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Characterisation of a mining-related arsenic-contaminated site, Cornwall, UK☆

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Abstract

Arsenic contamination in Cornwall is widespread due to the historic mining of polymetallic ores and the calcination of ores. In areas such as Camborne/Redruth and Hayle in West Cornwall, arsenic values typically exceed 100 mg kg^{-1} in sampled topsoils, with high values also being present in the subsoil. To investigate the dispersion of arsenic from a calciner stack and from fugitive dusts, the New Mill site at Roseworthy, near Camborne, Cornwall was chosen for detailed investigation. The site contains a calciner which was fed with handpicked ore and a refinery where arsenic was refined to a saleable product. In total, an area of 700×600 m on a grid with a spacing of 100 m was sampled. Seventy-eight soil samples were obtained from pits up to 30 cm deep and analysed by ICP-MS, while seven water samples were also analysed for arsenic. Two soil samples were analysed in more detail. Measured properties were pH, particle size distribution, the arsenic distribution in the different size fractions, and the mineralogy of arsenic in the soil using XRD, SEM and QemSCAN. Twenty samples crossing the area were subjected to water extraction and speciation analysis by HPLC-HG-AFS. High values of total arsenic, above 4000 mg kg^{-1}, were recorded in the soils in the valley floor adjacent to the calciner. Lower values, close to 500 mg kg^{-1} arsenic, were measured near the stack, with a background value of up to 125 mg kg^{-1}. Agricultural disturbance by ploughing and down-slope leaching has probably dispersed the arsenic contamination in the soil. The majority of the arsenic contamination was found to occur in the silt and sand fractions. Speciation of the water-soluble component revealed high values of As^{5+} plus As^{3+}, between 0.3% and 1.7% of the total arsenic value. QemSCAN results indicate that coal/coke/fly ash particulates are a significant carrier of arsenic contamination. Furthermore, locked and liberated particles associated with silicates and oxides often contain arsenic-iron oxide as rims and infillings. Water sample concentrations are below 50 μg l^{-1}, indicating relatively low mobility of arsenic contained in soils. This could be due to the oxidation state of arsenic and redox conditions. However, a large reservoir of arsenic could be remobilised if there is a change in ambient conditions, allowing for potential retoxification of the site.

Keywords: Arsenic; Contamination; Mining; Calciner; Pollution; Speciation; Cornwall

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☆ Characterisation data obtained from this study is available from the authors by contacting Prof. Glass at H.G.Glass@csm.ex.ac.uk.

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1. Introduction

Arsenic in soils is increasingly drawing the attention of environmental scientists due to its potential toxicity to humans and fauna and flora in general. It may be derived from naturally occurring minerals or be introduced anthropogenicaly by industrial activities. Part of this industrial activity is related to the mining and processing of metalliferous ores. There have been instances of arsenic poisoning in various parts of the world due to the processing of arsenical ores, or related to the residues of such operations (Mandal and Suzuki, 2002). To assess the environmental impact, better methods are required for evaluation of such contamination (Ferguson et al., 1998).

It is now recognised that exposure of humans to elevated levels of arsenic should be avoided (Thornton et al., 1986; Farago et al., 1997). Inorganic arsenate and arsenite are the most toxic natural forms. Of these, arsenite is considered to be more acutely toxic than arsenate (National Academy of Sciences, 1977; Naqvi et al., 1994). A provisional drinking water guideline, WHO (1993), recommends a value of 10 μg l^{-3}. Recently published Soil Guideline Values (SGV's) (2002) in the UK specify 20 mg kg^{-1} per dry weight of soil for residential areas and allotments while the value for commercial or industrial land is 500 mg kg^{-1} per dry weight of soil. If levels exceed these values, further assessment of the site is required.

Inorganic arsenic occurs either as pentavalent arsenate (As^{5+}) or trivalent arsenite (As^{3+}) while organic forms of arsenic are mainly methylated compounds and carbohydrate derivatives. Methylated arsenic oxyacids, found in soils (Masscheleyn et al., 1991), are less mobile than inorganic arsenic (Xu et al., 1988). Arsenic in water and soil can undergo a series of transformations, including oxidation-reduction reactions, ligand exchange and biotransformation (Mitchell and Barr, 1995). Arsenite predominates when the redox potential is low or when the soil is waterlogged (Sadiq, 1997). Haswell et al. (1985) reported that over 90% of the dissolved arsenic in aerobic soils occurred as arsenate. This drops to 15% to 40% in the waterlogged conditions prevalent in southwest England. At a pH of 5.8, As^{5+} is slightly more mobile than As^{3+}. As pH increases, the mobility of both species increases with As^{3+} becoming the more mobile species. In environmental studies, however, the distinction between the arsenic species is often overlooked: arsenic is usually reported as total arsenic.

