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INFLUENCE OF POSSIBLE SECONDARY SULPHATE MINERAL FORMATION ON THE IMPACT OF ACID MINE DRAINAGE TO SURFACE WATERS

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EXECUTIVE SUMMARY

Acid mine drainage (AMD) is a major environmental pollutant of both surface and ground waters (Kelly, 1988; Parsons, 1977). Intensive sampling of drainage from mine adits has revealed a seasonal variation in the Zn:Cu ratio. This is linked to 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. 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, results in higher river toxicity, even at high river discharge rates. This seasonal variation in toxicity of AMD from underground workings, or from mines with extensive surface spoil, has important ramifications for its control to surface waters.

DISCUSSION

The ores at the abandoned copper and sulphur mines at Avoca, 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.

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 and 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 ($p<0.001$), and as the regression equation shows ($y = -1.01+1.045x$) there is no significant difference ($p>0.05$) between discharge rates, although the discharge rate in the Ballymurtagh Adit recovers more slowly in winter than the Deep Adit. Significant weights of cations are 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 41.6, 70.0 and 65.4% of each metal respectively over the period of May 1994 to February 1995.

During the sampling period, 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. A similar phenomenon, although much less well defined, was also identified in the Ballymurtagh Adit. The variation in the Zn:Cu ratio corresponds 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 1). This variation in the Zn:Cu ratio corresponds closely to seasonal variation in expected rainfall (Fig 2), with highest Zn:Cu ratios recorded towards the end of the dry season.

The reason for this variation 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 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 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.

The variation in Cu in relation to Zn 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 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, 1995). It can be seen from Figs. 3 and 4 that while the toxicity exerted by the Zn 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 (Figs. 5 and 6). 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, then the total toxicity of the leachate varies 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.

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 during the winter period compared to summer low flow periods when minimum dilution is available.

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 once more. 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.

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Sullivan, M. (1995) Personal communication

Fig. 1. Variation of the Zn:Cu ratio with adit discharge rate.

