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Variation in metal contamination of riverine sediments below a Copper and Sulphur Mine in south east Ireland

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Abstract

The discharge of acid mine drainage (AMD) from the abandoned sulphur and copper mines at Avoca results in the formation of ochreous deposits on the substrate of the Avoca river. The riverine sediments were studied during a low flow period to establish the degree of contamination and to identify the major processes affecting sediment metal concentrations. Zinc adsorption and desorption in sediments is chiefly regulated by pH, showing a significant correlation ($p < 0.001$). The Zinc concentration in the sediment falls below background levels after the input of AMD. However, the metal came out of solution when the pH increased downstream of a fertilizer factory ($\text{pH} > 8.0$), some 7 km below the mine. In contrast Cu and Fe significantly increased ($p < 0.001$) both in the sediment (0-30 mm depth) and the surface ochre immediately below the mixing zone. Iron concentration decreased with distance from AMD source, whereas Cu showed another peak below the fertilizer factory. Copper removal appears to be primarily by co-precipitation with iron showing a significant relationship. Higher sediment enrichment factors for all metals were obtained in the surface sediment layer (ochre) deposited on larger stones and in floc material collected in sediment traps, compared to the subsurface sediment. Copper showed particularly strong enrichment in surface layer and floc. Cadmium was not recorded in any of the sediment collected at the detection limit used ($\mu\text{g g}^{-1}$). Metal deposition in the sediments was found to be spatially variable, so sub-sampling is required, although replicates showed less variation. Seasonal variation in metal concentration in the sediments was examined by sampling in late summer early spring.

Introduction/Aims

Oxidation of pyrite results in the release of acidic waters containing sulphuric acids and dissolved heavy metals often in toxic concentration, and the formation of solid iron precipitates ('ochre'). This phenomenon is usually referred to as ACID MINE DRAINAGE (AMD).

The aims of this study were to assess spatial and temporal variation with regard to the distribution of Fe, Cu and Zn in riverine sediments and to identify major processes taking place.

The discharge of AMD from the abandoned sulphur and copper mines at Avoca results in the formation of ochreous deposits on the substrate of the Avoca River (Plate 1). The mining area is principally drained by two major leachate streams, the Deep Adit at Tigroney (drains east) and the Ballymurtagh Adit (west) (Plate 1a). The mean annual AMD discharge in 1993/94 for the two leachate streams was 1.16 and 1.10 m³/day respectively ranging from approximately 0.81 m³/day during low flow to 2.3 m³/day during high AMD discharge. While during low flow conditions the metal contamination is principally attributed to AMD discharge from these two leachate streams, during heavy and prolonged rainfall surface runoff from spoil heaps contributes largely to metal input into the river system. The mean annual AMD discharge of Fe, Cu and Zn taking a total of the two main leachate streams was 461, 111 and 11 kg/day, respectively in 1993/94.

Methods

- Sediment samples were taken from both the subsurface sediment layer (0-30 mm) and from the deposited ochre material (surface layer).
- Sediments were collected during low river and AMD discharge in June and August, 1994, and immediately after a period of high river flow and AMD discharge in March/April, 1995.
- At each site three sub-site samples were taken to obtain a reasonable estimate of the contamination at each site; during the summer survey sub-site replicates were also taken.
- Approximately 3 kg of subsurface samples were presieved in the field through < 1 mm plastic sieves and frozen until subsequent analysis.

- Sediments were wet sieved in the laboratory and the < 0.063 mm fraction retained and oven dried for further analysis.
- Subsurface and surface sediments were digested in concentrated nitric acid and analysed using flame atomic adsorption spectrophotometry (AAS).
- Organic matter of the < 63 μm fraction in subsurface sample was determined by loss on ignition.

Results

Spatial distribution:

Site 1 is located approximately 500 m upstream of the mining are and not contaminated by AMD, whereas sites 2, 3 and 4 are located 3, 11 and 12.5 km downstream of the mines respectively. Complete mixing of AMD and river water was attained at site 2.

Mean metal results of sub-site samples are shown in Figs. 2, 3 and 4. Results show that Zinc concentrations in the < 63 μm sediment fraction increased only at site 4 when the pH of the river water also increased significantly. This suggested that Zn is not adsorbed onto sediments at sites 2 and 3 where the pH of the surface water is low. It is suggested that the pH is the key parameter regulating Zn concentrations in sediments.