Arsenic in the natural environment may occur in both organic and inorganic forms. While the global average concentration of arsenic in uncontaminated soil is 5 to 6 mg kg^{-1} (Adriano, 1986), values for the UK are between 2 and 53 mg kg^{-1}, with a median value of 10 mg kg^{-1} (Archer and Hodgson, 1987). Concentrations in Cornwall in areas away from former mining activity can range between 29 and 51 mg kg^{-1} (Culbard and Johnson, 1984) or between 26 and 67 mg kg^{-1} (Elghali, 1994). In contaminated areas such as the area around Camborne/Redruth/Hayle in West Cornwall values reach 727 mg kg^{-1} in sampled topsoils, and a maximum of 500 mg kg^{-1} in the subsoil (Abrahams and Thornton, 1987).

Historic non-ferrous metalliferous mining and ore concentration has resulted in the contamination of large tracts of Cornwall by metals and metalloids (Thomas, 1980). Contamination was identified in stream sediments (Hosking et al., 1965; Aston et al., 1975; Web et al., 1978; Thornton, 1979), soils (Colburn et al., 1975; Abrahams, 1983; Xu and Thornton, 1985; Abrahams and Thornton, 1987; Li and Thornton, 1993; Mitchell and Barr, 1995; Camm and Moon, 2001), soil pore waters (Haswell et al., 1985), estuarine sediments (Pirrie et al., 1997, 1999a,b, 2000), acid mine drainage (Johnson and Thornton, 1987; Moon, 1993; Brown et al., 1994; Hunt and Howard, 1994; Hamilton et al., 1999; Brown et al., 2002) and bioavailability studies (Kavanagh et al., 1997). The metalloid part of the contamination is derived from the calcination of arsenical ores and concentrates (Earl, 1983, 1996), either to remove the arsenic and/or for arsenic recovery. During the period from 1860 to 1900, Cornwall was the world's major producer of arsenic (Thornton et al., 1986). Airborne dispersion of arsenic can be traced to the plumes of calciner stacks, waste product dumps, and the activity associated within the calciner site, including the transport of the raw or refined product. Waterborne pollution stems from particulate and soluble components. Abrahams and Thornton (1987) state that 11.9% of the total area surveyed by soil and stream sediment sampling in southwest England is contaminated by heavy metals or metalloids. Cornwall therefore is an excellent area to study the long-term impact of mining related activity on the environment.

A site in West Cornwall (Fig. 1) was chosen for a detailed characterisation study. The site allows investigation of the contaminant plume from the calciner stack, the effect of calciner "fugitive" dusts (Davies, 1983) from former industrial activity, and spillage of material during transportation of the raw and refined products.