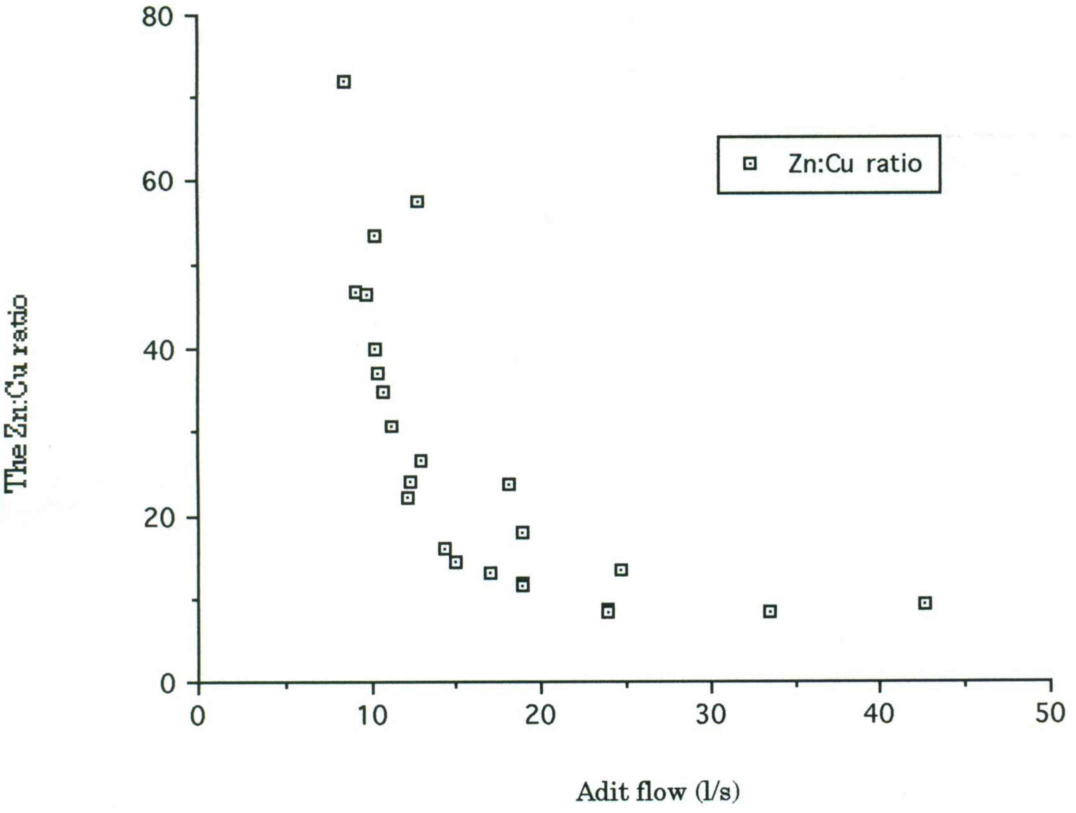

Fig. 2. The variation in the Zn:Cu ratio showing the increase during the dry summer period and rapid decline once the wet winter period becomes established.

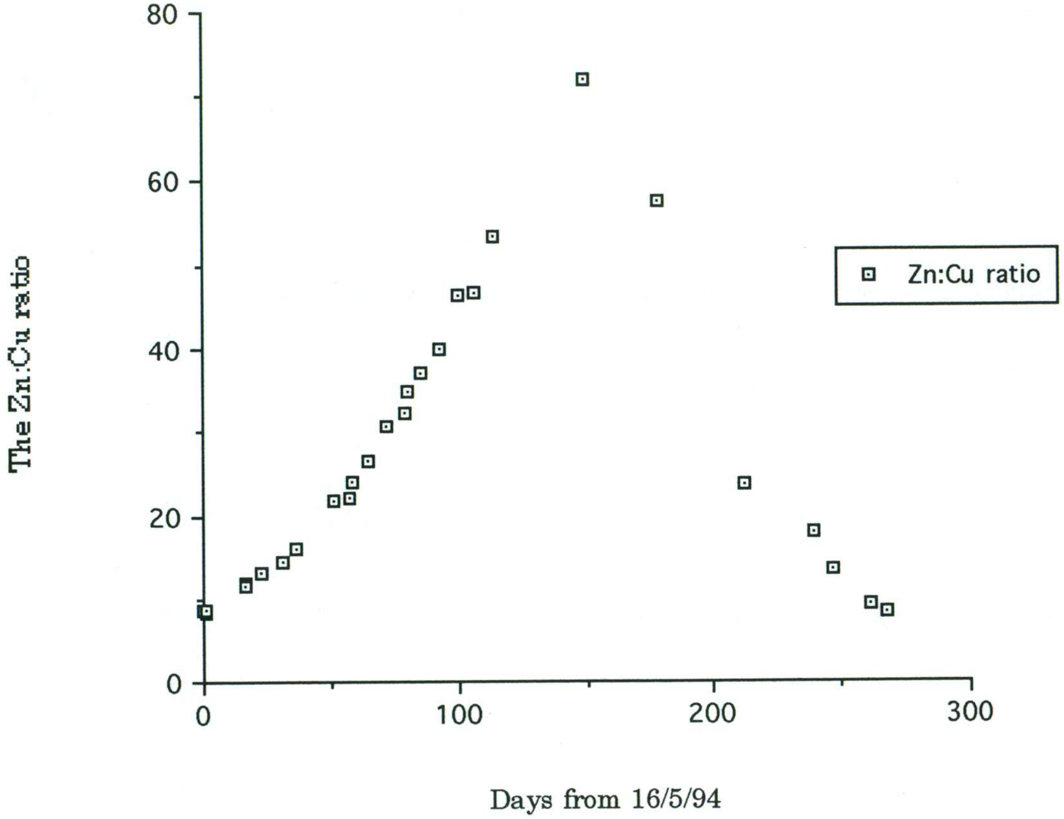

Fig. 3. Total toxicity in adit discharge caused by Zn and Cu in toxicity units per litre