Copper and Fe concentrations increased significantly at site 2 and decrease gradually downstream, with Cu showing a second peak at site 4. A significant correlation ($p < 0.001$) between Cu and Fe suggested co-precipitation of Cu with Fe hydroxides.

The average pH of AMD from the leachate streams was 3.4 and 3.8 respectively, resulting in a pH decrease of the riverwater from mean pH of 6.5 upstream of the mines to 5.8 at site 2 and a significant increase after the fertilizer factory to a mean pH of 9.

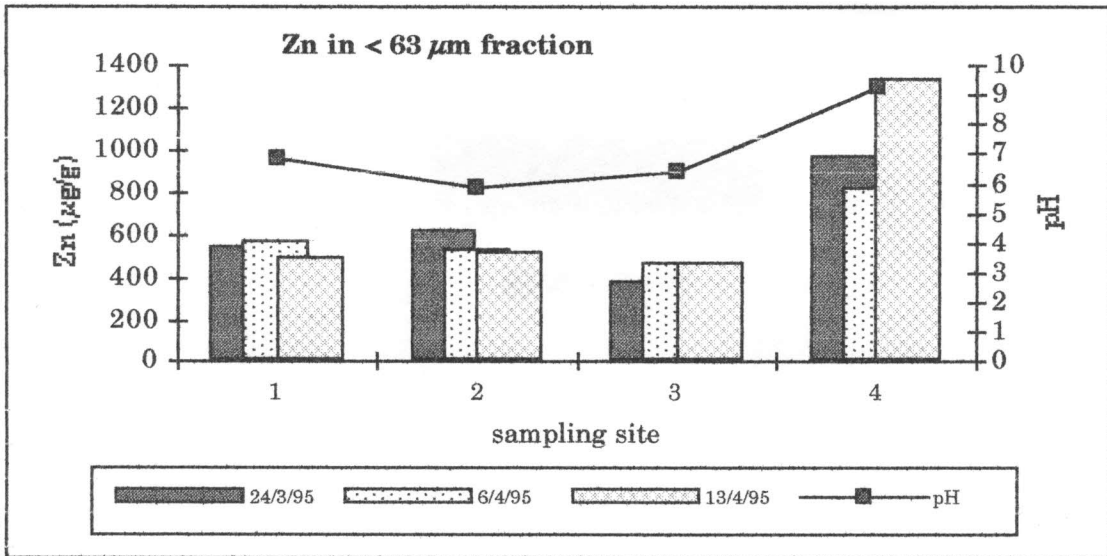


Fig. 2

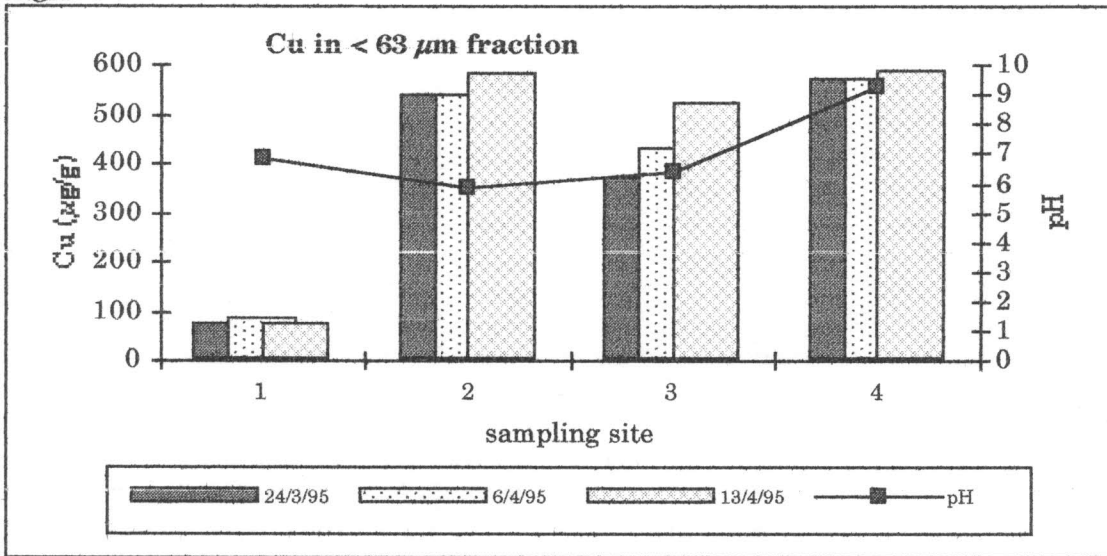


Fig. 3

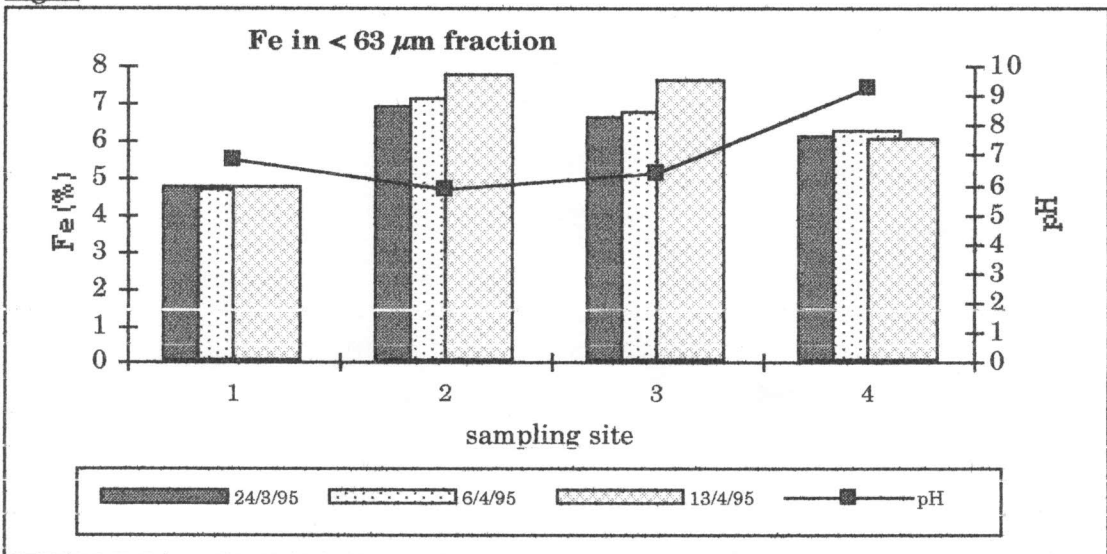
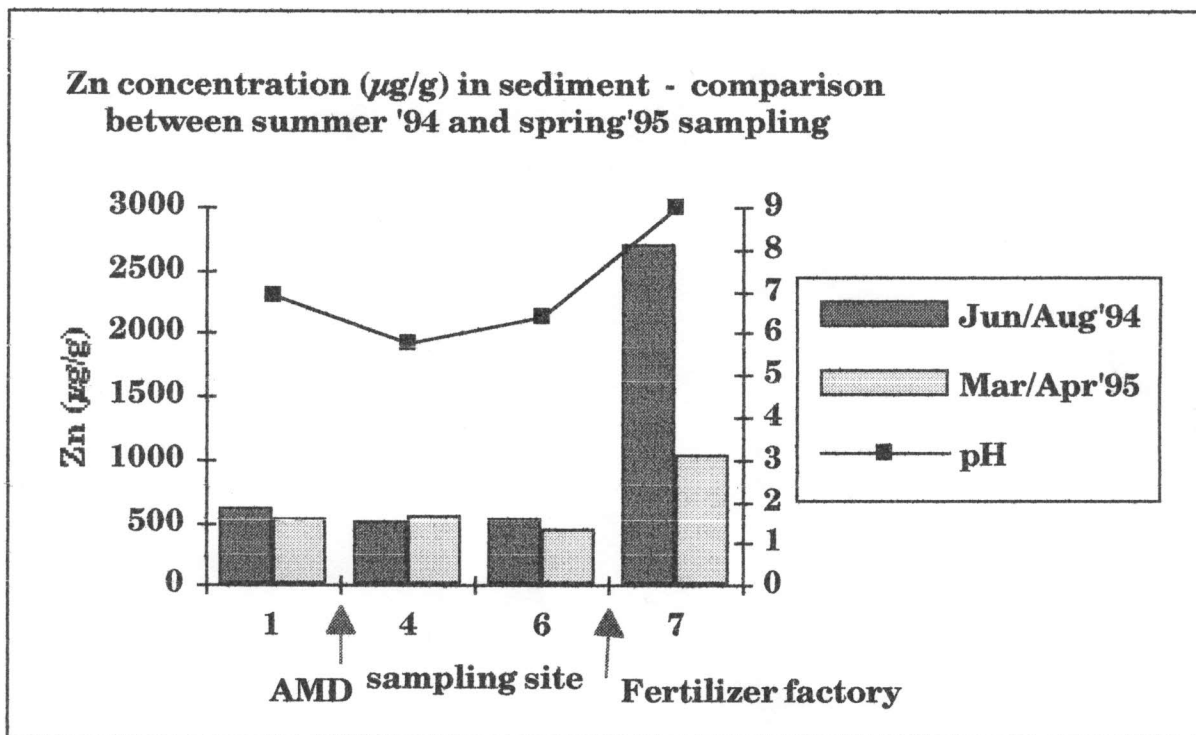


