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# A SURVEY OF SOIL AND VEGETATION IN THE AREA SURROUNDING THE AVOCA MINES, Co. WICKLOW

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#### **SUMMARY**

Metal content was determined in soil and vegetation around the eastern zone of the disused Sulphur and Copper mines at Avoca (south-east Ireland). A 250 x 250 m grid survey was conducted covering a total area of 4 km<sup>2</sup>. The mining belt was in the centre of the investigated site and was sampled separately. Iron, Zn, Cu and Cd concentrations in soil and plant material were determined in addition to soil organic matter content and soil pH. Soil samples taken from the spoil showed elevated Cu and Cd concentrations, low soil pH and organic matter contents. At least 50 % of the agricultural sites examined surrounding the East Avoca Mine, showed elevated Cu and Cd concentrations, whereas Zn and Fe concentrations were within the range for unpolluted soils. However, none of the vegetation analysed had elevated Zn, Cd, Fe or Cu concentrations. Overall there is no indication of serious metal contamination either in soils or vegetation surrounding the mine in spite of extensive dust deposition during open pit mining activity 20-50 years ago. There is however a plume of elevated Cu in the soil originating from a large spoil heap for some 2.0 km spread by the prevailing wind.

#### INTRODUCTION

Open pit mining of pyrite ores can lead to the contamination of the local environment and cause severe environmental impact to aquatic and terrestrial ecosystems (Soldevilla et al., 1992). Historical mining activities and bare spoil heaps from previous mine workings are often a source of metal contamination to surrounding agricultural land. In the UK the most extensive areas of contaminated soils are caused by mining and are associated with mineral processing activities (Thornton, 1980). Wind-blown dust containing high metal concentrations from unvegetated spoil heaps may be deposited on soil and plants, and can enter the food chain. For example Martin and Coughtrey (1982) found surface enrichment of lead, zinc, cadmium, mercury and copper in an area local to a mine but undisturbed by it.

Avoca Mines are situated in County Wicklow in south-east Ireland The ores are volcanic sulphide deposits of Ordovecian age. The principal minerals of economic importance are chalcopyrite (CuFeS<sub>2</sub>), pyrite (FeS<sub>2</sub>), sphalerite (ZnS) and galena (PbS). Mining of copper ore (chalcophyrite) began in 1720 in East Avoca in underground mining operations. During the nineteenth century pyrite was also mined and processed. Up until the mid twentieth century all sulphide mining operations were subsurface. As mining in Avoca became more economical due to new mining and processing techniques, the excavation of open pits and the processing of lower grade ore deposits was encouraged. Platt (1975) reported that open-pit operations at Avoca created substantial amount of dust and in exposed situations the spoil was prone to continuous wind erosion. However no large scale dust control programme was implemented since the dust was only periodically problematic and was primarily related to the east mining area only. It was felt that rainfall alone was sufficient as dust suppressant (Platt, 1975). Despite this, severe deposits of dust over a prolonged period were a cause of complaint and legal action during the operation of the mine. A number of large unvegetated spoil heaps are still present in the East Avoca mining district and are subject to wind erosion. The residents of the area feel that metal contamination in soils has led to localized toxicity problems.

Polluted soils generally have lower rates of decomposition, biological activity, mineralisation, soil biomass, and sporophore production by macrofungi than

uncontaminated soils (Tyler, 1984). This can lead to high soil organic matter content. Normally the upper soil horizons contain less than 15% organic matter although up to 90% can be found in the case of unaltered material at the surface (Fitzpatrick, 1983). In mine sites organic matter tends to be low and therefore metal availability is high.

Soil pH determines the solubility of metals (Chase and Wainwright, 1983; Shetron 1983; Williamson et al., 1982) by affecting their binding and thus determines the release and precipitation of metals in soil (Martin and Coughtrey, 1982). Metals become mobile once soluble, and hence may be leached from the soil solution. Zinc is one of the most readily mobilised metals upon acidification (Wallace and Berry, 1978). In normal soils a large proportion of the total metal is unavailable since it is either complexed with organic matter forming insoluble compounds or comprises part of a mineral structure.

Factors influencing the concentrations of elements found in vegetation include plant species, tissue type, level and availability of the element in soil, distance of the plant from the source of the element, season and climate. Only a small proportion of the metals entering the roots are transported to the other parts of the plant (Tyler, 1984).

Since the closure of the Avoca Mine in 1982 large unvegetated spoil heaps mark the area surrounding the Avoca Mines. They are predominant at the East Avoca mining district and are still subject to wind erosion. A survey to investigate metal enrichment of soil and vegetation in the vicinity of the East Avoca mines was conducted during June and July, 1995. The principal soils surrounding the mines are brown podzolics; the agricultural land is principally used for grazing of cattle and sheep and tillage production. Soil and vegetation samples were also taken from the spoil heap at Mount Platt. All samples were analysed to determine metal content of Fe, Zn, Cu and Cd, soil organic matter and soil pH in the 4 km<sup>2</sup> area surrounding the East Avoca mining district (Fig.1).

#### **METHODS**

# Sampling

The mining region at Avoca surrounding Mount Platt was divided into a 250 x 250 m grid covering a total area of  $4 \text{ km}^2$  (Fig. 1). Soil and plant material was removed from as close to the centre of each section of the grid as possible. However, the actual sampling location was dependent on local conditions such as the position of fences, trees and buildings.

Soil samples were taken from a 100x100 mm area to a depth of 100 mm at all sites. The surface vegetation was cut at ground level. Samples were placed in clean dry plastic bags and transported to a laboratory. The land use of the sites examined was determined as the samples were taken and the visibility of Mount Platt from the sites noted.

Vegetation samples were washed thoroughly in order to remove surface contamination, dried in an oven at 100°C and then desiccated to remove all water present. Fresh soil samples were sieved through a 2 mm stainless steel mesh. Part of the sample was dried in an oven at 100°C and then desiccated to remove all water present. Insufficient plant material from some sites meant only one or two replicates were obtained for some samples.

Some sites could not be sampled for plant material as little or no vegetation grew in some parts of the mines and some of the pastures were heavily grazed. Samples of *Calluna vulgaris* and *Erica cinerea* were taken where present. Grass samples were taken from all sites sampled. Needle samples were also taken from pine trees growing in sections E5-H5 and E4-H4 in order to determine metal uptake and translocation by deep rooting species (Fig. 1). Grass samples could not all be identified to species level due to the absence of flowering heads in most samples.

pH

A soil paste was prepared using fresh sieved soil sample and distilled water in a ratio of 1:2. It was allowed to settle for 30 minutes and the pH was then measured using a glass electrode.

# Organic matter content

Sieved, oven-dried, desiccated soil samples were placed in crucibles and weighed. They were ignited at 500°C for three hours and then cooled in a dessicator. They were reweighed when cold and the percentage loss on ignition calculated.

# Metal analysis

The total metal concentration of iron, zinc, copper and cadmium in soil and vegetation was analysed by flame atomic absorption spectrophotometry (AAS) using a Perkin Elmer<sup>®</sup> 3100 spectrophotometer. Three replicates of each sample were analysed wherever possible.

Samples were prepared by digestion of approximately 0.5 g dried sample in 10 mls of concentrated nitric acid (70%) for two hours at 170°C on a Tecator® digestion block. The acid was then evaporated down to 1-2 mls. Soil samples were filtered through Whatman No. 1 filter papers. Vegetation samples did not need to be filtered. All samples were made up to 50 mls in volumetric flasks using deionised distilled water. Samples were stored for analysis in clean, dry polyethylene 50 ml bottles.