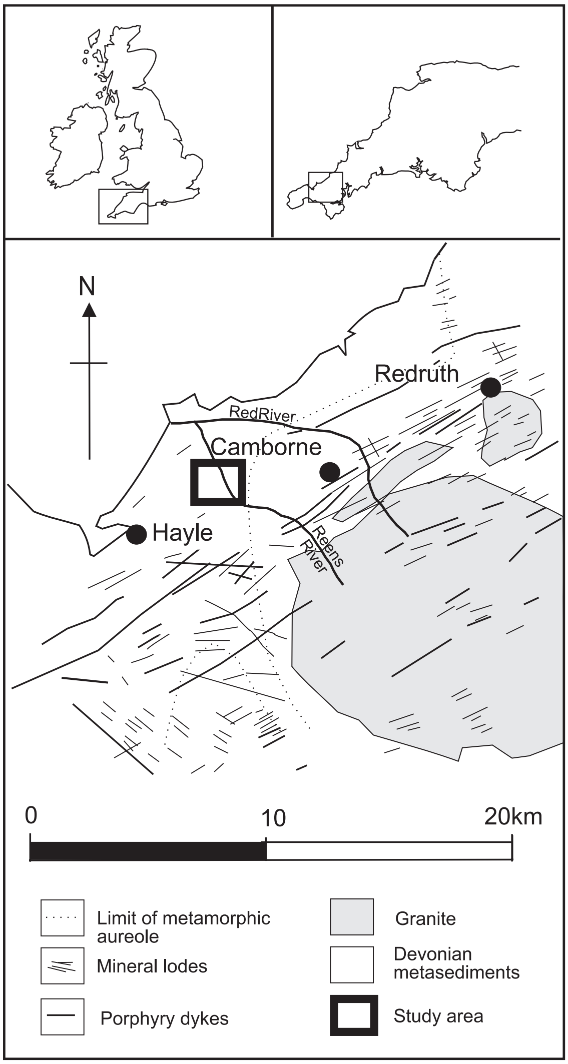

Fig. 1. Location map of west Cornwall showing the study area west of the Camborne–Redruth orefield and thermal metamorphic contact of the Carnmenellis Granite.

The objectives of this study are:

(a) to characterise the spatial distribution and concentrations of arsenic in soil and the soil pH around a calciner site and stack,
(b) to determine the concentrations of arsenic in the sand, silt and silt clay soil grain size fractions,
(c) to examine the mineralogy of selected soil size fractions by X-ray diffraction (XRD) and scanning electron microscopy (SEM),
(d) to determine the arsenic speciation of the water-soluble component at selected sample sites within the study area.

2. Historical background

Cornwall has a very long history of metalliferous mining dating back to the Bronze Age. During its peak in the 1800s, it was the largest producer of tin and copper in the world (Dines, 1956). Arsenic occurs in the tin and copper lodes primarily as arsenopyrite (FeAsS) with minor amount of löllingite ($FeAs_2$) and enargite ($3Cu_2S.As_2S_5$). In addition, associated secondary minerals occur in the upper oxidised parts of the lode structures. High levels of arsenic in concentrates had a detrimental effect on the smelting of such ores. Roasting or calcination of ores to remove arsenic and sulphur probably began in the 1700s when placer and gossan ore supply was naturally replaced by the primary, more sulphidic ore types. Sulphidic ore is reduced in size and roasted with coal or coke as a fuel and arsenic driven off as an oxide, condensing on cooler surfaces. The recovery of arsenic is therefore primarily connected to the processing of tin ores as these are intimately associated with arsenic minerals. Concentrates were roasted to remove the metalloid as well as the sulphur component. From the 1860s, arsenic recovery and refining became more extensive (Earl, 1983, 1996). When arsenic became valuable due to the discovery of pigments, especially 'Paris Green' and 'Kings Yellow', and later as an insecticide (calcium-arsenate) and as a glass decolouriser, mine waste dumps were handpicked for arsenic-bearing ores and arsenic-rich ore was purposely mined. The roasting process to remove the arsenic, with discharge to the atmosphere, was gradually replaced by the recovery of arsenic by the implementation of elaborate condensing features. Large areas were therefore highly contaminated by arsenic before the Alkali Inspectorate introduced controls of 2.9 g of arsenious oxide per cubic metre of air in the late 1800s.

The metalliferous mining activity in Cornwall left tailings and rock dumps and has produced soils (Abrahams and Thornton, 1987) or superficial deposits, including river and estuarine sediments (Pirrie et al., 1997, 2000; Pirrie and Camm, 1999). In practice, these are contaminated with arsenic and heavy metals. For example, some 410 km^2 in the Hayle–Camborne–Redruth–St. Day–St. Agnes area is contaminated (Abrahams and Thornton, 1987). Besides contamination from anthropogenic sources, soils may be enriched from natural weathering of a parent rock containing elevated arsenic values (Thornton, 1979; Camm and Moon, 2001). To investigate the contamination of soils from calcination alone without the over or underprint of tailings or other hardrock mining activity related material, a site was chosen at New Mill, Roseworthy near Camborne for examination.

The New Mill calciner was constructed in 1889 for refining of arsenic soot from mines in the area as well as the calcination of handpicked arsenical ore from the mine waste dumps. Historically, the site was chosen due to its close proximity to the Redruth–Camborne orefield, its access to waterpower, and its distance from habitation. Arsenic recovery was effected by shaft furnaces and waste products were dumped to the north of the calciner on the west bank of the Reens River which could handle a coarse feed from dump material mixed with coal/coke. The calciner complex continued until circa 1923 as the English Arsenic Works. Production data from this calciner are, however, not available. The site is now derelict with the condensing chambers and residue dump still visible near the valley floor and with the stack on the hill above.