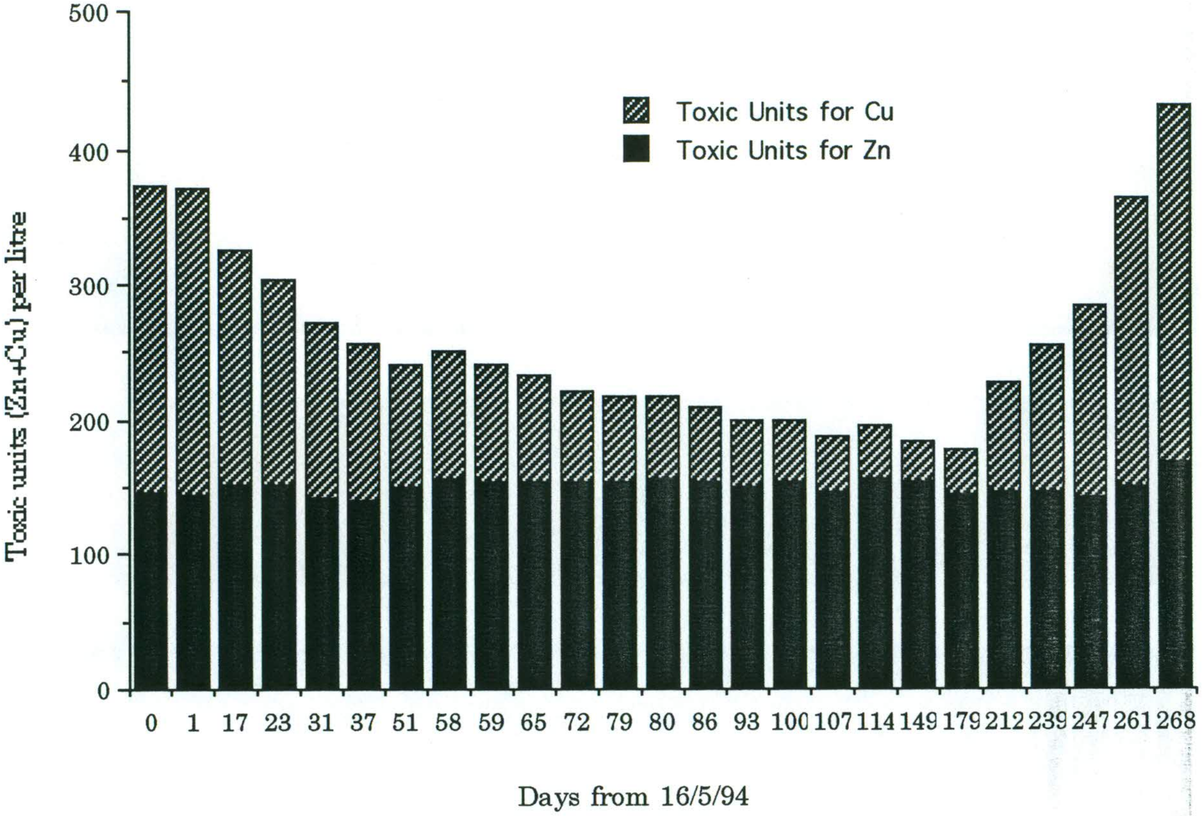

Fig. 4. Variation in toxicity of Zn and Cu, and total toxicity (Zn+Cu), over sampling period.

