AERIAL AND AQUEOUS DISPERSION OF INORGANIC CONTAMINANTS - SIGNIFICANCE FOR THE CORNISH FARMING INDUSTRY[1]

Caroline P. Waller[2], Richard P. Edwards[2] and Carolyn Wilkins[3].

Abstract: Cornwall has numerous derelict Cu-Sn mine sites scattered throughout the county - a legacy of past intensive mining activity. Due to the toxic concentrations of heavy metals many sites are poorly vegetated which leads to continued dispersion of toxic metals into the surrounding farming environment.

The aim of this research is to establish the extent of contamination, to determine its form, and to ascertain how much dispersion is currently occurring. A case study of the Tresavean Mine near Redruth, west Cornwall, UK, has shown that the distribution of As and Cu from the mine extends up to 150 m. An extensive soil survey of the farmland surrounding the mine revealed two distinct distribution patterns for As and Cu. Arsenic distribution appears to correlate with the prevailing wind direction at the site, whereas the Cu distribution follows the down slope drainage pattern.

Sequential extractions were made on soil samples taken at intervals along a transect from the mine to determine which soil fractions Cu and As are held in; i.e. water-soluble, exchangeable, adsorbed, organic, Fe-Mn oxides or residual. These sequential extractions indicate the Cu is held mainly in the residual and organic fractions and As is held mainly in the residual and iron-organic fractions. Although the absolute concentrations of As and Cu decrease with distance from the mine site, as expected, the percentage of As and Cu in each fraction does not follow this pattern in every case.

Additional Key words: Copper, arsenic, mine waste, soil, sequential extractions.

Introduction

During the heyday of Cornish mining from 1750 to 1900 numerous Cu-Sn mines were operating throughout the county. The "boom-bust" activity of these mines has left a legacy of derelict mine sites scattered across south-west England. Reclamation was virtually unheard of during the height of Cornish mining, and the closed mines were left in a state of dereliction with no remedial action taken. This left high concentrations of heavy metals at the surface which has deterred natural revegetation of some sites. This is how they have remained to the present day. The lack of vegetative cover exacerbates the continued dispersion of metals into the surrounding farmland.

Previous work carried out in south-west England has highlighted the problem of As-Cu contamination in this region (Abrahams and Thornton 1987, Colbourn et al. 1975, Gaukroger 1986). Copper and As are potentially toxic to animals and man if present in large amounts (Thornton 1980). Copper can also be phytotoxic (Kabata-Pendias and Pendias 1991, Lepp 1981) and therefore needs to be monitored in the farming environment. In Cornwall, where background values of both of these elements are naturally high (Abrahams and Thornton 1987), guidelines need to be followed for land which is subject to a change of use, for example, returning derelict mine sites to farmland (ICRCL 1990) or where planning permission is required (ICRCL 1983). However, "trigger values" ("trigger value" is defined as "that below which the soil is considered to be safe, i.e. the concentration present should not give rise to phytotoxicity or zootoxicity effects" (ICRCL 1990)) given in these ICRCL

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[2]Caroline P. Waller, Postgraduate, Richard P. Edwards, Senior Lecturer, University of Exeter, Camborne School of Mines, Pool, Redruth, Cornwall, UK.
[3]Carolyn Wilkins, Geochemist, CSM Associates Ltd., Rosemanowes, Herniss, Penryn, Cornwall, UK.

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guidelines are difficult to use in Cornwall because the county's naturally elevated background concentrations are very close to the "trigger values". The local farming community (which farms predominantly livestock) has experienced the problems of high soil-As concentrations. Animals grazed in high soil-As areas endure a period of poor health while becoming accustomed to the higher As levels. As these problems of As and Cu contamination are inherent in Cornwall, this paper will concentrate on these two elements.

The study area for this research was the Tresavean Mine, Lanner, near Redruth, west Cornwall, United Kingdom (fig.1). Tresavean is an old, disused, underground mine with records dating back to 1745. It was a rich mine with relatively high quality copper ore. During its history it has been closed and reopened a number of times due to fluctuating markets, but finally closed in 1928. Dines (1956) states that Tresavean produced over 3,000 tons of black tin (tin concentrate for smelting), 13 tons of arsenic and 228,000 tons of copper ore.

Tresavean straddles the contact of the Carnmenellis Granite (part of the Cornubian granite batholith) and metasedimentary country rock. The contact strikes ESE and dips 35°-45° to the NE with metasediments overlying the granite.

There were four principal lodes at Tresavean (fig. 2) containing copper sulphides and cassiterite as the main ore minerals. Impurities in Cornish lode ore, such as arsenopyrite and pyrite, interfere with the smelting process and were removed during the ore-dressing stage by calcining. This is the process of roasting heaps of ore to decompose the arsenopyrite and pyrite by atmospheric oxidation to As_2O_3 and SO_2, which were removed in the fumes.

Figure 1. Location map.

Soil Metal Distribution

The initial soil survey at Tresavean was designed to cover all the adjacent farm fields. Surface (0 to 20cm) soil samples were taken on a regular grid pattern (50 by 100 m) over the site, using a soil auger and combining three sub-samples at the sample site. Table 1 summarises the results obtained for the soil analysis of total elements. The results for Cu and As are also presented as element distribution maps in figures 3 and 4. Values for isolines were determined from population graphs of the data. The threshold concentration of Cu in soils at Tresavean was found to be 300 μg/g; anything above this is considered to come from an anomalous population. The data also suggest a further population split at 550 μg/g. For As the threshold value is 220 μg/g, with a further population split at 450 μg/g.