The concentration of copper, iron, zinc and cadmium in mg/l contained in the digests was determined by AAS. The concentration of each element in the samples was calculated using the following formula:

$$\mu g/g = A-B \times 50$$
  
wt (g)

where

 $\mu g/g$  = the concentration of the element in soil or vegetation

A = the reading obtained for the samples in mg/l

B = mean blank value

= the volume of digest prepared

wt (g) = the weight of the sample used to prepare the digest.

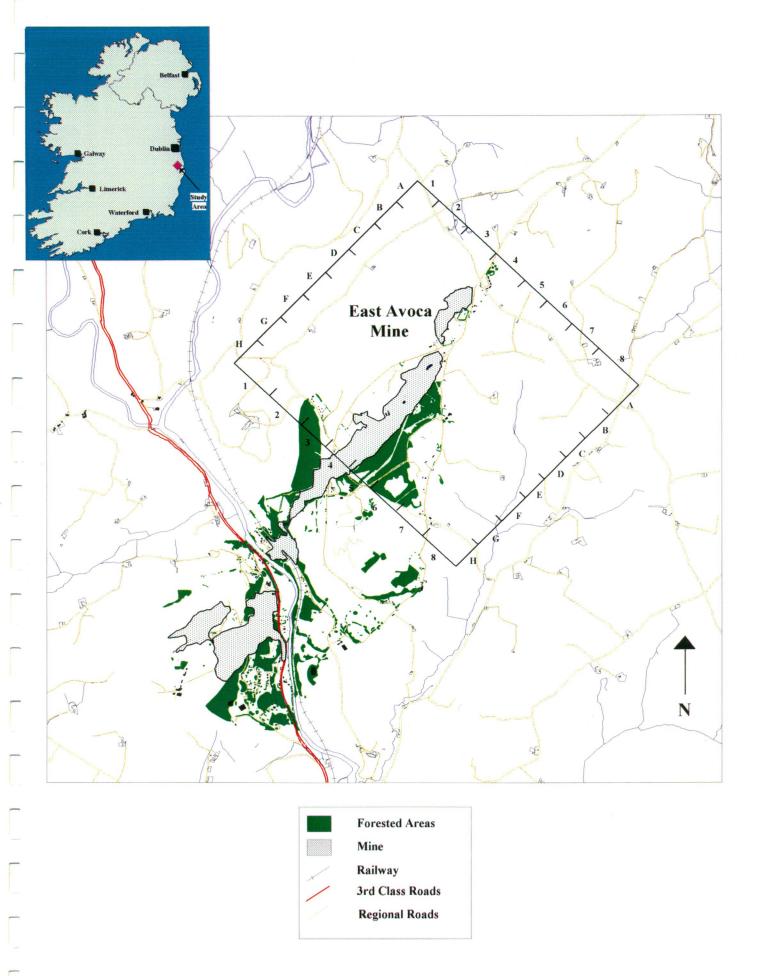


Figure 1: Map showing the location of East Avoca Mines and Sampling Grid

#### RESULTS

A description of each site, land use and visibility of Mount Platt is given in Appendix I. The results of the soil analysis carried out are given in Appendix II, the mean concentrations of elements in vegetation in Appendix III, and the concentrations in specific plant species from each site in Appendix IV. Among the sites surrounding the mines were a number of control sites which did not lie in the path of prevailing winds. These were B1, B2, C1 and C2.

#### Soil

Summary statistics for the parameters analysed in soil samples taken from the mine spoil and surrounding pasture are shown below in Tables 1 and 2 respectively.

Table 1. Summary statistics for soil parameters measured in samples taken from the mine spoil (n=14)

	Mean	SD	Median	Min	Max	Normal range*
LOI (%)	3.52	0.97	3.52	1.55	4.94	
pН	3.5	0.68	3.6	2.6	4.5	
Cu (µg/g)	658	317	566	261	1235	5-80
$\operatorname{Zn}\left(\mu g/g\right)$	342	344	179	86	1184	20-300
$Cd (\mu g/g)$	1.14	1.06	0.83	0.00	3.62	0.03-0.3
Fe (%)	5.5	2.4	4.9	2.6	9.9	0.5-10

<sup>\*</sup> Normal range for mineral soils (Allan, 1989)

# Organic matter

The average soil organic matter content was 16%. Sites covered with forest and woody vegetation showed higher organic matter content than pastures as lignin takes a long time to decay. Soil organic matter content of sites E4, E5 and H4 were on average 10-15 % higher than all other sites. These sites are located on the edge of the mine and the high loss on ignition may indicate inhibition of the breakdown of organic matter by the soil microflora. The

lowest values were in sites 1-14, on Mount Platt with concentrations ranging from 1.55 to 4.94 %. This is due to the sparse vegetation cover in the area.

pH

The pH of all spoil sites sampled was less than pH 4.5. As the sites had little organic matter to bind elements and nutrients, there is potential for leaching in this area. Minerals essential for plant growth may have been lost from the soil through this process. However this study was confined to metal contamination and therefore nutrient availability was not investigated.

Table 2. Summary statistics for soil parameters measured in soil samples taken from pastures surrounding the mines (n=54)

	Mean	SD	Median	Min	Max	Normal range*
	Mean	DD	Micaran	1/1111		110111111111111111111111111111111111111
LOI (%)	16.2	10.5	13.2	6.1	61.2	
pН	6.2	0.9	6.3	3.5	7.9	
Cu (μg/g)	145	159	77	15	769	5-80
$\mathrm{Zn}\left(\mu\mathrm{g}/\mathrm{g}\right)$	131	68	113	39	342	20-300
$Cd (\mu g/g)$	0.9	0.6	1.0	0.0	2.6	0.03-0.3
Fe (%)	2.8	1.2	2.7	0.3	6.8	0.5-10

<sup>\*</sup> Normal range for mineral soils (Allan, 1989)

Some of the sites surrounding Mount Platt also had low pH, namely E5, F5, G5 and H6. All these sites were woody and were located close to the mines. The only other wooded site, H2, had a slightly higher pH of 5.04. The pH of soil in sites around the mines ranged from 3.5 to 7.7. Low pH values were detected at grid sites E-H, 4 and 5 in addition to H2, F7 and A4 with a range of 3.5 to 5.8, significantly more acidic than the other sites examined.

# Copper

All sites sampled on Mount Platt were found to contain Cu concentrations exceeding the normal range of 5-80  $\mu$ g/g with the exception of site 3 which had

a high associated standard deviation (Table 1 and Appendix II). High concentrations of this element were expected here since Cu was the principal element mined.

Almost half of the sites surrounding the mines exceeded the normal range of copper of 5-80  $\mu$ g/g indicating that contamination from the mines has spread to the surrounding area (Table 2 and Appendix II). The sites with highest Cu concentrations are those in the upper mining area and the southern site of the mining district (Fig. 2). The contaminated sites lay mainly in the direction of the prevailing wind which appears to be the source of the contamination. The remainder of the contaminated sites are located to either side of the mines and appear to be the product of other, more localised factors. The control sites were uncontaminated.

#### Zinc

The mean Zn concentration on Mount Platt was 342  $\mu$ g/g, slightly above the normal range of 20-300  $\mu$ g/g for mineral soils (Allan, 1989). However, the median of 179  $\mu$ g/g indicated that more than 50% of the samples had low Zn concentrations (Table 1). High zinc concentrations were found on the mines in sites 8, 9 and 12 with a range of 716 to 1184  $\mu$ g/g.