3. Location, physiography and geology

The calciner is situated some 4 km to the WSW of Camborne in Cornwall, southwest England. The industrial site lies on the western side of the valley floor in a cut into the hillside adjacent to the Reens River, which is a tributary of the Red River (Fig. 2). The chimney is at an elevation of some 50 m above ordinance datum or 35 m above the valley floor and is positioned on an interfluve between two small streams, feeding down to the main river. The main river catchment includes the most westerly extent of the Camborne–Redruth orefield, and as such would have been a conduit for mine tailing discharge in the 1800s through to the earlier part of the 1900s. The area is partially farmed with the majority of the area as pasture, along with some arable and areas of scrub and semi-managed woodland (Fig. 3). Natural soils are usually slightly acidic. Soils in both the pasture and arable land have been enriched with amendments in the form of calcareous beach sand and fertilisers and disturbed by ploughing. The soil type in the area is generally a high clay loam (brown earths) with alluvium in the valley bottom (Staines, 1979). Prevailing winds are westerlies and the average rainfall is 1400 mm per annum. The solid geology of the study area is dominated by the Devonian Mylor Slate Formation with fine silt laminae and rare thin beds of sandstones and interbedded metabasites (Goode and Taylor, 1988). Although on the edge of the metamorphic aureole and associated mineralisation, there is a record of a small mine named Rose-in-Valley Mine (Hamilton Jenkin, 1963), mining two east–west copper, zinc and lead bearing lode structures in the area. Little evidence of this mining activity now remains.

4. Previous studies

The site mainly consists of agricultural land with the exclusion of one small area containing the calciner. It was first investigated by Abrahams (1983) with SW/NE traverse sampling. Metal and metalloid contamination due to past mining activity is reported in Thornton et al. (1986) and Abrahams and Thornton (1987). A total of 51 out of 58 samples showed arsenic values exceeding the moderately contaminated threshold of 110 mg kg^{-1} (Fig. 6). Locations adjacent to the stack and to the calciner on the valley floor gave values between 600 and 2200 mg kg^{-1}, respectively, with unexplainable outliers above 59,000 and 1200 mg kg^{-1} to the southwest. It was concluded that the contamination was widespread and worthy of further investigation. Samples for arsenic determination were analysed by ICP-AES.

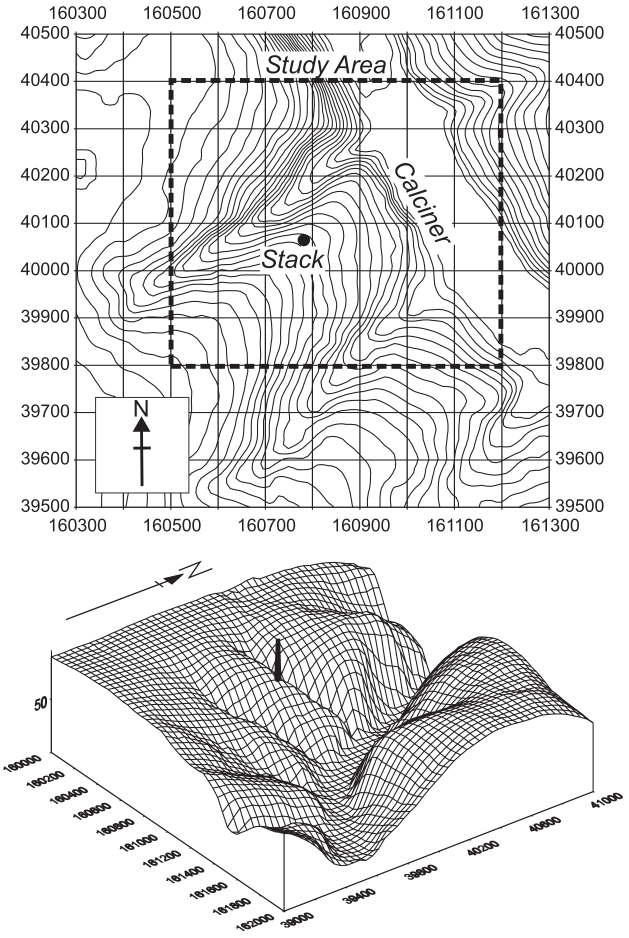

Fig. 2. Topography and area of interest showing the Reens River valley and site of the calciner and stack.