Figure 2. Geology with principal lodes at Tresavean Mine.

The 300 μg/g isoline for Cu largely follows the boundary of the mine site on the western side, but on the eastern side the isoline encroaches much further into the fields, by up to 150 m (fig. 3). The pattern is similar for As; however, there is more encroachment of the isoline into the fields in the south-east and slightly less into the fields in the north-east (fig. 4). The results show more intense As contamination to the south-east compared with Cu, and greater Cu contamination to the north-east.
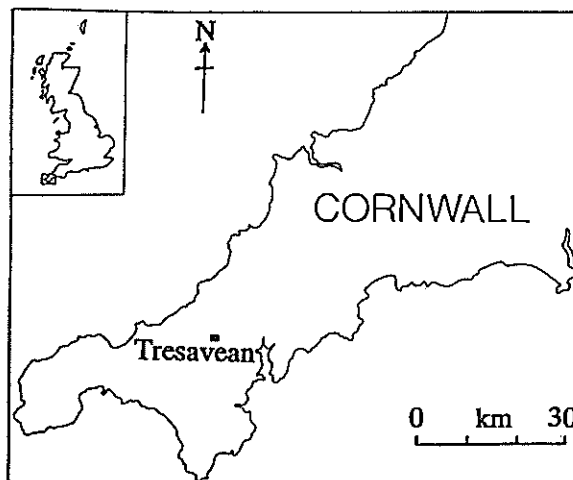
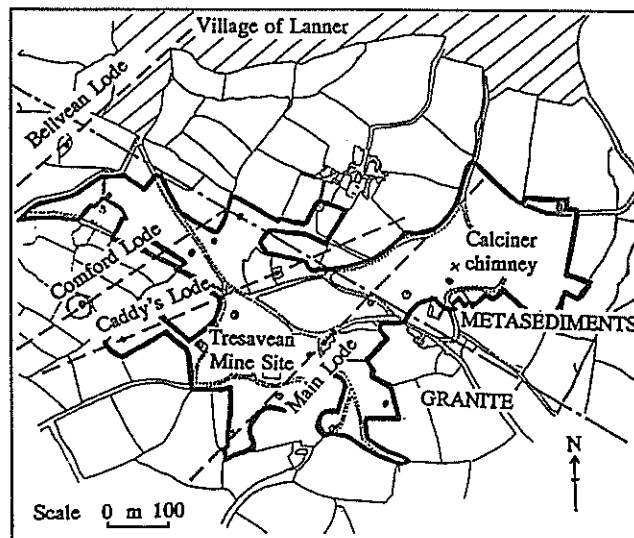Table 1. Results obtained from surface soil samples at Tresavean.

	Total element concentration, $(\mu g/g)$[1]						
	Cu	As	Pb	Zn	Ni	Mn	Fe
Maximum	2,750	1,410	580	1,680	48	1,350	47,800
Minimum	60	30	30	80	0	100	16,200
Mean	250	180	130	360	16	380	26,100
Std. dev.	270	150	80	200	9	240	5,900
n =	147	147	147	147	147	147	147

[1]Samples were air-dried at 30°C, sieved to obtain the minus 2 mm fraction, and digested by a nitric-perchloric acid mixture (Hesse 1971).
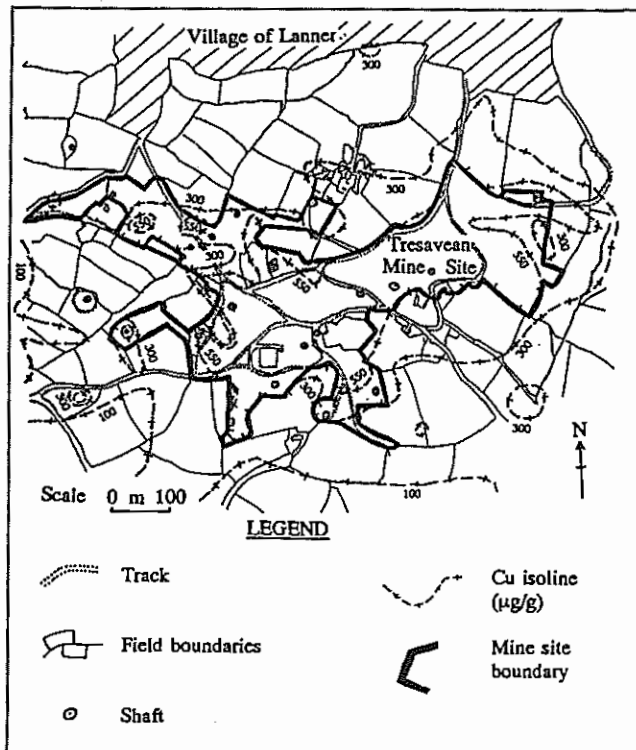

