50 to >250 TU/l (Fig. 9). This has been confirmed by re-examining earlier and less intensively sampled data when a similar seasonal pattern of toxicity emerges. Using just zinc and copper for toxicity assessment purposes, then the total toxicity of the leachate varies from 177 toxicity units per litre (TU/l) in the late autumn to 531 TU/l in spring, due to the variation in Cu concentration.

The total toxicity discharged from the adits shows clear seasonal variations (Figs. 10 and 11) being least toxic during the autumn (August to November) reaching maximum toxicity during spring (February to April). 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 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 during the winter period compared to summer low flow periods when minimum dilution is available.

Fig. 9. Total toxicity in Deep Adit discharge to river caused by Zn and Cu in toxicity units per litre (TU/l). Values are monthly means.

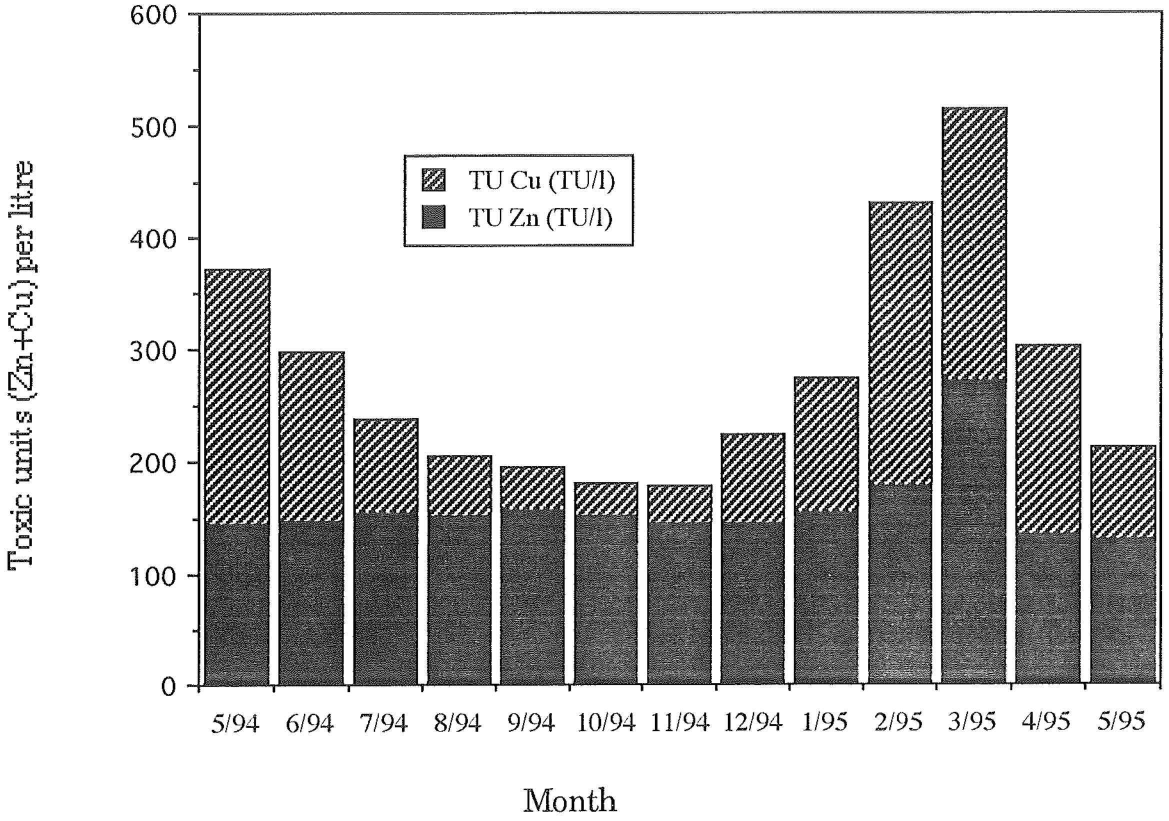


Fig. 10. Mean monthly variation in total toxicity discharged from Deep Adit.