Fig. 4

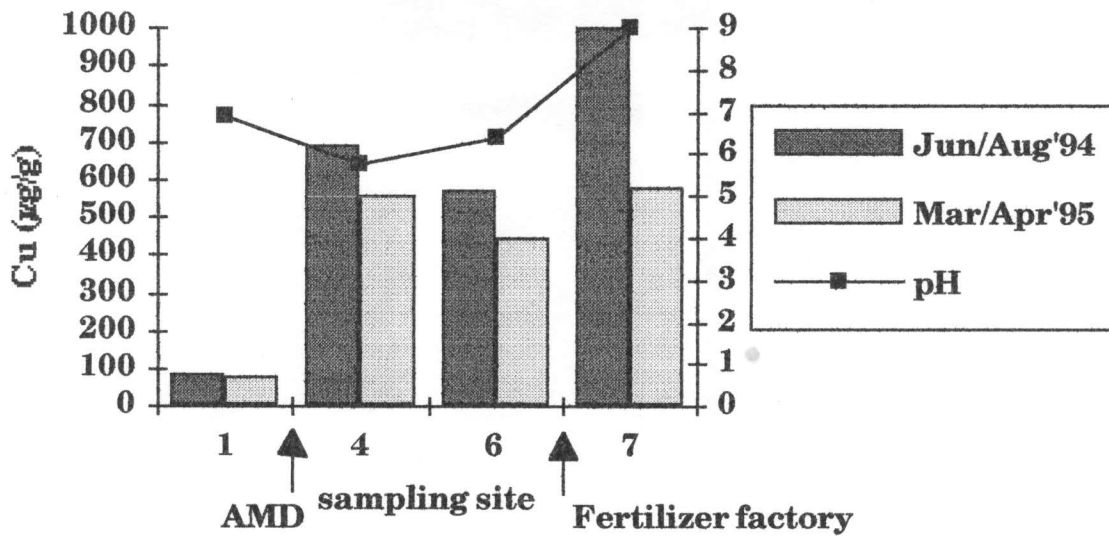
Temporal distribution:

Sediment samples were collected in summer '94 on 29.6.94 and 4.8.94 and in spring '95 on 24.3.95, 6.4.95 and 13.4.95. Results show the same trends in terms of metal distribution for both sampling periods in 1994 and 1995, although metal concentrations were generally somewhat lower during the 1995 surveys.