Li and Thornton (1993) studied part of the New Mill site near the chimney. Topsoil (0–15 cm) and subsoil (15–30 cm) were sampled. Three soil samples were extracted using a 2.5 cm soil auger to produce a composite sample of nine borings within a 2 m×2 m square, while two subsoil samples consisted of three sub samples. The arsenic concentration ranged between 210 and 925 mg kg^{-1} in the topsoil (0–15 cm), 257 to 962 mg kg^{-1} arsenic in the subsoil (15–30 cm) and 190 to 236 mg kg^{-1} arsenic in the subsoil (30–45 cm).

Frizzel (1993) used a 90 m transect at the calciner site to extract soil samples of 10 cm depth. High levels of arsenic were measured in the direct vicinity of the calciner and adjacent buildings, with values between 800 mg kg^{-1} and 16% from soil samples.

5. Field methods

Given that the calciner site was previously identified as highly contaminated and containing ‘made ground’, no samples were taken there. Sampling was restricted to the area with ‘natural’ soils. Most of the soil has been in agricultural use. Official guidance on spatial sampling strategies is not very helpful (Ferguson, 1992). Because the site contains two potential sources, the stack and calciner site, a staggered square grid on 100 m centres, with a 50 m interval between staggers was designed. This produced a grid pattern, which covered the largest area (700×600 m) with a W pattern and allowed for infill if required (Fig. 3).

Sample positions were initially located using compass, tape, and ranging poles using the field hedge