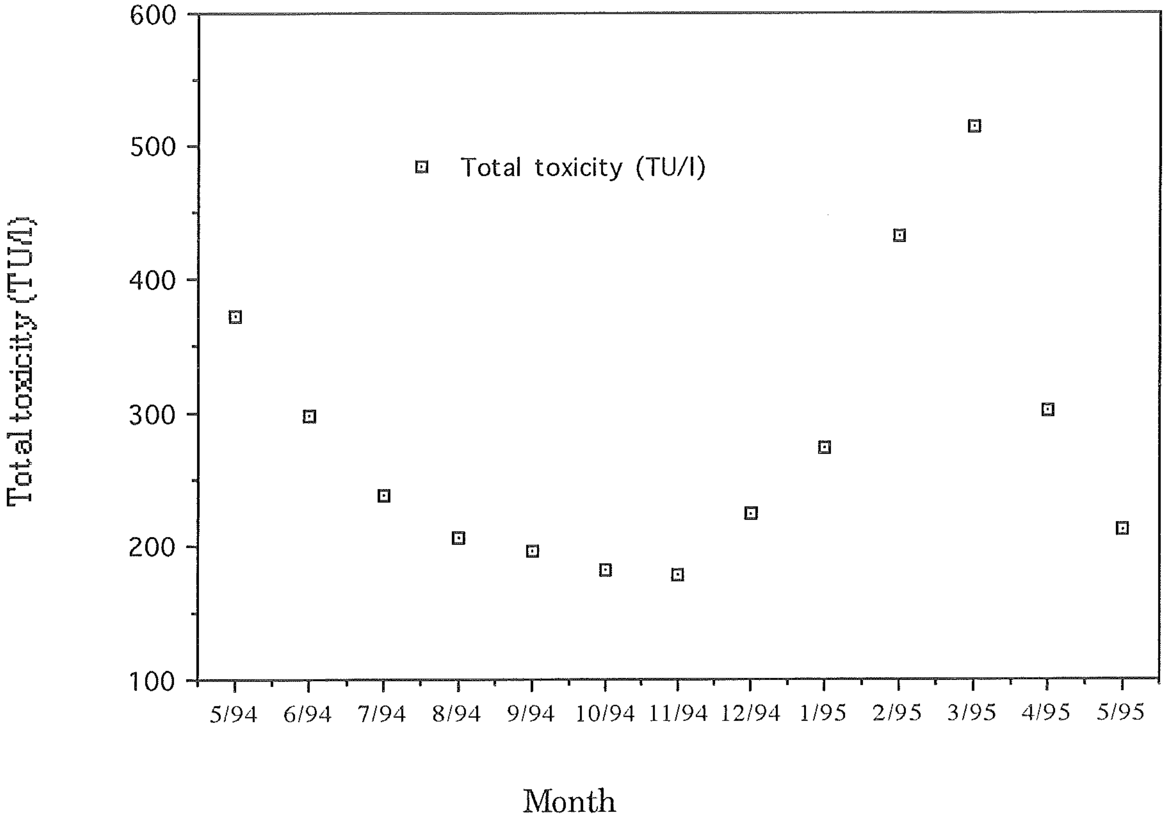
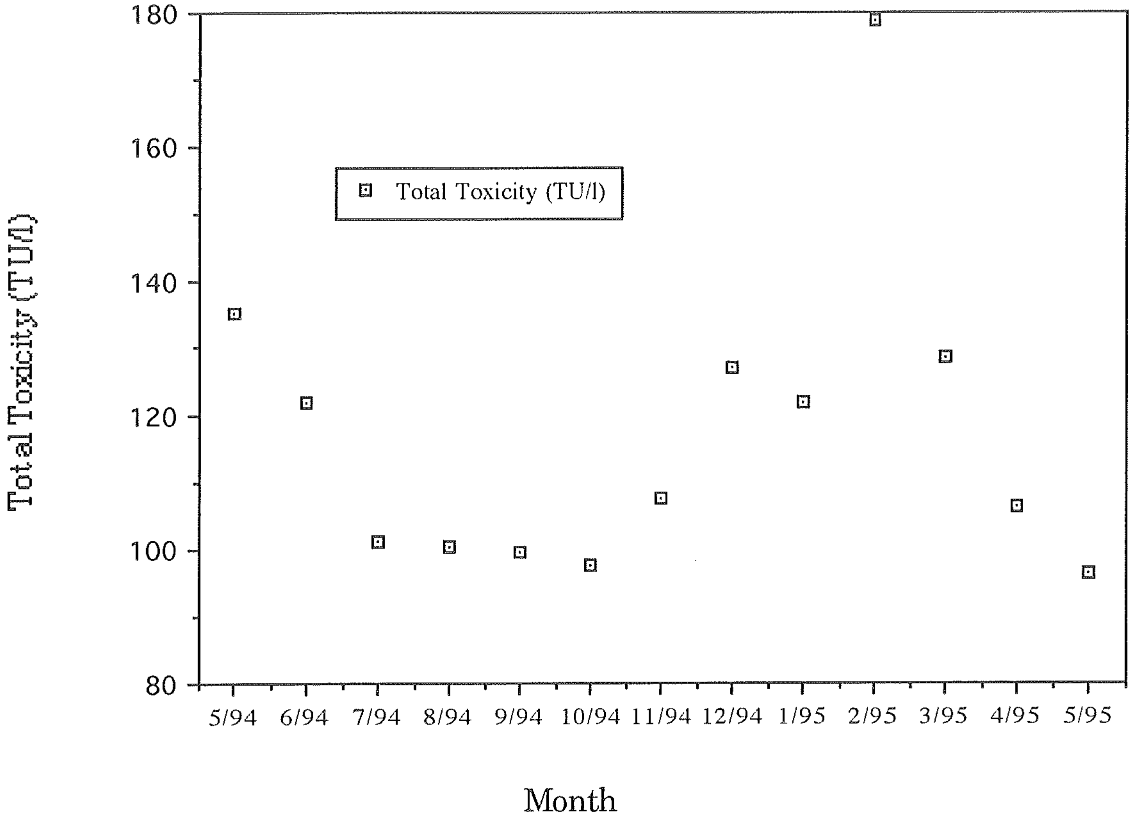