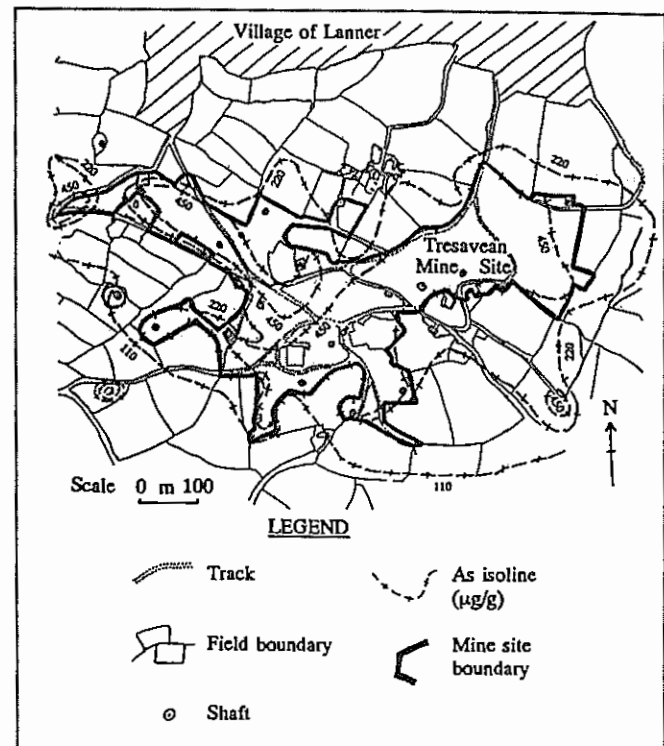Figure 3. Distribution map of Cu in soil at Tresavean.

Figure 4. Distribution map of As in soil at Tresavean.

Sequential Soil Extractions

Sequential extractions are a useful way of providing information on the partitioning of heavy metals into certain soil fractions. This in turn provides information about the origin, mode of occurrence, biological and physico-chemical availability, mobilisation and transport of heavy metals (Tessier 1979). For example, metals which are water soluble are likely to be more mobile and potentially phytotoxic compared with metals which are sequestered on to iron oxides (hydroxylamine hydrochloride extract). These metals, solubilised by the latter extractant, are in a more stable condition within the soil (hence the need for a stronger extractant). A number of authors have used sequential extraction procedures for specific purposes, modifying them to suit their own needs (Tessier 1979, Rose and Suhr 1971, Gatehouse et al. 1977, Hoffman and Fletcher 1979, Kersten and Förstner 1986). Consequently there is no standard single sequence of extractants. Some of the common extractants are reviewed by Beckett (1989).

The sequence starts with weak extractants, which remove those metals most loosely bound, gradually increasing in strength to the final extractant, which effectively removes any remaining metals within the crystal lattices of the resistate minerals. The extracts are not <u>completely</u> specific; therefore, all the metals removed by a particular extractant are not solely related to one phase. However, the <u>majority</u> of the element extracted in one part of the sequence can be attributed to that soil fraction.

Using sub-samples of the soils analysed for total metal content, a series of sequential extractions was undertaken to determine the soil fractions which held Cu and As. Due to the time-consuming nature of these experiments, analysis was restricted to a transect across an area at Tresavean which appeared most interesting from the total element analysis (fig. 5). It is necessary to use two different sequential extraction methods because cations and anions behave differently in soils. As a metal, Cu tends to form cations, whereas As is a metalloid and as such usually forms anions in soils. Two methods were used for the sequential extractions: one to determine the Cu cation distribution and one to determine the As anion distribution. The methods used for these extractions are given in figures 6 and 7.

The sequential extraction technique used for heavy metals divides the soil into seven fractions: water soluble, exchangeable, adsorbed, organic, sulphides, iron and manganese oxides and residual. These fractions are based on Viets' (1962) five pools of micronutrient cations in soil: (1) water soluble, (2) cations exchangeable by a weak exchanger like NH_4^+, (3) adsorbed, chelated, or complexed ions exchangeable by other cations possessing high affinities for exchange sites or extractable with stronger chelating agents, (4) micronutrient cations in secondary clay minerals and insoluble metal oxides, (5) cations held in primary minerals. Pool 3 has here been sub-divided into adsorbed and organic fractions as it was considered important to discriminate between these two fractions in the soil. An "extra" extract purely for sulphide determination has been included because Cu is present in the mine waste as sulphide. The extractants used for each of these fractions are, respectively; water, ammonium acetate, sodium acetate, sodium pyrophosphate, sodium hypochlorite, hydroxylamine hydrochloride and nitric-perchloric acid.

Figure 5. Topographical map of Tresavean with traverse and sample sites marked.

The series of extractants for As divides the soil into the following fractions: water soluble, Al-associated, Fe-associated, Ca-associated, occluded Al-associated (i.e. that which has been incorporated into the Al oxide or hydroxide crystal structure) and residual. The extractants used are, respectively; water, ammonium fluoride, sodium hydroxide, sulphuric acid, ammonium fluoride and nitric-perchloric acid, based on the sequential extraction technique of Woolson et al. (1973). Very little work on As extractions has been reported in the literature; the work of Woolson et al. (1973) is based on a modified Jackson procedure for soil phosphorus (Petersen and Corey 1966). However, this technique addresses the inorganic forms of soil P extraction and results may be open to misinterpretation if organic-anion compounds are likely. The sequential extraction is shown in figure 7 with the inorganic forms of As expected to be extracted. However, it must be borne in mind that sodium hydroxide may extract As related to Fe compounds, organic-Fe compounds and/or organics in the farmland soils.