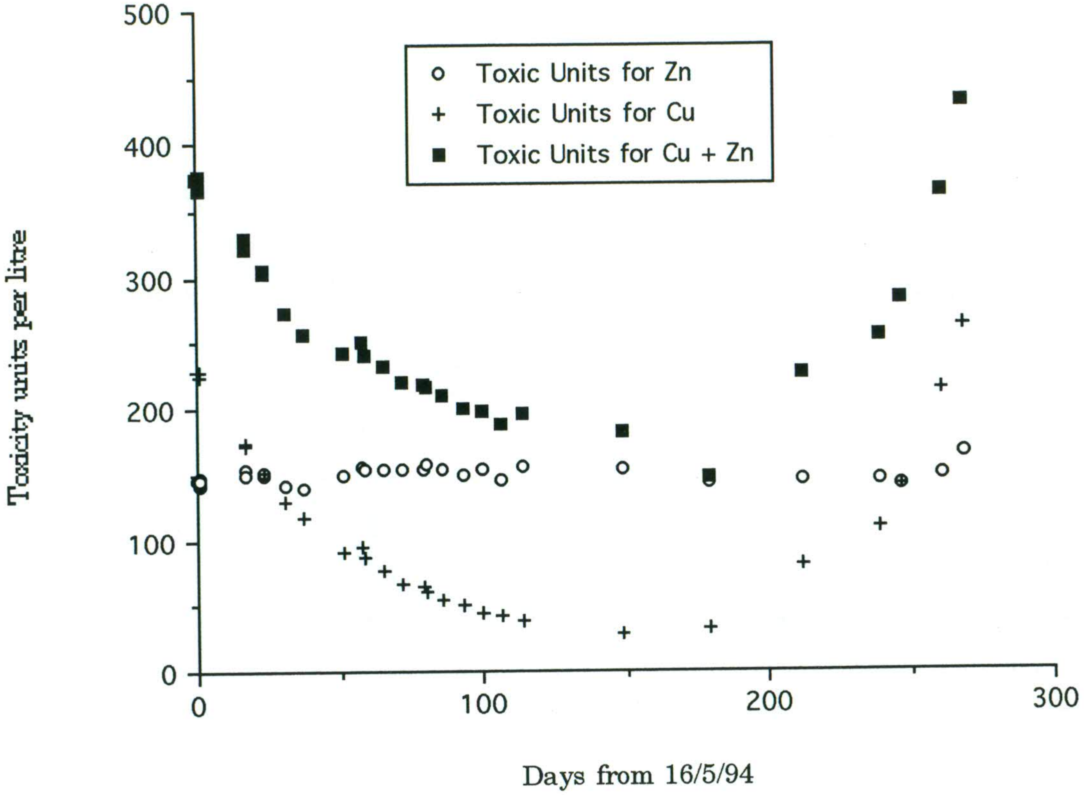

Fig. 5. Variation in toxicity with the Zn:Cu ratio.

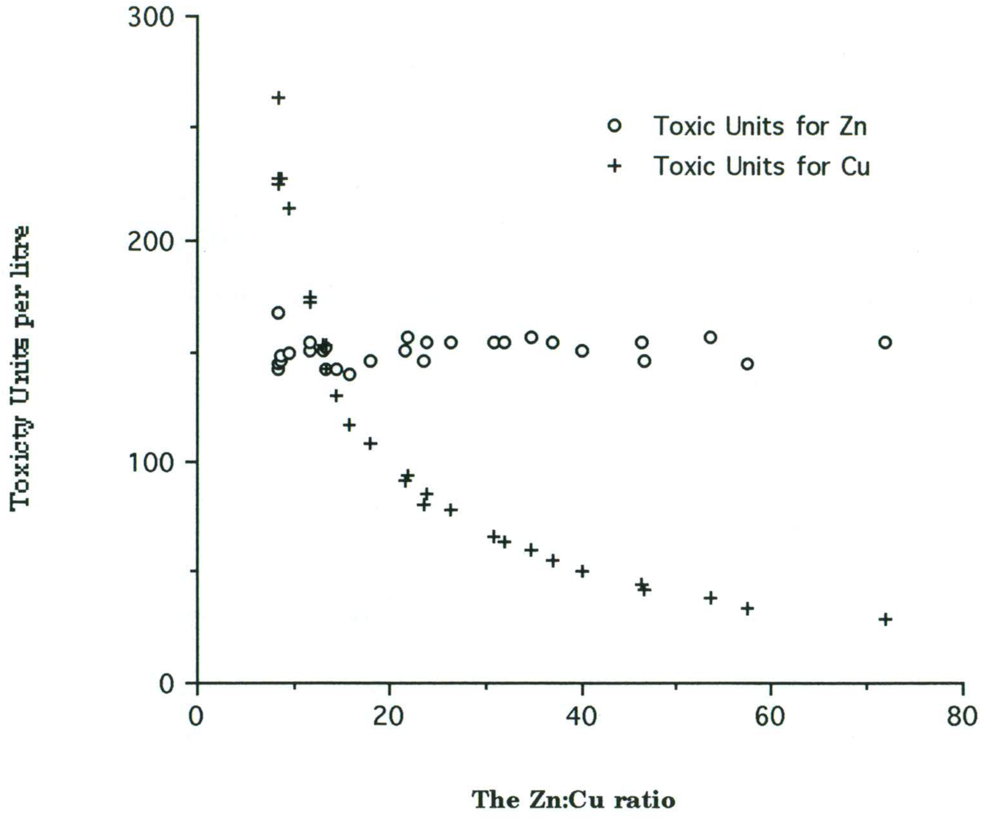

Fig. 6. Variation in toxicity with the Zn:Cu ratio