Fig. 11. Mean monthly variation in total toxicity discharged from Ballymurtagh Adit.



Fish migration

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 eliminates all biological life from the last 9 km stretch of the river to the sea, thus providing an effective barrier for salmonid migration to spawning areas upstream. 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 once the water begins to clarify 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 returning to a 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 series to successfully past the mining area up into the unpolluted catchment. The water quality objective for the section of the Avoca River which is polluted by AMD is *to permit salmonids to migrate upstream to colonize its major unpolluted tributaries* (i.e. the Aughrim, Avonmore and Avonbeg). In terms of water quality criteria, the impact on the substrate/sediment can be ignored for fish migration upstream even though the damage to the substrate causes total elimination of the flora and fauna. The primary objective is to protect water quality at specific times of the year when migration occurs sufficiently to permit migratory fish to swim freely and safely upstream through the affected zone to the unpolluted catchment. To this end fish toxicity units have been used to model the impact in the river rather than absolute metal concentrations.

Returning salmonids may take only 24 hours to swim from the estuary up the Avoca River past the mines into unpolluted waters, and less than 12 hours if moving from the Avoca River at Woodenbridge into the Aughrim sub-catchment (Fig. 1). Returning adults do not feed on their return journey upstream to breed, so the condition of the riverine substrate is unimportant. In contrast, as young salmon leave the catchment they pass relatively slowly downstream actively feeding as they make their way to the sea. In the Avoca River this emigration may take up to a week, or even longer, to complete. For fish leaving an AMD-impacted river system the importance of FeOH floc on the river substrate and the effect of adsorbed and precipitated metals on sediment toxicity can not be ignored. Therefore, in order to re-establish a productive and self-sustaining salmonid fishery consideration of water toxicity alone is insufficient as the re-establishment of a reasonably healthy flora and fauna is also necessary. Water quality objectives must not only identify acceptable water toxicity levels for the major AMD parameters, but also acceptable levels for sediment toxicity and substrate modification (Gray, 1995b). In the Avoca River it is proposed that the toxicity level of the water outside the mixing zone should be below 1 TU/l as calculated using Atlantic Salmon (Sullivan and Gray, 1995). This could be achieved by selective removal of copper from the two main adits. Substrate modification can only be prevented by removing all the iron from the adits. A remediation strategy for the Avoca River is presented elsewhere (Gray and Innes, 1995).

Impact assessment of river toxicity

Using the equations below then the toxicity in the river water caused by the AMD can be predicted, with 95% precision, if the river discharge rate is known as well as the discharge rates in the two main adits. The total toxicity of the drainage from the Deep Adit is closely linked (logarithmic) to discharge rate due to the predictable nature of the Zn:Cu ratio with discharge rate (Fig. 12). In contrast, due to the different hydrological nature of the west Avoca mining area the total toxicity of the discharge is more complex to model. There is a similar seasonal relationship between discharge rate and the Zn:Cu ratio, although less defined due to a lower surface area underground for secondary sulphate formation. However, at higher discharge rates, and during short period afterwards, the Cu concentration is reduced due to dilution (Fig. 13). This is not apparent with either the Zn or Fe (Fig. 6) which continue to increase in strength with increasing adit discharge rate. For predictive purposes the contribution of metals and so toxicity from the Ballymurtagh Adit have to

Fig. 12. The toxicity of the discharge from the Deep Adit in toxic units per litre (TU/L) can be estimated from the adit flow rate using the equation:

y = - 228.56 + 424.28*LOG(x) R^2 = 0.762

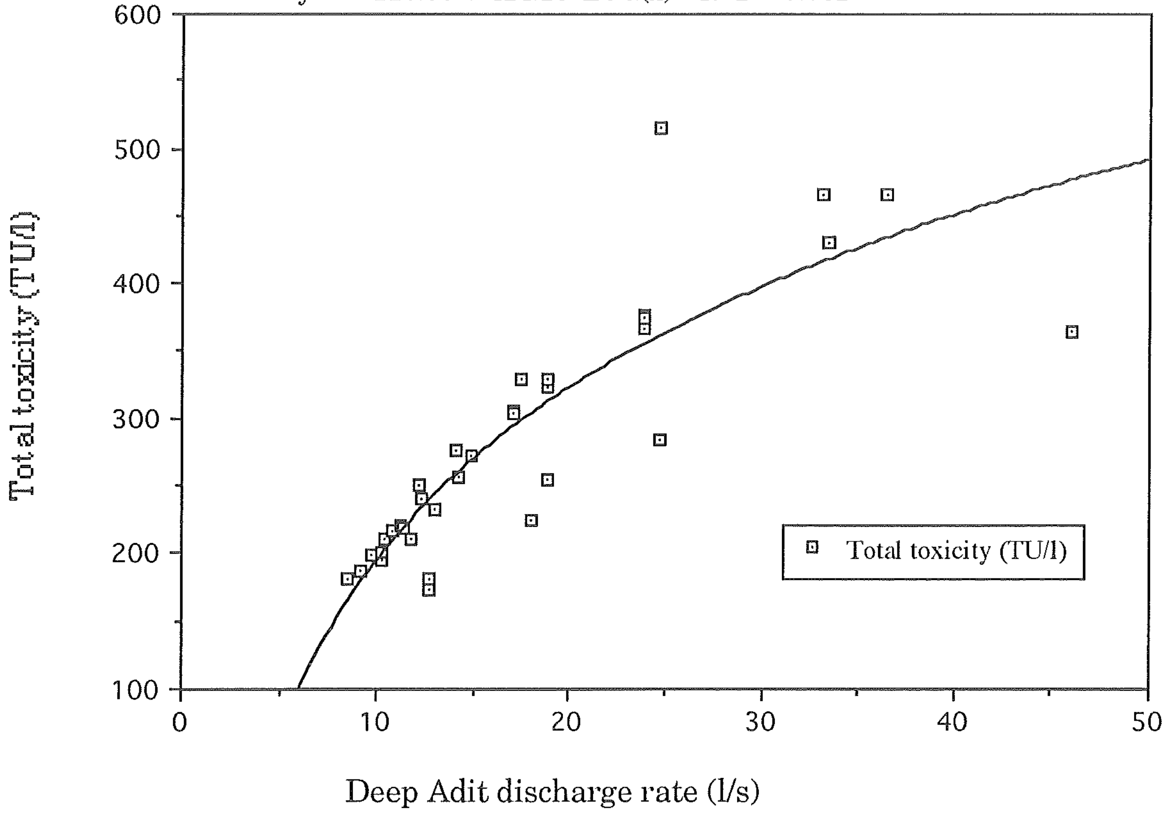