To determine the residual fraction for both methods, the summation of the extracted element was subtracted from the total content previously determined by the nitric-perchloric digestion. Results from these two sequential
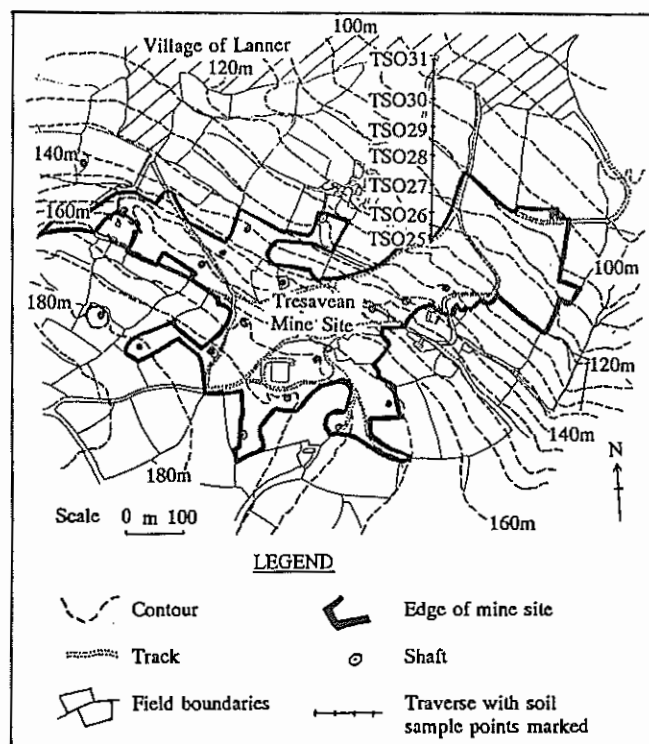
extractions are presented in figures 8-11.

Extraction Method   **Fraction Extracted**

To 10 g soil add 50 mL distilled water (pH 7) and shake for 5 h Centrifuge and remove supernatant liquid

Water soluble

To residue add 50 mL of 1$\underline{M}$ ammonium acetate solution (pH 7) and shake for 1 h Centrifuge and remove supernatant liquid, wash residue with 25 mL distilled water Centrifuge to remove water and add to supernatant

Exchangeable

To residue add 50 mL of 1$\underline{M}$ sodium acetate solution buffered to pH 5 with acetic acid Shake for 5 h, centrifuge and remove supernatant liquid Wash as for ammonium acetate

Adsorbed

To residue add 50 mL of 0.1$\underline{M}$ sodium pyrophosphate (pH 7) and shake for 15 h centrifuge and remove supernatant liquid Wash as for ammonium acetate

Organic

To residue add 75 mL of 0.1$\underline{M}$ sodium hypochlorite adjusted to pH 9.5 with 6$\underline{M}$ HCl Leave for 10 h shaking every 2 h then centrifuge and remove supernatant liquid Repeat addition of sodium hypochlorite, shaking and centrifuging Add supernatant liquids together then leach residue by adding 50 mL of distilled water and acidifying to pH 3 by addition of 1.5$\underline{M}$ HCl Centrifuge and add supernatant to sodium hypochlorite extractant

Sulphides

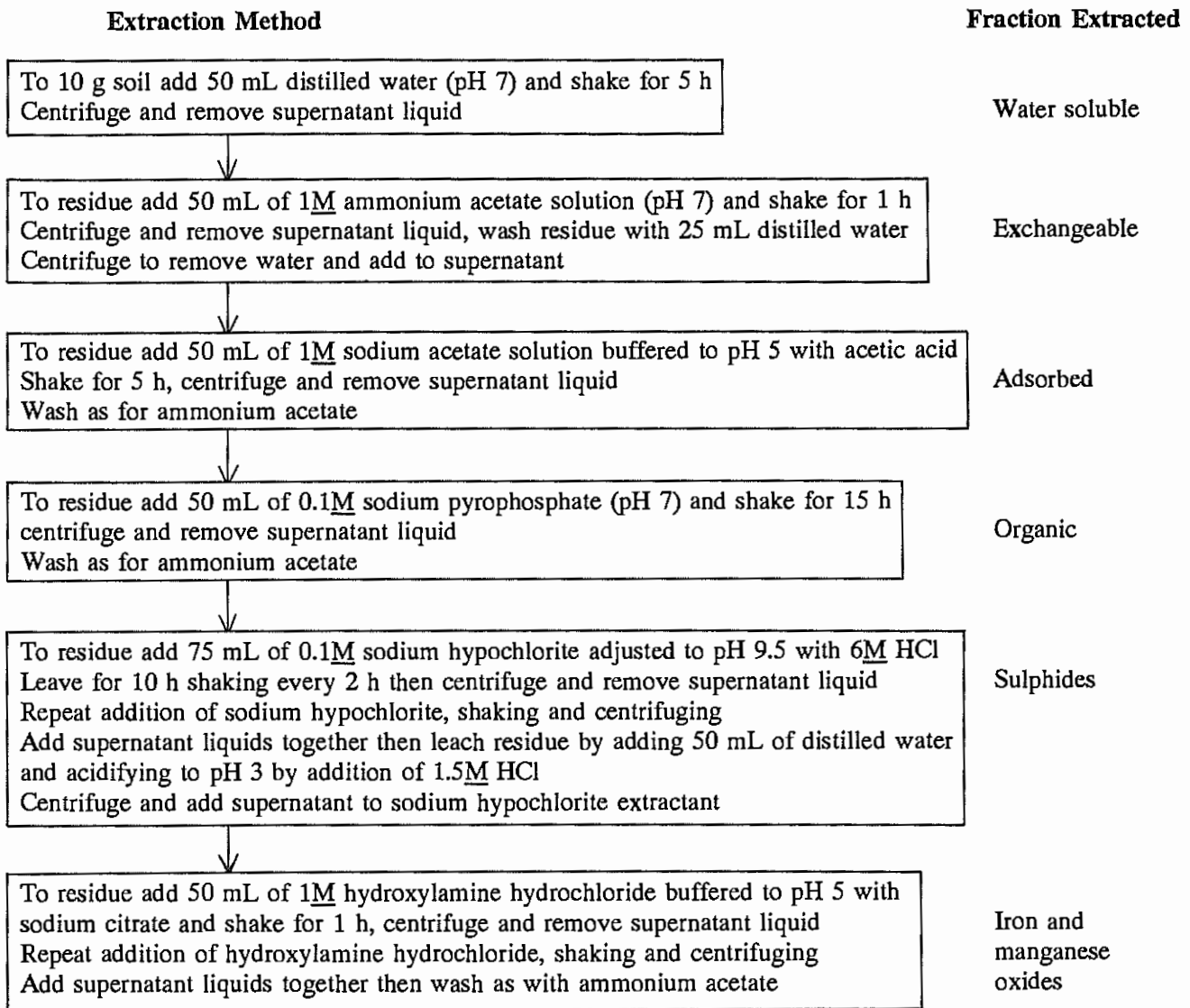| To residue add 50 mL of 1$\underline{M}$ hydroxylamine hydrochloride buffered to pH 5 with
sodium citrate and shake for 1 h, centrifuge and remove supernatant liquid
Repeat addition of hydroxylamine hydrochloride, shaking and centrifuging
Add supernatant liquids together then wash as with ammonium acetate |
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Iron and
manganese
oxides