In the area surrounding the mines zinc concentrations are generally low with a mean of 131  $\mu$ g/g (Table 2). Only sites C4 (327  $\mu$ g/g) and H5 (392  $\mu$ g/g) were slightly elevated, probably because of their close proximity to the mine spoil. Therefore there is no evidence of zinc contamination spreading in the area.

#### Cadmium

The cadmium concentrations in the spoil were found to be low in comparison to the surrounding land. Overall cadmium concentrations are high with a mean of  $0.9 \,\mu\text{g/g}$  which is three times above the threshold limit (Table 2). It is unlikely that the elevated Cd concentrations are due to wind blow from the mine spoil as the concentrations in the spoil are comparatively low.

Singh and Steinnes (1994) reported that NPK fertilizers contain between 0.1 to 10  $\mu$ g/g Cd, depending on the source of rock phosphate, resulting in elevated

Cd concentrations in soils due to fertilizer application. Therefore fertilizer could be the source of the elevated concentrations in soil surrounding the mines. As most values recorded were close to the detection limit of 0.01 mg/l, Cd results must be considered as being less accurate than those of other metals.

#### Iron

No sample was found to contain excessive concentrations of iron, i.e. over  $100,000 \mu g/g$  (Allen, 1989).

#### Correlation of soil results

A Pearson Product-Moment correlation was carried out on the results obtained from analysis of soils surrounding the mines and a number of significant correlations were found (Table 3). All metals investigated showed strong significant correlations with each other (p<0.001). A strong significant negative correlation (p<0.001) was found between pH and soil organic matter. A negative relationship of pH with copper (p<0.05) was also seen.

Table 3. Pearson Product-Moment correlation of soil parameters, land use category and visibility of the mine for sites surrounding Mount Platt.

	рН	% loi	Cd	Cu	Fe
% loi	-0.708***				
Cd	0.100	-0.059			
Cu	-0.310*	0.249	0.562***		
Fe	0.063	-0.149*	0.495***	0.656***	
Zn	0.019	-0.099	0.534***	0.648***	0.619***

significance levels: p<0.001\*\*\*, p<0.01\*\*, p<0.05\*

When Pearson Product-Moment correlations were carried out on the results of spoil analysis significant relationships were found between cadmium and zinc (p<0.001) and copper and iron (p<0.05) as can be seen in Table 4.

Table 4. Pearson Product-Moment correlation of soil parameters, land use category and visibility of the mine for samples taken from Mount Platt.

	рН	% loi	Cd	Cu	Fe
% loi	0.287				
Cd	-0.056	-0.106			
Cu	-0.156	0.243	0.254		
Fe	0.336	0.312	0.116	0.508*	
Zn	-0.201	-0.256	0.844***	0.062	0.387

significance levels: p<0.001\*\*\*, p<0.01\*\*, p<0.05\*

The relationship between visibility of Mount Platt from the sites examined and the soil parameters analysed was determined by means of Analysis of Variance. Visibility was found to be a source of variance of loss on ignition (p<0.01). High loss on ignition is associated with low visibility indicating a negative relationship between the parameters. A relationship at the 95% interval was found between visibility and soil cadmium concentration.

Analysis of Variance found land use category to be a significant source of variance (p<0.001) for pH, loss on ignition, copper, cadmium and iron. Land use was a less significant source of variation for zinc (p<0.05). Manure from grazing animals increases the organic matter content of soil and provides potential for metal immobilization. Liming affects pH, which in turn affects metal solubility and potential for leaching. Fertilizer increases the nutrients in the soil and encourages the growth of different species. In tilled areas crop species are grown which are different to the natural vegetation of the area and decay at different rates, affecting organic matter content. As different species absorb different elements and nutrients from the soil, vegetation affects the soil composition. Untreated land is therefore chemically different to treated soil.

#### Vegetation

The results of analysis of vegetation are given in Appendices III and IV. The bulk of vegetation in the area surrounding the mines consisted of grass species. As there were few flowering heads identification of grasses could not be made to species level. A summary of analysis carried out is given in Table 5.

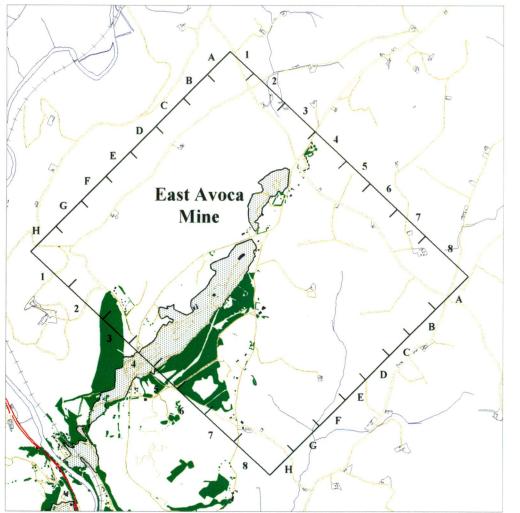




Figure 2: Contour plot of Cu concentration ( $\mu g/g$ ) on spoil and surrounding agricultural land

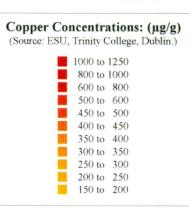


Table 5. Mean and standard deviation of copper, zinc, cadmium and iron concentrations in  $\mu$ g/g in plant species growing on sites surrounding the mines.

	n	Copper (sd)	Zinc (sd)	Cadmium (sd)	Iron (sd)
Juvenile Pinus	3	12	46	0.33	33.6
		(6.3)	(12.5)	(0.29)	(9.1)
Pinus needles	4	3.5	64	0.48	64
		(0.8)	(16)	(0.41)	(16)
grass species	56	12	44	0.08	171
		(4.7)	(37)	(0.19)	(126)
Calluna vulgaris	4	13	47	0	139
		(6.3)	(31)	(0)	(15)
Erica cinerea	6	9.1	42	0	118
		(2.7)	(17)	(0)	(40)
Normal range		2.5 - 25	15-100	0.03-0.3	40-500
(Allan, 1989)					

# Element analysis

The mean Cd concentrations were elevated in Juvenile *Pinus* and *Pinus* needles exceeding the normal range of 0.03-0.3  $\mu$ g/g. This indicates that trees, which have deeper roots than herbaceous species, are taking up higher concentrations of the element. This may be due to the presence of higher concentrations of the element deep in the spoil, which are then absorbed by the roots and translocated to the leaves.

A number of species not commonly found throughout the sampling region were also sampled (Appendix II). Among the garden plants examined, Parsley was found to contain significantly higher concentrations of Cd than the normal range (Allen, 1989). However the sample number was small and further replicates would have to be taken to confirm the validity of this result.

Vegetation growth on the disturbed mine site itself was very sparse. Results of analysis of vegetation taken from the spoil heap are given in Table 6. Mean

Cu concentrations in grass were slightly above the normal range. Mean Zn concentrations were found to be elevated in grass species and Calluna vulgaris, exceeding the normal range for plant material. However there was a high standard deviation associated with replicate in the latter case which negates its significance. Mean Cd concentrations were within the range of 0.03-0.3  $\mu$ g/g for all species while Fe concentrations exceeded the normal range in grass species. Most areas of the spoil were not vegetated due to factors such as toxicity, high porosity and low organic matter content leading to low water availability and poor slope stability.