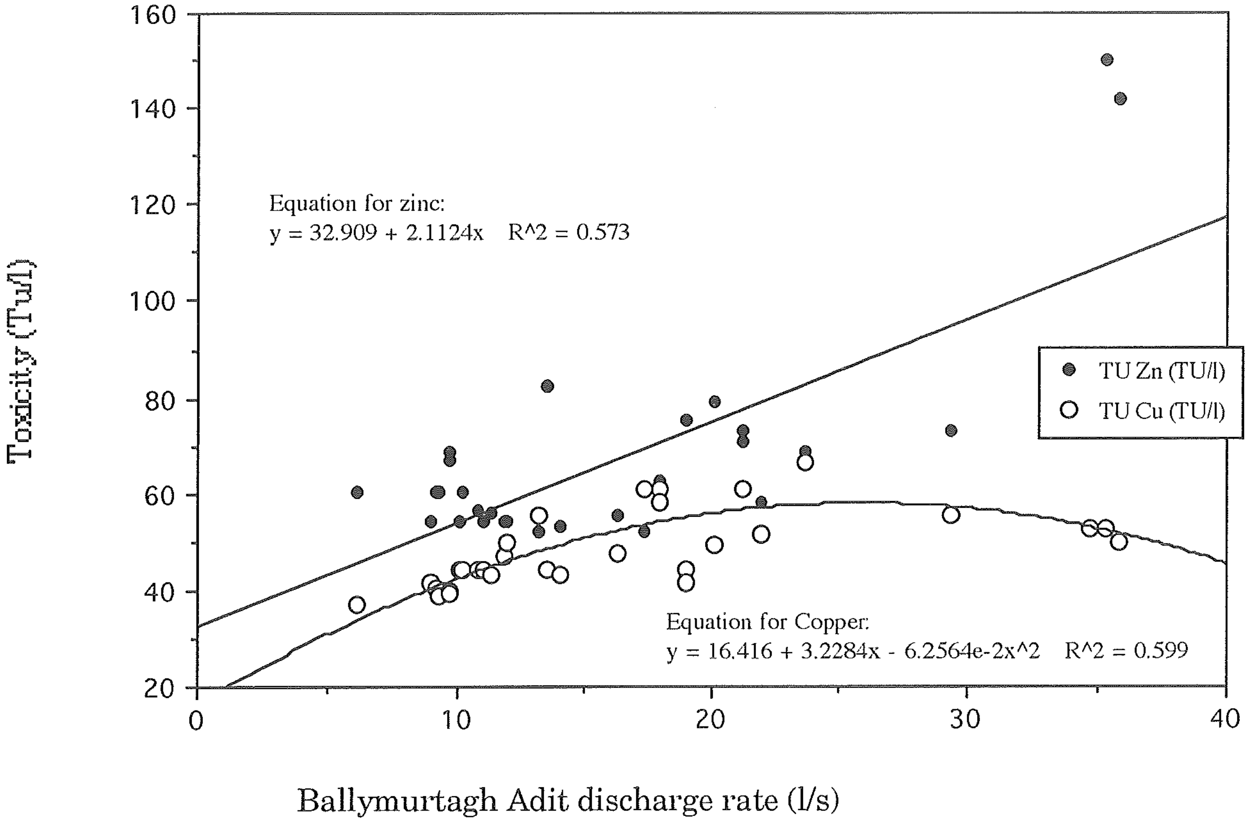