Figure 6. Sequential extraction method for copper (modified from Tessier et al. 1979).

Results of Copper Fractionation in Soil

The Cu concentration in each extract is shown in figure 8. As a whole, the concentrations for each extractant decrease with distance from the mine site and, as such, mimic the total Cu content of the soils. However, with regard to Cu content in each fraction as a percentage of total Cu, all bar the residual and organic fractions behave similarly and appear to be constant. In each soil sample the majority of the Cu (fig. 9) is held in the residual phase. This ranges between approximately 45% and 60% of the total Cu content and shows a slight increase with distance from the mine. The second highest percentage of the total Cu, in every case, is the organic fraction, extracted by sodium pyrophosphate. This organic fraction, unlike the others, shows a decrease with distance from the mine site. It decreases from 33% to 21% over the 300 m traverse. The actual Cu concentrations in the organic fraction drop from 195 µg/g to about 60 µg/g from TSO25 to TSO31. By the end of the traverse the concentration appears to have levelled off (fig. 8).
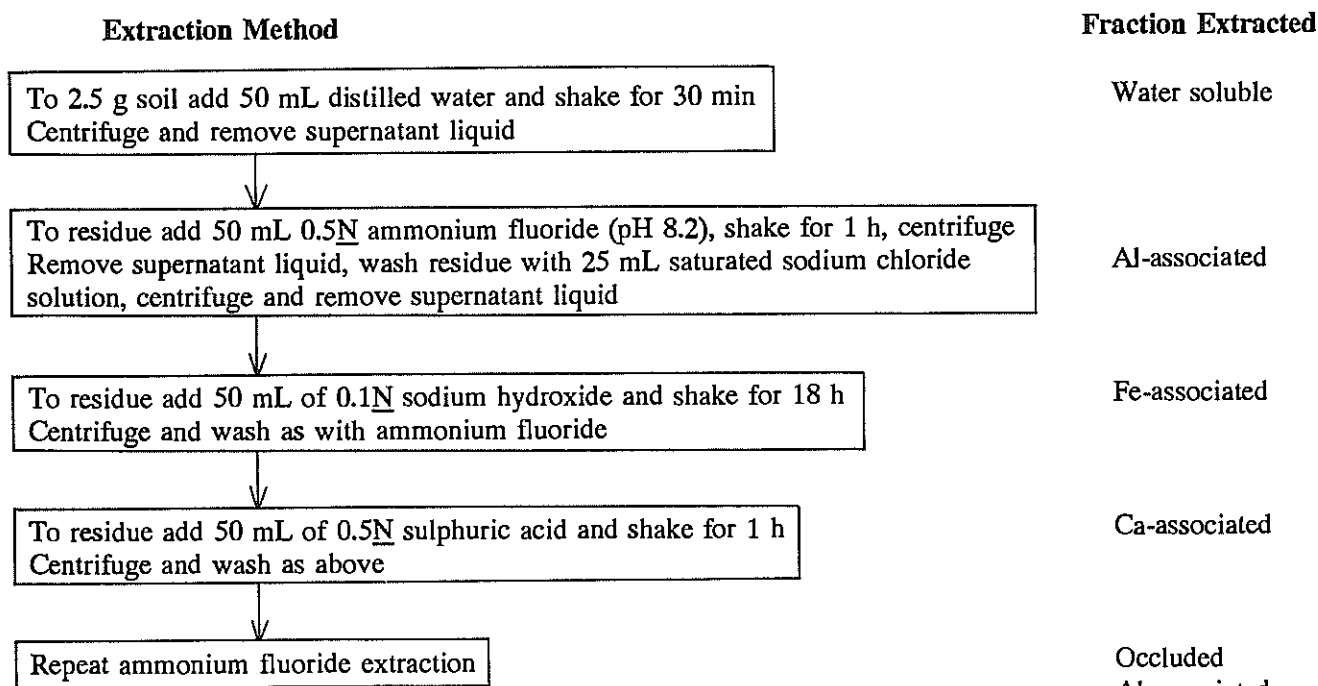
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Extraction Method	Fraction Extracted

| To 2.5 g soil add 50 mL distilled water and shake for 30 min
Centrifuge and remove supernatant liquid | Water soluble |