Table 6. Mean and standard deviation of copper, zinc, cadmium and iron concentrations in  $\mu$ g/g in plant species growing on the mine spoil.

	n	Copper (sd)	Zinc (sd)	Cadmium (sd)	Iron (sd)
Juvenile Pinus	4	16.3	42.4	0.09	116
		(2.6)	(7.0)	(0.17)	(60)
Pinus needles	6	7.2	101	0.23	248
		(2.2)	(22.3)	(0.29)	(153.1)
grass species	4	28	197	0.17	1022
		(5.3)	(209)	(0.34)	(617)
Calluna vulgaris	1	15	363	0	946
Erica cinerea	2	14	49.5	0	501
		(4.2)	(4.9)	-	(114)
Ulex europaeus	1	11	39	0	194
Normal range		2.5 - 25	15-100	0.03-0.3	40-500
(Allan, 1989)					

### Analysis of individual sites

Species were examined on a site by site basis. The results can be seen in Appendix IV. Three sites were found to contain species exceeding the maximum normal Cd concentration (i.e. F5, H5 and H7). Sites F5 and H5 were located next to the mines and H7 had only one species, parsley, which contained high concentrations. All the sites also contained some species with typical levels of the element.

Sites 1 and 4 were found to contain some vegetation with excessive copper concentrations. Sites 1, 4 and 5 were found to contain vegetation with higher than normal iron concentrations. Sites 1 and 2 were found to contain species with excessive zinc concentrations. All these sites were located on the mines and contained species with normal concentrations of the elements. Therefore it can be seen that different species take up different concentrations of each element.

# Correlation of vegetation results

A Pearson Product-Moment correlation was carried out on the results obtained from analysis of vegetation growing in the area surrounding the mines and on the mine sites. The results can be seen in Table 7 and Table 8 respectively. In vegetation from the area surrounding the mines the relationship between Fe and Cu is significant (p<0.01). On Mount Platt the relationships between Fe and both Cu and Zn were found to be significant (p<0.001) indicating that the elements are transported together in vegetation.

Table 7. Pearson Product-Moment Correlation of vegetation samples taken from the area surrounding Mount Platt

	Cd	Cu	Fe	Zn	
Cd	1.000				
Cu	-0.175	1.000			
Fe	-0.157	0.351**	1.000		
Cd Cu Fe Zn	-0.037	0.017	0.036	1.000	

significance levels: p<0.001\*\*\*, p<0.01\*\*, p<0.05\*

Table 8. Pearson Product-Moment Correlation of vegetation samples taken from Mount Platt

	Cd	Cu	Fe	Zn	
Cd	1.000				
Cd Cu	-0.110	1.000			
Fe	-0.164	0.723***	1.000		
Zn	-0.114	0.368	0.813***	1.000	

significance levels: p<0.001\*\*\*, p<0.01\*\*, p<0.05\*

#### DISCUSSION

Some of the sites surrounding the Avoca Mines showed elevated Cu and Cd concentrations. High Cu concentrations were mainly detected on sites which lay in a south-westerly direction and also on the southern site of the mine (Fig. 2). Sites to the south of the mine site consisted mainly of uncultivated land used for sheep grazing. Merrington and Alloway (1994) found Cu accumulated in soils to a greater degree than Zn and Cd per unit input during their investigation of deposition rates and retention of metals in mined polluted soils.

Singh and Steinnes (1994) reported that maximum concentrations of some elements (As, Cd, Cu and Zn) in fertilizers such as N, P, NPK and liming material exceed background levels for soils. However, cases of soil contamination from these sources have only been linked to Cd, and not to Cu or Zn. The high levels of Cd found in some Avoca soils may have been introduced through application of fertilizer. Further investigation would be required to determine whether this is the case. Land use was found to be a significant source of variance for pH, loss on ignition, Cu, Cd and Fe concentrations. Therefore it is likely that fertiliser is one of the factors contributing to the variation.

The lowest losses on ignition and pH values were found on Mount Platt. The substrate consists mainly of spoil, overburden and waste material and therefore is probably lacking in cation exchange sites. Therefore little binding of metals is likely to take place on the mines and there is great potential for leaching which can result in loss of nutrients. Some of the soils surrounding the mines were found to have high loss on ignition indicating slow breakdown of material. This is likely to be due to the woody plant material growing on these sites rather than inhibition of micro-organisms.

Vegetation samples were only collected at about 50% of the mine sites, as others did not support any vegetation. The low pH, lack of soil structure due to low organic matter, poor nutrient content and elevated metal concentrations in some of the spoil probably account for the lack of vegetation.

Phytotoxicity was recorded on some pine trees growing on the mines, and at site E5. This could be a product of low pH or poor nutrient conditions in the substrate, and may not necessarily be linked to metal toxicity. Further studies would have be carried out in order to determine the precise cause of the damage and to determine whether invisible damage such as reduction in dry matter production, lower plant yield, and tissue damage is also occurring. The main problem areas were found to be sites at the edge of the spoil possibly due to extensive runoff. One site contained vegetation exceeding the normal range for three elements and another site for two elements. Toxic symptoms are said to be usually only found in plants when the total concentration of individual metals in soils exceeds 1,000  $\mu$ g/g (Bradshaw and Chadwick, 1980). Some of the mine sites showed concentrations exceeding this for both Cu and Zn. However some of these sites were vegetated indicating some plants have developed tolerance to the element. Considerable quantities of acid mine drainage are generated within the spoil with pore water highly acidic (pH < 2.5) and high in metals, making conditions for plant growth extremely difficult. At site E5 considerable phytotoxicity of pine trees was observed. This site was heavily contamined by a small spoil heap part of which is still visible in the centre of the 250 x 250m grid square...

The region surrounding the mines appeared to be well vegetated with no visually apparent damage plant tissue. Vegetation sampled comprised mainly of grass species. Increased metal content in grass species due to soil-plant transfer was not evident. The trace element concentrations of the above ground portion of plants reflect only to a small degree amounts present in soil due to the limited uptake and translocation of the elements (Abrahams and Thornton, 1994). The mean Cd concentrations were above the normal range of 0.03- $0.3~\mu g/g$  for Juvenile *Pinus* and *Pinus* needles. In experiments using *Lolium perenne* and *Brassica rapus* Eriksson (1989) found indications that the Cd content decreased in both crops as the pH level increased. The effect was more pronounced in rape seed.

Soil and grass species examined for Cu, Fe and Cd concentrations at agriculture sites within the Hayle-Camborne-Redruth mining province of south-west England, principally important for mining of Sn and Cu, were compared with results gained in this study as can be seen in Table 9. Soils in south-west England show a similar Cu, Zn and Fe concentrations to Avoca, while herbage samples from the Avoca sites indicate a wider range of Cu and

Zn concentrations. Soil-plant transfer of metals is not apparent. However there is clear evidence that contamination from dust deposits from the mining operation and spoil has occurred, particularly in those areas affected by the prevailing winds.

Table 9. Soils and herbage species examined for Cu ( $\mu$ g/g), Zn ( $\mu$ g/g), Cd ( $\mu$ g/g) and Fe (%) in agricultural land in a metalliferrous area in S.W. England (Abrahams and Thornton, 1994) compared to Avoca.