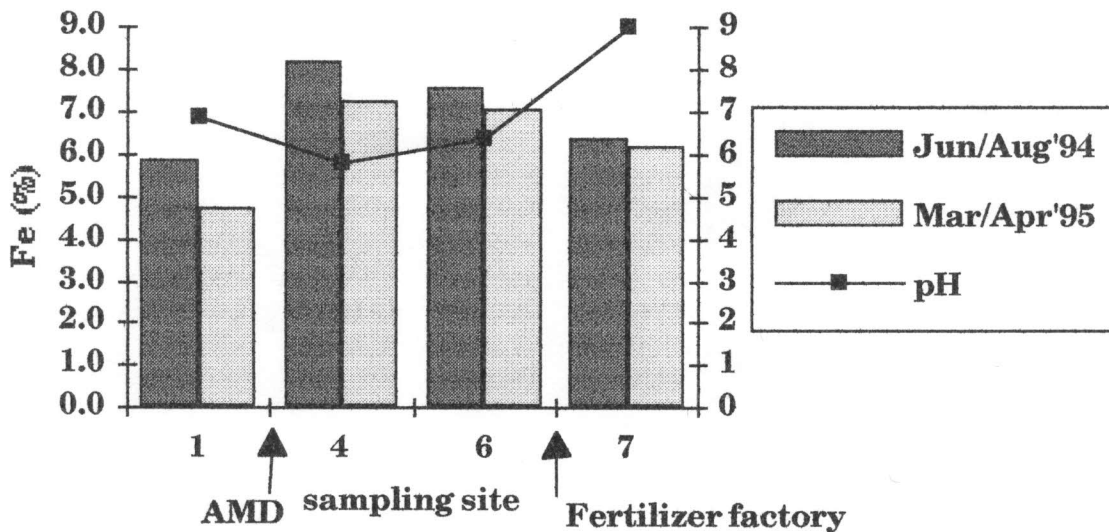
While the summer sampling in 1994 showed no obvious differences in terms of metal concentration of the subsurface sediment, sampling surveys in spring 1995 showed a gradual increase of Cu and Fe concentration in the sediment at all sites affected by AMD discharge. This was due to a dry weather spell where river discharge decreased faster than the AMD discharge and therefore resulted in a build up of surface precipitate of Fe-hydroxide from the first to third sampling episode. Thus it can be assumed that hydrological factors play a major role in the accumulation of metal in subsurface as well as in surface sediments. Concentrations of Zn in the sediments are more variable, not reflecting the increase seen with Cu and Fe.



Cu concentration ($\mu\text{g/g}$) in sediments - comparison between summer'94 and spring'95 sampling



Fe concentration (%) in sediments - comparison between summer'94 and spring'95 sampling



Metal accumulation in surface floc

In stagnant areas or extremely slow flowing water (Plate 2 and 3) floc material accumulates. Metals become concentrated in the floc and eventually when the

floc dries out associated with the sediment (Plate 4 and 5). Metal concentrations are spatially variable. Analysis of the floc during the summer surveys in 1994 showed concentrations of Zn of 539 $\mu\text{g/g}$ at site 2 and 1949 $\mu\text{g/g}$ at site 3, Cu was 1818 $\mu\text{g/g}$ at site 2 and 2099 $\mu\text{g/g}$ at site 3. Iron concentrations fluctuated around 5%. Concentrations of Zn and Cu were generally lower in dry areas (Plate 5, 6). Results showed Zn concentrations of 227 $\mu\text{g/g}$ at site 2 and 1165 $\mu\text{g/g}$ at site 3 and Cu concentrations of 1116 $\mu\text{g/g}$ at site 2 and 1253 $\mu\text{g/g}$ at site 3. Iron concentration dropped from 7.6% at site 2 to 5.8% at site 3.

Metal accumulation in ochre

Results of analysis of ochreous precipitate also showed that metals, specifically Cu and Fe (1118 $\mu\text{g/g}$ and 17.1%), were strongly concentrated in the surface layer. Comparison between subsurface and surface layer showed that Cu and Fe concentrations increased approximately two fold at site 2. Copper was enriched in the surface layer by a factor of 26 compared to an enrichment of Cu in the subsurface sediment by a factor of 15. This suggested that Cu may be preferentially co-precipitated with Fe-hydroxide.

Conclusions

- Zinc concentrations in sediments of the Avoca River are found to be primarily regulated by pH
- Copper and Fe concentrations in sediment are highest at the sampling site closest to the AMD discharge (at site 2), whereas Zn only becomes associated with the sediment when the pH is high for the metal to precipitate
- Temporal variation seems to be evident when the river discharge decreases faster than the AMD discharge
- Hydrological factors play a major role in metal accumulation in the sediment, as the surface ochre and floc material is easily scoured
- Metals are highly concentrated in the floc, and subsequently associated with the sediment.
- Copper seemed to be concentrated in the surface sediments (ochre) and primarily co-precipitated with Fe.
- Further research is necessary to evaluate toxicity of sediments