| To residue add 50 mL 0.5N ammonium fluoride (pH 8.2), shake for 1 h, centrifuge
Remove supernatant liquid, wash residue with 25 mL saturated sodium chloride
solution, centrifuge and remove supernatant liquid | Al-associated |

| To residue add 50 mL of 0.1N sodium hydroxide and shake for 18 h
Centrifuge and wash as with ammonium fluoride | Fe-associated |

| To residue add 50 mL of 0.5N sulphuric acid and shake for 1 h
Centrifuge and wash as above | Ca-associated |

| Repeat ammonium fluoride extraction | Occluded
Al-associated |

Figure 7. Sequential extraction method for arsenic (modified from Woolson et al. 1973).
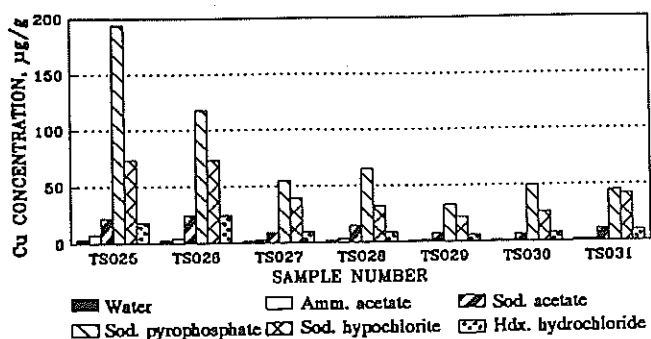
Figure 8. Sequential soil analysis for extractable
    Cu (μg/g) for soil traverse at Tresavean.
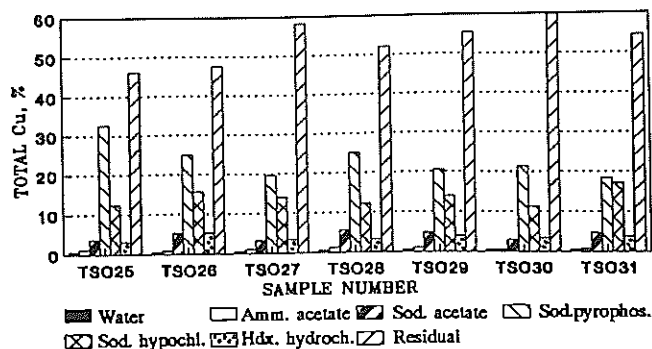
Figure 9. Sequential soil extraction for Cu
    (expressed as % of total Cu in each sample).
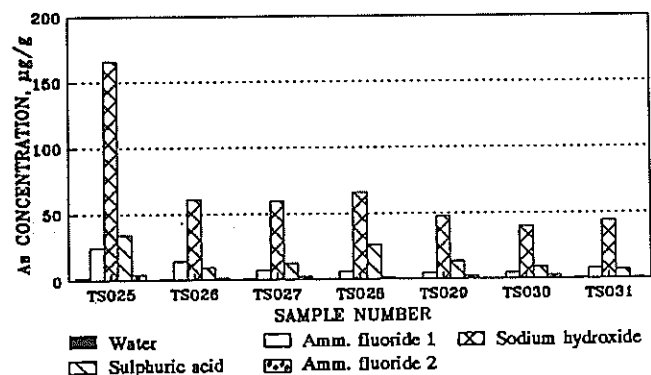
Figure 10. Sequential soil analysis for extractable
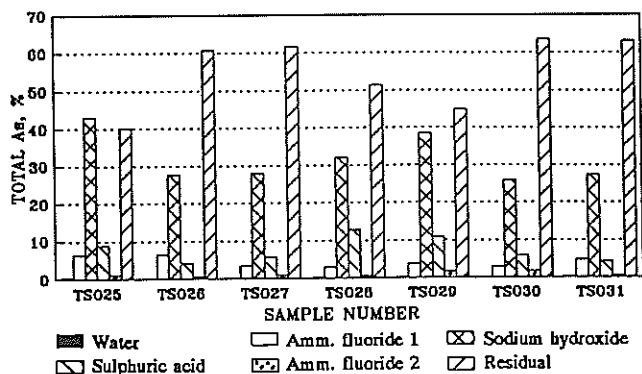   As (μg/g) for soil traverse at Tresavean.

Figure 11. Sequential soil extraction for As
    (expressed as % of total As in each sample).

The remaining extractants are listed in order of decreasing importance with regard to Cu concentration: sodium hypochlorite (sulphides) > hydroxylamine hydrochloride fraction (Fe-Mn oxides) ≥ sodium acetate fraction

(adsorbed) > ammonium acetate fraction (exchangeable) ≥ water soluble fraction.

Results of As Fractionation in Soil

A general decrease of As content in each soil fraction occurs with increasing distance from the mine (fig. 10). When presented as a percentage of the total As in each sample, the pattern is not so clear (fig. 11). Apart from TSO25, the residual fraction contains the most As in each case. For TSO25, which is the sample nearest the mine, the residual fraction is only slightly less than in the sodium hydroxide extract (40% compared with 43% respectively). For all the other samples the sodium hydroxide extract (Fe-organic As) contains the second highest percentage of As. The remaining extractants are listed in order of decreasing importance with regard to As concentration: sulphuric acid (Ca-associated) > the first ammonium fluoride extract (Al-associated) > the second ammonium fluoride extract (occluded Al-associated) > water. The first ammonium fluoride extract of TSO31 contains more As than the sulphuric acid extract (4.8% and 4.3% respectively), but this is only marginally greater.