		Soil		Herbage			
	S.W.	Avoca	North-	S.W. England	Avoca		
	England	Ireland	Somerset		Ireland		
	n=12	n=55	n=174				
Cu (µg/g)	12-319	15-342	2.8-145	8-23	4-25		
$\mathrm{Zn}\left(\mu\mathrm{g}/\mathrm{g}\right)$	29-365	39-342	14-8344	25-62	0-199		
$Cd (\mu g/g)$	-	0-2.6	0.5 - 127	-	0-0.8		
Fe (%)	1.1-5.9	0.3-6.8	-	$42\text{-}1224~\mu\mathrm{g/g}$	$52\text{-}413 \mu\mathrm{g/g}$		

It was concluded that individual species are not severely affected by metals associated with mining as concentrations were generally within the normal ranges. The only sites to exhibit contamination were located on or close to the spoil. These sites contained higher than normal concentrations in some species but not others. The main problem areas were sites 1 and 4 as site 1 contained vegetation exceeding the normal range for three elements and site 4 for two elements. However as these were mine sites this is unlikely to be problematic in terms of area management. Sites with elevated Cd concentrations could give rise to problems for agriculture.

Overall the vegetation is in good condition and no difficulties are posed to agriculture due to plant uptake. There are some problems posed to rehabilitation of the mines. Further studies would have to be carried out to determine the most suitable rehabilitation scheme for the area and the most suitable cultivars. Damage to existing species on the mines, principally pine, would have be assessed to determine the precise cause. There appears to be little damage to the area surrounding the mines although prevailing winds appear to be associated with some spread of copper.

#### REFERENCES

**Abrahams, P.W. and Thornton, I.** (1994). The contamination of agricultural land in the metalliferrous province of Southwest England: implications to livestock. *Agriculture, Ecosystems and Environment*, **48**, 125-137.

**Allen, S.E.** (1989). Chemical analysis of ecological materials. Blackwell Scientific Publications, Oxford.

Bradshaw, A.D. and Chadwick, M.J. (eds.) (1980). The restoration of land. Blackwell Scientific Publications, Oxford.

Chase, D.S. and Wainwright, S.J. (1983). The vertical distribution of copper, zinc and lead in weathered tips of copper smelter waste in the lower Swansea valley. *Environmental Pollution*, **5**, 133-146.

**Eriksson, J. E.** (1989). The influence of pH, soil type and time on adsorption and uptake by plants of Cd added to the soil. *Water, Air, and Soil Pollution* **48**, 317-335.

Fitzpatrick, E.A. (1983). Soils. Their formation, classification and distribution. Longman Scientific and Technical.

Martin, M.H. and Coughtrey, P.J. (1981). Impact of metals in ecosystem function and productivity. In: *Effect of Heavy Metal Pollution on Plants: 2*, (Ed. N.W. Lepp). Applied Science Publishers, London.

Merrington, G. and Alloway, B.J. (1994). The flux of Cd, Cu, Pb and Zn in mining polluted soils. *Water*, *Air and Soil Pollution*, **73**, 333-344.

**Platt, J.W.** (1973). Avoca. In *Mining Ireland* (Ed. H. Legge). Irish Publishing Company Ltd., Dublin.

**Platt, J.W.** (1975). Environmental control at Avoca Mines Ltd, Co Wicklow, Ireland. In *Mining and the environment*. (Ed. M.J. Jones). The Institution of mining and metallurgy, London, 731-758.

**Shetron, S.G.** (1983). Alfalfa, *Medicago sativa* (cultivar Vernel), establishment in mine mill tailings: 1 - plant analysis of Alfalfa grown on iron and copper tailings. *Plant and Soil*, **73**, 239-246.

Singh, B. R. and Steinnes, E. (1994). Soil and water contamination by heavy metals. In *Soil processes and water quality*, (Ed. R.Lal and B.A. Steward) Advances in Soil Sciences, Lewis Publications, London, 233-271.

Soldevilla, M., Maranon, T. and Cabrera, F. (1992). Heavy metal content in soil and plants from a pyrite mining area in Southwest Spain. Communication in Soil Science and Plant Analysis, 23, 1301-1319.

**Thornton, I.** (1980). Geochemical aspects of heavy metal pollution and agriculture in England and Wales,. In *Inorganic Pollution and Agriculture*. Ministry of Agriculture and Fisheries and Food, HMSO, London, 105-125.

**Tyler, G.** (1984). The impact of heavy metal pollution on forests: a case study of Gusum, Sweden. *Ambio.*, **13**, 18-24.

Wallace, A. and Berry, W.L. (1978). Trace elements in the environment - effects and potential toxicity of those associated with coal. In *Ecology and coal resource development* (Ed. M.K. Wali).. Pergamon Press, New York. 95-104.

Williamson, N.A., Johnson, M.S. and Bradshaw, A.D. (1982). *Mine wastes Reclamation*. Mining Journal Books Ltd., London.

# APPENDIX I

The sites examined, description of vegetation, category of land use, and visibility of Mount Platt from the site where + indicates visibility, and - indicates absence of visibility.

Site	Type of land use	Land use Category	Visibility of source
A4	Edge of football pitch, gorse, heather	9	-
B1	Silage, freshly cut	2	-
B2	Permanent pasture	3	-
B3	Barley, limed, poor growth	5	+
B4	Permanent pasture	3	
B5	Barley	5	+
B6	Barley	5	+
B7	Rough permanent pasture	1	+
B8	Barley - tillage	5	+
C1	Silage, freshly cut	2	-
C2	Permanent pasture, cattle	3	-
C3	Permanent pasture, cattle, luxuriant grass	$\frac{2}{3}$	+
C4	Permanent pasture	3	-
C5	Barley	5	+
C6	Barley	5	+
C7	Permanent pasture, silage	2	+
C8	Permanent pasture, silage	2 2 5	+
D1	Barley	3	+
$D_2$	Permanent pasture, cattle	9	+
D3 D4	Rough grazing, overgrown bog	3	_
$D_5$	Permanent pasture Permanent pasture, cattle	3	_
$D_{6}$	Permanent pasture, cattle	3	+
$\overline{D7}$	Permanent pasture, cattle	3 3 5	+
D8	Permanent pasture cattle	3	+
E1	Barley	5	+
E2	Permanent pasture, cattle	3	+
E3	Permanent pasture, sheep	4	-
E4	Permanent pasture, hay	3	-
E5	Pine forest, c.a. 15 yrs old, some dieback		
	of trees, receiving AMD	6	-
E6	Permanent pasture, cattle	3	+
E7	Silage	2	+
E8	Permanent pasture, silage	2 2 5	-
F1	Barley	5	-
F2	Permanent pasture, cattle	3	+
F3	Steeply sloped rough pasture	3	-
F4	Rough land, heather, gorse	9	-
F5	Pine forest - clearing with grass and		
	heather - some dieback of trees	6	-
F6	Permanent pasture (sheep)	4	+
F7	Scrub, Gorse, grass, ferns	9	+

F8	Permanent pasture, sheep	4	+
G1	Oats	5	+
G2	Permanent pasture	4	+
G3	Permanent pasture	4	-
G4	Rough pasture	1	+
G5	Pine forest - clearing with grass and		
	heather - some dieback of trees	6	-
G6	Permanent pasture (sheep)	4	+
G7	Permanent pasture, sheep	4	+
G8	Permanent pasture, sheep	4	+
H1	Permanent pasture	3	-
H2	Beech woodland, very deep litter	7	-
H3	Permanent pasture	3	+
H4	Rough pasture, gorse	1	+
H5	Pine forest, c.a. 15 yrs old, some dieback		
	of trees, receiving AMD	6	-
H6	Mature larch forest no grass, heather,		
	mainly moss	6	-
H7	Permanent pasture	4	-
H8	Permanent pasture, sheep	4	+