Fig. 13. The toxicity of Cu and Zn must be calculated separately for the Ballymurtagh Adit as the Zn:Cu ratio is independent of flow due to the different hydrological nature of the west mining zone.



be calculated separately using linear regression for Zn and a second order polynomial relationship for Cu.

To predict the toxicity of the river water below the mixing zone then:

I. Calculate toxicity emanating from the Deep Adit (β^{DA})

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

II. Calculate toxicity emanating from the Ballymurtagh Adit (β^{BA})

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

III. Calculate contribution of main adits to overall AMD discharge to river (Ø). This is done by using the sulphate ion as a conservative tracer and mass balance analysis. 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

IV. Toxicity of adit discharges. At this point the total toxicity from the two main adits is $((\beta^{DA}) + (\beta^{BA}))$, while the total toxicity of AMD discharged into the river is $((\beta^{DA}) + (\beta^{BA}) / Ø)$.

V To calculate the toxicity after complete mixing within the river in TU/l (Ω) then the following mass balance equation is used:

$$\Omega = \frac{(((\beta^{DA}) + (\beta^{BA}) / \varnothing) \times ((f^{DA}) + (f^{BA}) / \varnothing)) + ((\beta^{R}) \times (f^{R}))}{((f^{DA}) + (f^{BA}) / \varnothing) + f^{R})} \text{ TU/l}$$

VI. To include the effect of surface runoff during an intense and prolonged storm the calculation to estimate the toxicity after complete mixing within the river in TU/l (Ω) is modified as follows:

$$\Omega = \frac{(((\beta^{DA}) + (\beta^{BA}) / \varnothing) \times (f^{DA}) + (f^{BA}) / \varnothing)) + ((\beta^{SR}) \times (f^{DA} + f^{BA})) + ((\beta^{R}) \times (f^{R}))}{((f^{DA}) + (f^{BA}) / \varnothing) + (f^{DA} + f^{BA}) + f^{R})}$$

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 surface runoff the toxicity will vary from 86 to 1,748 TU/l, the variation due to dilution and flushing of stored acidity from spoil.

CONCLUSIONS

The AMD water quality protocol comprises five stages:

I. The establishment of water quality criteria and standards for the receiving water.
II. Calculation of the natural assimilation capacity of AMD by the receiving water.
III. Impact assessment including projections over a 20 year period based on future development of the site, long-term AMD generation assessment, and the effect of any site remediation work.
IV. AMD control.
V. Compliance monitoring and review of discharge standards.

It is important to fully evaluate discharge characteristics of the key adits over a minimum period of 12 months in order to fully assess, and to be able to predict, the impact of AMD on the receiving water as shown in the example for the River Avoca.

Water quality objectives based on toxicity levels are ideal for returning salmonids, as they do not feed on their way upstream to spawn. However, young salmonids do feed as they make their way slowly downstream to the sea at the start of the migration cycle. Therefore, in order to re-establish a productive and self-sustaining salmonid fishery then acceptable levels for sediment toxicity and substrate modification must also be identified as well as setting normal water quality standards.

The current method of predicting the toxicity of AMD outside the mixing zone of the river is based on mass balance. While toxicity data is based on actual toxicity trials (Sullivan and Gray, 1992), the current procedure gives maximum expected values rather than actual values which may be significantly less due to various sorption processes reducing the availability of metals to the biota.

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