The large drop in concentration between samples TSO25 and TSO26 in each soil fraction is obvious, but is most notable in the sodium hydroxide extract (that relating to Fe-organic As), which drops from 166 μg/g to 61 μg/g (fig. 10). The sodium hydroxide extract shows a further decrease in As content with distance from TSO26 to TSO31, but at a much reduced rate.

Comparison of Sequential Extraction Results for Mine Waste and Soil

The distribution of Cu is very different in mine waste when compared with soil (fig. 13). The most striking differences are in the proportions found in the sodium acetate fraction and the residual fraction. For soils the residual fraction at 52% is by far the largest, but for mine waste this fraction only accounts for approximately 20%
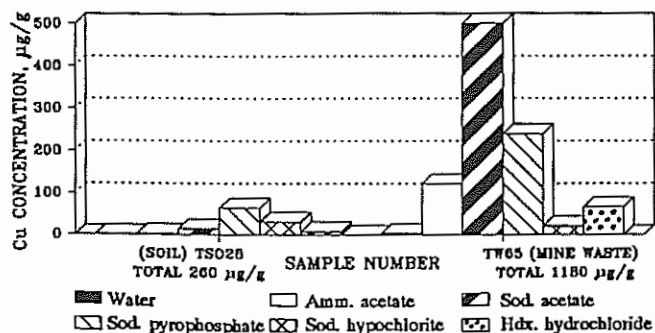

Figure 12. Comparison of sequential analysis of soil and mine waste for extractable Cu.
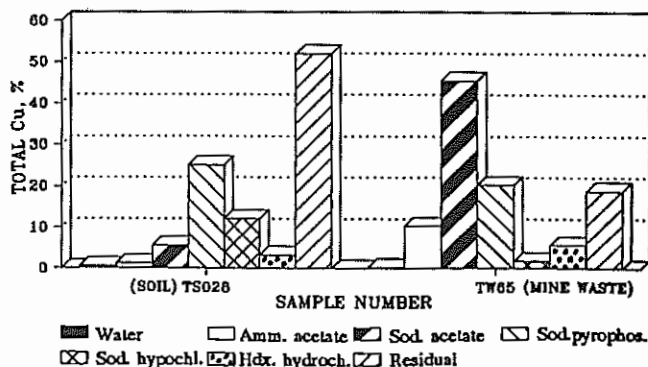
Figure 13. Comparison of sequential analysis for Cu (expressed as % of total Cu in each sample).

of the total Cu. In mine waste, Cu appears to be mostly held in the sodium acetate extractable fraction, i.e. that equivalent to adsorbed Cu. The organic Cu fraction of the two samples appears to be similar at around 20% of the total Cu concentration. This fraction in both cases is the second most important in terms of Cu concentration, but for the mine waste sample it is only just greater than the residual Cu concentration. The mine waste again differs from the soil in the amount of Cu found in the ammonium acetate extractable fraction. For mine waste this is 10% of the total Cu, but for the soil it is only 1%. The hydroxylamine hydrochloride fraction appears to be similar for both soil and mine waste at around 5% of the total Cu concentration. The sodium hypochlorite fractions (sulphide content) also differ. Surprisingly, soil contains more Cu in this fraction than does the mine waste (12% compared with 2%), but absolute concentrations are about the same (between 20 μg/g and 30 μg/g). Water soluble Cu is approximately the same in terms of percentage of total Cu, but in absolute values for mine waste it is at least twice the soil concentration.

Results from the sequential analysis of soil and mine waste for As are given in figures 14 and 15. The

results in figure 14 are the actual concentrations found in each fraction; as expected, the mine waste contains more As in each fraction than is found in the soil. Figure 15 shows that the distribution of As in soil and mine waste is extremely similar. It is important to note that the sodium hydroxide fraction (Fe-organic) is the most important extract, removing approximately 30% of the total As present in both soil and mine waste.
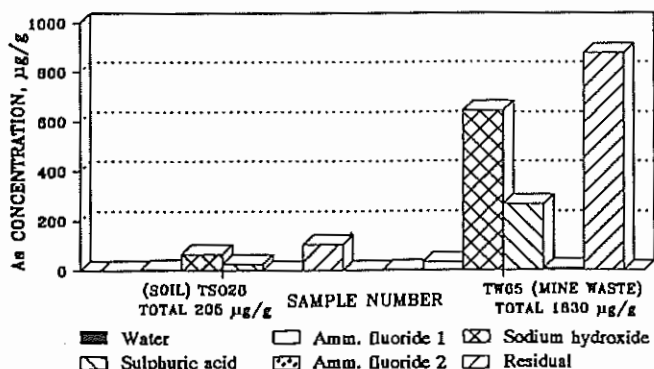

Figure 14. Comparison of sequential analysis for soil and mine waste for extractable As.
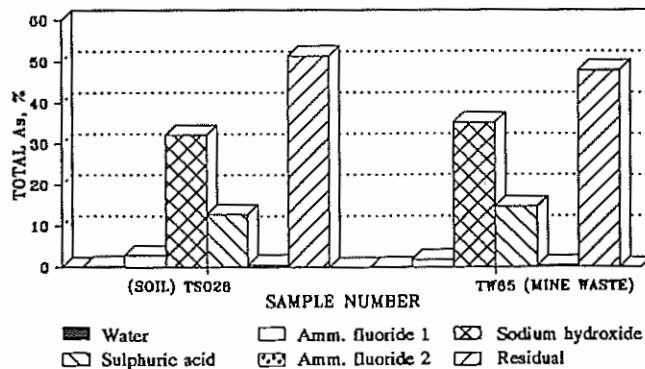
Figure 15. Comparison of sequential extractions (expressed as % of total As in each sample).