#### **Mine sites on Mount Platt**

- On edge of upper pit, fence. Revegetation occurring, sparse development, pines mainly stunted
- 2 As 1 but more open area of stony material. Grass on top of rabbit dung only.
- 3 Edge of Mount Platt, forest side of road, pine, grass on rubbish
- 4 As 1 opposite side of road to fence, sparse development, no grass, individual pine and birch.
- 5 Opposite road, spoil heaps with low-form Pine and birch. All young. Some heather
- No vegetation on Mount Platt, within fence, half way up, near Mottee stone. Stunted pine and some heather. No other vegetation
- 7 Dry whitish material, no vegetation.
- 8 Dry, darker material, very friable, very dry and warm
- 9 As 8
- 10 Dry, friable, dusty ochre-coloured material
- 11 Dry, less compacted, finer material
- 12 As 11
- 13 At entrance of Mt. Platt. Small red material
- 14 Near spring at base of Mt. Platt.

APPENDIX II

Mean and standard deviation of soil parameters measured in soil samples taken from Avoca.

Site	pН	sd	loi	sd	Cd	sd	Cu	sd	Fe	sd	Zn	sd
1	3.58	0.01	3.02*	0.24	0.34	0.59	422	4.0	52350	1622	170	3.8
2	3.88	0.02	4.81	0.06	1.37	0.62	1107	77	99216	2529	174	11
3	4.47	0.02	4.32*	0.03	0.36	0.62	368	395	43329	38008	148	94
4	3.81	0.03	3.2	1.39	1.73	0.57	875	156	74931	4669	227	43
5	4.45	0.02	4.94*	0.32	1.0	0.01	261	26	48486	5626	86	28
6	4.40	0.03	4.04*	0.01	0.34	0.59	1077	4.36	89379	5041	122	10
7	2.79	0.06	3.17*	0.06	0.35	0.61	317	20	31516	2930	253	194
8	2.59	0.03	3.59*	0.06	2.42	1.61	1235	55	25728	982	716	296
9	3.53	0.02	3.44*	0.01	2.46	0.55	494	24	28460	1346	1184	94
10	3.57	0.07	1.55*	1.30	0	0	428	24	40874	4136	120	25
11	2.85	0.03	2.37*	0.30	1.02	0.01	548	51	47929	4351	324	52
12	3.67	0.03	2.51*	0.11	3.62*	0.89	584*	28	59597*		936*	159
13	2.76	0.08	4.06**	-	0.34	0.58	838	19	91064	1582	145	18
14	2.62	0.07	4.32	0.55	0.65	0.57	654	52	36918	1477	184	38
A4	5.01	0.04	19.47	0.25	1.01	0.01	85	4	29279	1356	144	25
B1	6.35	0.01			1.04	0.04	25	0.58	26126	2430	101	15
B2	6.27	0.10	31.03	2.11	1.01	0.03	50	7.6	23799	2872	118	13
B3	6.05	0.07	7.61	0.12	0.61	0.54	57	3.1	17706	717	112	4.5
B4	5.88	0.02	14.39	0.26	1.01	0.01	165	1.73	24509	571	158	3.61
B5	7.31	0.09	9.02	0.27	1	0.02	70	1.73	29398	919	124	11
B6	6.92	0.09	10.25	0.50	0.98	0.02	77	3.2	32750	627	159	13
B7	5.95	0.04	11.56	0.16	0	0	36	1.15	20575	1698	59	6.6
B8	6.80	0.06	7.36	0.12	0.97	0.06	62	1.73	30357	623	138	55
C1	7.13	0.14	-	-	0.70	0.60	18	2.1	33059	714	89	19
C2	5.92	0.11	13.1*	0.28	0	0	15	1.5	10627	1718	44	16
C3	6.53	0.04	12	0.15	0.99	0.09	110	2.1	27440	465	196	26 15
C4	7.71	0.03	16	0.12	2.0	0.02	420	14	26176	$1660 \\ 1445$	327 99	9.3
C5	6.86	0.09	9.5	0.14	0.64	0.56	69 50	4.6	28254 32966	1582	$\frac{99}{144}$	61
C6	6.37	0.03	8.9	0.08	0.96	0.06	59 39	$\frac{2}{1}$	36017	304	86	3.5
C7	6.24	0.03	14	$0.46 \\ 0.33$	$\frac{1}{0.34}$	$0.03 \\ 0.59$	60	6.4	32537	1757	196	128
C8	5.98	$0.08 \\ 0.03$	9.8 7.3*	0.33	1.0	0.02	20	1	22565	665	93	13
D1	6.78						22	1.9	13266	14513	39	7.9
D3+	5.56	0.09	23.6	$0.30 \\ 2.2$	$0.17 \\ 1.0$	$0.42 \\ 0.03$	$\frac{22}{370}$	$\frac{1.9}{32}$	54515	1171	118	3.2
D4	7.29	0.03	20.1	0.72	1.7	0.03	57	3.1	25194	1539	81	11
D5	6.17	$0.09 \\ 0.04$	20.9	0.72 $0.35$	1.1	0.01	58	13	23783	961	113	13
D6	6.60	0.04 $0.21$	12 13*	0.35	0.52*	0.01	77*	1.4	29123*		239*	89
D7	6.15				1.03							
D8	7.42	0.07	6.1	0.49	0.95	0.03	41	1.2	27273	372	88	5.3
E1 E2	6.72	0.08	12.1*	0.35	0.49*	0.69	30*	4.2	19583*		253*	221
E3	6.47	0.04	14.9	0.23	1	0.01	118	5.8	15612	933	65	3.6
E4	5.67	0.03	16.6	0.15	0.98	0.02	149	3	26819	287	110	13
E5	4.17	0.04	25.6*	0.71	0.97	0.03	483	22	22073	660	86	14
E6	7.86	0.15	12*	0.35	1.1	0.01	135	4	27704	2529	167	15
E8	6.51	0.06	9.08	0.24	0.60	0.53	132	24	28861	2722	137	7.4
F1	7.43	0.05	9.3	0.32	1.9	0.08	50	0.58	28710	646	112	14
F2	6.59	0.09	6.7*	0.1	0.33	0.57	70	9.7	11544	1097	97	25
F3	5.87	0.09	13.6	0.28	1.0	0.02	34	1.5	10309	511	54	23
F4	5.12	0.11	38.8	1.1	0	0	137	6.2	31358	1489	84	5.6
F5	4.22	0.04	38	1.8	1.0	0.03	120	2.5	16087	1199	104	12
F6	6.21	0.04	12.9	0.32	0.97	0.05	472	18	48503	2216	195	14
F7	4.96	0.08	16.4	0.35	0	0	45	2.6	18574	1563	69	8.1
F8	6.89	0.07	9.3	0.04	1.2	0.53	135	8.4	28957	383	177	16
G1	6.30	0.05	11.8	0.38	0	0	31	0.58	25555	688	125	37

G2	6.47	0.08	10.4	2.2	0.97	0.02	64	21	18024	1233	69	41
G3	6.44	0.08	13.3	0.31	0.97	0.03	97	1.7	34314	400	72	19
G4	5.33	0.08	23.5	0.83	2.6	0.53	461	10	40299	1693	203	12
G5	4.08	0.05	45.1	3.6	1.1	0.01	270	7.0	9011	205	69	6.7
G6	6.15	0.05	14.0	0.37	0.98	0.08	387	20	34031	2521	105	13
G7	6.61	0.03	9.9	0.14	0.97	0.06	211	6.4	37520	1538	104	1.7
G8	6.24	0.05	14.6	0.15	1.01	0	195	13	31315	1478	174	37
H2	5.04	0.10	61.2*	0.85	0	0	27	1	2719	70	166	155
H3	6.31	0.04			1.0	0.01	71	4.0	16961	1619	45	11
H4	5.84	0.12	23	0.38	2.0	0.02	488	6.9	60466	1996	307	17
H <sub>5</sub>	3.52	0.04	10.6*	0.57	2.0	0.02	769	11	68172	2611	342	17
H <sub>6</sub>	4.42	0.04			0.33	0.57	78	4.5	25677	614	67	15
H7	7.15	0.05	13.7	0.20	0.96	0.08	256	16	30017	3677	138	4.9
H8	6.58	0.04	13.8*	0.35	0.33	0.57	123	3.8	27128	225	155	5.5

<sup>+- 6</sup> readings for all metals analysed \* - two readings \*\* - one reading

loi - loss on ignition sd - standard deviation

#### APPENDIX III

(i) Cadmium concentrations  $(\mu g/g)$  contained in each species in sites surrounding the mines where results are obtained from the mean of species over all sites examined

species	mean	median	no.	sd	min	max
Calluna vulgaris	0	0	12	0	0	0
Erica cinerea	Õ	Ŏ.	18	0	0	0
Hordeum distichon	0	Ö	6	0	0	0
Juvenile <i>Pinus</i>	0.40	0	5	0.58	0	1.02
Pinus needles	0.48	0.43	12	0.50	0	1.06
Plantago lanceolata	0	0	3	0	0	0
Pseudotsuga menziesii	0	0	6	0	0	0
grass	0.08	Ö	155	0.33	0	2.29
grass flowers	0	Ŏ	4	0	0	0
leek bulb	Õ	Ŏ	3	0	0	0
leek leaves	Õ	0	3	0	0	0
leek roots	Õ	ŏ	1	-	0	0
parsley	0	Ŏ	3	0	0	0
parsley leaves	0.98	0.93	3	0.10	0.92	1.1
maturing <i>Pinus</i> cones	0.00	0.00	3	0	0	0
onion leaf	0	ŏ	3	Ŏ	0	0
onion stem	0	Ŏ	3	Ŏ	Ŏ	Õ
	0	0	3	0	0	Õ
spinach	<u> </u>	U	<u> </u>	0		

(ii) Copper concentrations  $(\mu g/g)$  contained in each species in sites surrounding the mines where results are obtained from the mean of species over all sites examined

species	mean	median	no.	sd	min	max
Calluna vulgaris	13	11	12	7.2	8.8	34
Erica cinerea	9.1	8.9	18	2.9	5.2	17
Hordeum distichon	8.5	8.5	6	0.4	8	9.1
Juvenile <i>Pinus</i>	13	10	5	5.6	6.9	20
Pinus needles	3.5	3.2	12	0.96	2.0	5.9
Plantago lanceolata	7	6.8	3	0.38	6.6	7.4
Pseudotsuga menziesii	4.1	4.3	6	0.87	3.1	5.0
grass	12	11	155	5.8	4.1	49
grass flowers	22	24	4	9.8	9.5	33
leek bulb	0.67	0.85	3	0.60	0	1.16
leek leaves	8.7	5.5	3	6.0	5.0	16
leek roots	24	24	1	-	24	24
parsley	10	11	3	0.8	9.6	11
parsley leaves	4.5	4.6	3	0.15	4.4	4.6
maturing <i>Pinus</i> cones	13	13	3	0.47	12	13
onion leaf	0.94	0.96	3	0.07	0.86	0.99
onion stem	1.3	0.99	3	0.61	0.98	2.05
spinach	13	11	3	5.1	8.7	18

(iii) Iron concentrations  $(\mu g/g)$  contained in each species in sites surrounding the mines where results are obtained from the mean of species over all sites examined

species	mean	median	no.	sd	min	max
Calluna vulgaris	139	137	12	19	115	183
Erica cinerea	118	105	18	41	65	194
Hordeum distichon	145	150	6	29	110	179
Juvenile <i>Pinus</i>	35	41	5	9.2	25	44
Pinus needles	69	59	12	29	44	123
Plantago lanceolata	48	47	3	5.7	44	55
Pseudotsuga menziesii	50	51	6	7.5	37	59
grass	174	120	155	162	41	1628
grass flowers	83	80	4	11	75	98
leek bulb	305	34	3	482	20	861
leek leaves	47	43	3	8.8	41	57
leek roots	361	361	1	-	361	361
parsley	55	51	3	17	41	73
parsley leaves	54	53	3	2.9	51	57
maturing Pinus cones	7.5	7.7	3	0.7	6.6	8.0
onion leaf	46	26	3	38	23	90
onion stem	14	13	3	2.4	12	16
spinach	94	71	3	58	50	160

(iv). Zinc concentrations ( $\mu g/g$ ) contained in each species in sites surrounding the mines where results are obtained from the mean of species over all sites examined

species	mean	median	no.	sd	min	max
Calluna vulgaris	47	48	12	33	14	125
Erica cinerea	42	44	18	19	7.3	68
Hordeum distichon	287	28	6	590	5.7	1484
Juvenile <i>Pinus</i>	43	43	5	10.5	31	59
Pinus needles	64	63	12	18	40	104
Plantago lanceolata	48	47	3	21	27	69
Pseudotsuga menziesii	72	41	6	62	20	151
grass	45	33	155	61	0	583
grass flowers	38	38	4	11	25	51
leek bulb	0	0	3	11	0	10.2
leek leaves	17	23	3	16	0	28
leek roots	31	31	1	-	31	31
parsley	16	20	3	9.9	4.3	22
parsley leaves	9.7	9.8	3	6.9	2.8	17
maturing <i>Pinus</i> cones	87	83	3	11	79	99
onion leaf	0	0	3	1.6	0	0
onion stem	0	0	3	9.3	0	0
spinach	17	8.2	3	21	2.0	40
no = number $sd = stand$	dard devi	ation	min = mini	imum	max =	maximum

Mine site results are contained in Table 6.

APPENDIX IV

Mean and standard deviation of metal concentrations analysed in each species taken from each site examined in Avoca ( $\mu g/g$ ).