Discussion

Metal Distribution

The Cu distribution map (fig. 3) shows that the more mobile Cu has tended to migrate down slope away from the mine in the direction of greatest slope, which is to the north and east (fig. 5). However, As (fig. 4) is more likely to have been dispersed by wind as it is generally not soluble in the low pH conditions found in the mine waste at Tresavean. Arsenic-rich dust will have been blown from west to east with the prevailing wind, as will any fumes from the calciner plant. Hence As would be expected to predominate on the eastern side with less on the northern side (as found in the distribution map, fig. 4). This, of course, does not preclude some of the Cu from being dispersed in this fashion. There is evidence of some Cu contamination to the east, but it is not as marked as the As. It is possible that much of the As dispersion is relict and occurred when the mine was in operation.

The distribution maps for As and Cu (figs. 3 and 4) also show that despite high concentrations of As and Cu in Tresavean mine waste (up to 1.9% As and 2.8% Cu), dispersion is apparently of limited extent (approximately 150 m); however, in samples directly adjacent to the mine, it is quite severe. This may suggest a lack of extensive wind dispersion, which may be attributable to Cornwall's relatively wet climate reducing airborne dust. The high rainfall will, however, leach the available Cu from the mine waste.

Metal Fractionation in Soil

It is important to note that the organic fraction is the most significant fraction of the partially extractable metals. Therefore any organic matter added to the fields surrounding the mine site (e.g. spreading of animal waste) may preferentially adsorb heavy metals dispersed from the mine. The organic fraction becomes less significant with distance from the mine, whereas the residual fraction appears to increase in percentage of total Cu.

From figure 11 it is apparent that residual As and Fe-organic associated As are by far the most important soil fractions, accounting for up to 90% of the total As. This concurs with the general association of As with Fe oxides and hydroxides (Woolson 1983, National Academy of Sciences 1977) and reiterates the importance of the organic fraction in soil (as mentioned above). Evidence from the literature indicates that As is strongly attracted to Fe oxides and hydroxides (Dudas 1987, Johnston and Barnard 1979) but not to soil organic matter (Johnson and Hiltbold 1969). Other authors report As may be bound to soil organic matter (National Academy of Sciences 1977, Woolson 1983).

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Comparison of Metal Content in Mine Waste and Soil

In the mine waste, about 75% of the Cu is present in the ammonium acetate, sodium acetate and sodium pyrophosphate fractions; that is, it is present in exchangeable, adsorbed and organic form. This compares with only 32% for these fractions in soil. Secondary minerals formed during the weathering of mine waste may partly account for this high percentage of easily extractable Cu. Any acid mine drainage would therefore be capable of removing large amounts of Cu from the mine waste. Fortunately there are no streams running through Tresavean, but surface drainage is likely to be a problem and has the potential to be a Cu dispersal mechanism.

As the sodium pyrophosphate fraction in the mine waste is a major Cu-containing fraction, the amount of organic matter found in a mine waste sample will also be very important. Generally the organic content of the mine waste is low (< 3% total organic carbon) and this may result in the saturation of the organic matter with Cu because of the very high Cu content of the spoil. The surprisingly high Cu concentration in the sodium hypochlorite fraction of soil compared with this fraction in mine waste may be due to inefficient extraction of organic Cu by the previous sodium pyrophosphate extraction. It seems very unlikely that soil will contain more Cu sulphides than the mine waste. Beckett (1989) has reported some research to have shown that sodium pyrophosphate can dissolve Cu sulphides. Therefore it is possible the sodium pyrophosphate fraction of the mine waste not only reports organic Cu but also some sulphidic Cu. This will in turn reduce the amount of Cu extracted by sodium hypochlorite (designed to remove sulphides) as it follows the sodium pyrophosphate extraction.

The As fractionation in the mine waste is very similar to that in the soil and appears to be associated mainly with the residual and Fe-organic fractions, with the Ca-associated fraction also being important. As mentioned earlier, As_2O_3 is present in the mine waste at Tresavean; as this is soluble in alkalis, both the ammonium fluoride and sodium hydroxide extractions may report it. The results show that the majority of the As in the mine waste is not held in the easily extractable fractions (i.e. the water and first ammonium fluoride extracts), which only account for approximately 2% of the total As. Hence any dispersion of As would have to be of a physical nature. For As to be dispersed any distance it would therefore be as wind-blown dust.

Conclusions

Element distribution maps produced from the extensive soil survey of farmland surrounding the Tresavean Mine have revealed two distinct patterns of Cu and As distribution. Arsenic distribution extends in an easterly direction and appears to correlate with the prevailing wind direction. Cu distribution extends more to the north and east and follows the down slope drainage pattern. Considering the high Cu-As content of the mine waste, the extent of dispersion is less than expected. This may be due to Cornwall's high rainfall reducing dust-blow.

Sequential extractions were used to determine the fractionation of Cu and As in soils at Tresavean. It was found that Cu is held mainly in the residual and organic fractions, whereas As is held mainly in the residual and iron-organic fractions. Although the absolute concentrations of As and Cu decrease with distance from the mine site as expected, the relative percentage of As and Cu in each fraction tends to be independent of distance from the mine. The sequential extractions performed on the mine waste show Cu to be present largely in the easily extractable fractions; As is mostly present in the less easily extractable fractions. Copper is therefore more likely to be subject to leaching and hydromorphic dispersion (e.g. by drainage), whereas As is more prone to mechanical dispersion (e.g. as wind-blown dust).

Acknowledgements

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