Site	Species	Cd	sd	Cu	sd	Fe	sd	Zn	sd
1	Juvenile Pinus	0.34	0.59	19	0.63	73	39	48	6.1
1	Pinus needles	0.32	0.55	6.6	0.18	174	18	115	3.0
1	grass	0	0	32	2.1	1876	189	502	53
	Juvenile Pinua	0	0	18	1.1	56	5.7	34	8.1
2 2	Pinus needles	0	0	6.5	0.39	123	2.6	82	11
2	Grass	0	0	26	7.5	726	386	159	53
3	Pinus needles	0.72	1.2	10	0.49	453	42	122	80
3	Grass	0.67	1.2	21	1.2	452	39	57	22
4	Juvenile <i>Pinus</i>	0	0	15	0.32	169	92	39	4.0
4	Pinus needles	0	0	9.5	2.3	432	21	64	7.2
4	Grass	0	0	32	0.75	1035	18	69	7.5
5	Calluna vulgarts	0	0	15	0.58	946	61	363	465
5	Erica cinerea	0	0	11	2.1	421	40	53	39
5	Juvenile Pinus	0	0	13	0.79	165	79	48	10
5	Pinus needles	0	0	4.2	1.1	118	17	111	29
5	Ulex europaeus**	0	0	11	0.15	194	0.9	39 46	12
6	Erica cinerea	0	0	17	0.15	582	93		64
6	Pinus needles	0.32	0.55	6.3	0.38	190	12 5.7	110 19	18
A4	Erica cinerea	0	0	14	3.3	167 360	183	68	10
A4	Grass	0 0.35	0 $0.61$	17 8.7	10 1.1	82	12	116	154
B1	Grass	0.33	0.01	13	0.89	240	12	47	28
B2 B3	Grass Grass	0	0	11	0.57	109	69	24	8.6
B4	Grass	0.35	0.60	19	4.2	95	1.1	50	9.9
B5	Grass	0.55	0.00	16	0.19	182	12	17	2.2
B6	Grass	0	0	17	0.91	187	11	84	28
B7	Grass	0	0	13	3.6	222	60	0.70	1.6
B8	Grass	0	0	7.8	0.27	119	6.6	0	3.4
C1	Grass	0.32	0.56	9.9	0.72	181	40	39	12
C2	Grass	0	0	7.9	0.93	164	84	55	5.9
C3	Grass	0	0	11	0.60	102	8.3	26	8.2
C4	Grass	0	0	25	21	89	13	34	17
C5	Grass	0	0	16	0.23	100	16	6.6	6.7
C6	Grass	0	0	17	1.7	223	1.8	34	13
C7	Grass	0	0	11	6.4	95	29	47	86
C8	Grass	0	0	11	1.7	144	21	199	333
D1	Grass	0	0	12	1.3	113	18	38	25
D2	Grass	0.41	0.71	6.7	0.66	72	9.9	35	11
D3	Calluna vulgaris	0	0	23	10	154	26	29	23
D3	Grass	0	0	8.1	1.3	87	11	55	12
D3	Grass flowers	0	0	21	12	86	12	38	13
D4	Grass	0	0	11	0.45	192	11	27	5.8
D5	Grass	0.38	0.66	9.7	2.7	92	14	25	11
D6	Grass	0	0	8.7	0.75	254	59	73	51
D7	Grass	0	0	8.2	0.61	248	24	35 19	12 7.5
D8	Grass	0	0	11	2.5	203 131	$7.3 \\ 33$	565	7.5
E1	Hordeum distichon	0	0	8.8	$0.27 \\ 1.2$	160	$\frac{33}{12}$	117	93
E2	Grass	0	0	9.8 18	8.1	263	220	43	22
E3	Grass	0	0	6.0	0.90	85	6.8	68	17
E4	Grass	0	U	27	0.30	75	0.0	38	11
E4	Grass flowers**  Erica cinerea	0	0	7.1	1.6	78	5.3	55	8.3
E5 E5	Juvenile <i>Pinus</i>	0.49	0.69	19	0.78	43	2.3	34	4.5
E5	Pinus needles	0.49	0.03	3.1	0.06	113	8.8	51	8.9
E5	Grass**	0	U	6	0.00	84	0.0	0	
E6	Grass	0.75	1.3	16	1.7	413	67	46	10
EO	Glass	0.10	1.0	10	2.1	110	- 1		

TIC	TIS TIS	118	H7	H7	H7	H7	H7	H7	H7	H7	H7	H6	H5	H5	H5	H5	H4	H4	H4	H3	H2	H2	H	G8	G7	B	GS	S	G5	G5	94	G3	G2	95	F) -	된.	F7	F6	된 !	F)	F5	F5	F4	F4	F4	F3	F2	F1	मू ह	F.7
GIUSE	I minugo mincomia	Diantago langolata	Parslev	Parsley leaf	Spinach	Onion stem	Onion leaf	Leek root**	Leek leaf	Leek bulb	Grass	Pseudotsuga menziesii	Grass	Pinus needles	Juvenile Pinus**	Erica cinerea	Grass	Erica cinerea	Calluna vulgaris	Grass*	Grass	Pseudotsuga menziesii	Grass	Grass	Grass	Grass	maturing Pinus cones	Grass	Pinus needles	Calluna vulgaris	Grass	Grass	Grass	Grass	Grass	Grass (2)	Grass	Grass	Grass	Pinus needles	Juvenile <i>Pinua</i>	Erica cinerea	Grass	Erica cinerea	Calluna vulgaris	Grass*	Grass	Hordeum distichon	Grass	Fraga
00	0 76	0	0	0.98	0	0	0	0	0	0	0	0	0	0.69	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.29	0	0	0	0	0	0	0	0	0	0.72	0.92	0.51	0	0	0	0	0	0.35	0	0	0
1	- c	<b>&gt;</b> (	0	0.10	0	0	0		0	0	0	0	0	0.60		0	0	0	0	0	0	0	0	0	0	0	0	0	0.50	0	0	0	0	0	0 (	0 (	0	0	0.62	0.07	0.72	0	0	0	0	0	0.60	0	0	0
0.0	6.6	70	10	4.5	13	1.3	0.94	24	8.7	0.67	00	3.7	21	2.7	6.9	8.7	0.9	9.2	12	14	14	4.6	11	27	5.4	13	13	15	4.5	9	10	10	8.2	4.2	8 P			17	00	3.6	10	8.3	11	6.8	9.5	15	6.7	8.2	13 i	χ .Σ
1	10	0.38	0.77	0.15	5.1	0.61	0.07		6.0	0.60	0.47	0.91	6.4	0.61		0.35	0.46	0.45	0.36	2.1	2.6	0.63	1.1	2.3	0.55	0.27	0.47	5.5	1.3	0.42	1.4	1.2	2.7	0.03	<u>ا</u> ا	1.4	1.9	0.94	1.6	0.63	0.21	0.99	1.6	0.51	0.71	0.59	1.3	0.29	0.52	0.39
	י הכ	48	ST ST	54	94	14	46	361	47	305	77	55	266	45	25	200	76	112	136	354	311	45	91	400	58	164	7.5	66	71	119	77	288	710	52	100	72	76	272	83	47	34	165	115	102	146	474	126	160	81	75
	70	7	17	2.9	58	2.4	38		8.8	482	20	3.6	67	0.83		5.7	0.75	42	10	15	151	6.8	9	28	8.4	15	0.73	7.2	1.6	3.8	6.7	90	795	15	OT !	1.7	12	68	5.2	1.8	10	27	42	5.7	8.7	163	13	19	12	3 7
	42	48	16	9.7	17	0	0	31	17	0	0.55	29	65	60	99	63	93	52	51	89	82	115	55	60	0.71	23	87	87	87	19	43	69	32	34	0	1.4	13	15	26	59	44	35	55	28	89	77	14	8.9	31	49
	18	21	9.9	6.9	21	9.3	1.6		16	11	5.5	10	19	4.4		5.0	4.0	11	6.5	22	31	63	10	15	3.2	7.0	11	33	19	4.4	5.1	71	1.6	9.3	2.9	1.2	33.57	7.4	14	17	1.6	6.1	24	15	30	41	6.4	5.3	12	12

<sup>\*\* = 1</sup> Rep only \* = 2 reps only