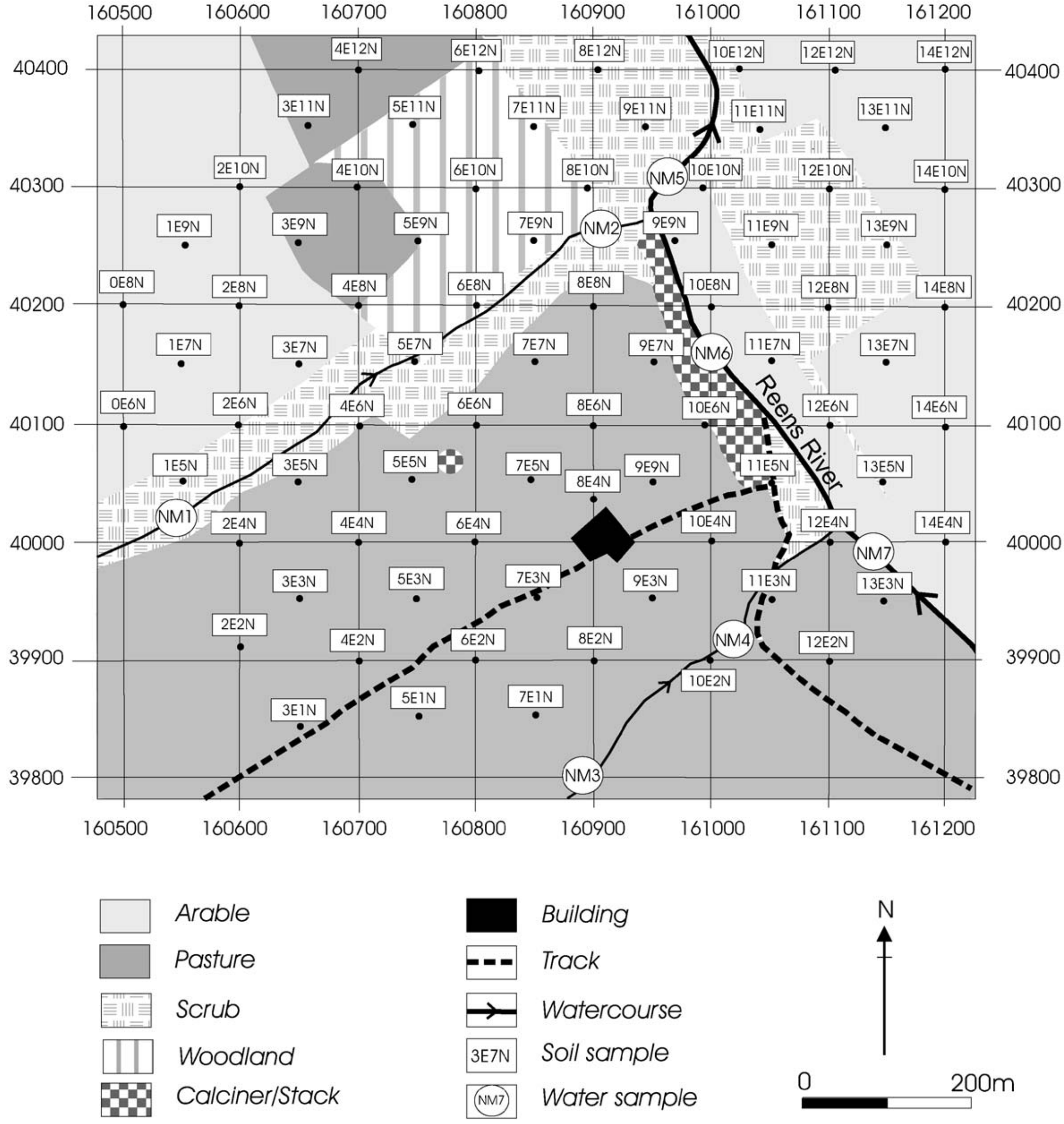

Fig. 3. Land use and soil/water sample positions within the study area.

boundaries as locators and with a back up of a Garmin 48 handheld GPS. Each sample was given a unique alphanumeric number with the grid origin to the southwest of the area of interest. A total of 78 sample sites were obtained with only six samples moved from their grid locations due to obstructions or unavailability.

At each sample site, a 30×30 cm pit was excavated by spade to the subsoil or to a maximum of 30 cm (deep plough depth) if the subsoil had not been encountered. A channel sample of the soil was then cut using a stainless steel trowel 8 cm wide, ranging to the organic layer at the top. Soil depths were measured, the soil type observed and recorded, and the samples (approximately weighting 250 g) placed into Kraft bags. At two sites, 9E9N in the valley floor and 5E5N on the hill near the calciner stack, further samples were taken for characterisation for 'down-profile' As values and particle size analysis. Channel sampling for size analysis cut a sample of approximately 250 g. Using a 10-cm-wide flat stainless steel scoop, soil samples were cut at 10 cm increments to the bottom of the 30 cm pits for down-profile values. The samples were placed in Kraft bags. To assist with the characterisation study, samples were cut into the bank on the west side of the river adjacent to the calciner from an exposure of the calciner residue dump.

To determine the aqueous contamination, water samples were taken at seven locations NM1 to NM7 from the two streams and the river running through the area (Fig. 3). Acid-cleaned 1 l plastic containers were used for the purpose of water collection.

6. Laboratory methods

Soil samples for analysis were air dried at 30 °C, weighed, disaggregated in a porcelain mortar and pestle and sieved at 2 mm through a stainless steel sieve. The oversize from sieving was bagged and retained and the undersize weighed, split by riffler to one quarter of the volume for size reduction, and the remainder retained. The quarter split was ground in a Tema mill with a chrome-steel barrel to -100 μm. The ground sample was riffle split into two parts, one for analysis and the other for retention as a replicate.

Samples for determination of the sand, silt and clay fractions were kept in the natural state, mixed and agitated with demineralised water and wet sieved through 2 mm and 63 μm stainless steel sieves using a vibrating shaker. The +2 mm fraction was thoroughly washed with demineralised water and discarded while the +63 μm fraction was washed by using demineralised water and transferred to a tray for air-drying. The -63 μm fraction and wash water were transferred to 5 l beakers and made up to 5 l with demineralised water. Four drops of 0.05% Calgon were added and agitated before solids were allowed to settle. The -2 μm clay fraction was decanted and the silt and clay fractions transferred to trays for air-drying. Samples were weighed and recorded prior to sample preparation. Sized samples (5E5N and 9E9N) of the sand, silt and clay were disaggregated in a porcelain mortar and pestle prior to riffle splitting. One-half of the sample was retained in the natural state for XRD and SEM analysis, the other of the sand and silt ground to -100 μm in a Tema mill for analysis. The clay fraction was disaggregated in a porcelain mortar and pestle, riffle split into two samples, one for geochemical analysis and the other for XRD and SEM examination.

All soil samples were analysed using Inductively Couple Plasma-Mass Spectrometry (ICP-MS) for 35 elements using 0.5 g of split sample leached in hot (95 °C) Aqua Regia before analysis at the ACME Laboratories, Vancouver, Canada. The samples were digested in a 2:2:2 mixture of ACS grade concentrated HCl, concentrated HNO_3; and demineralised water, is added to each sample. Samples are digested for 1 h in a hot water bath (>95 °C). The QA/QC protocol requires simultaneous digestion of two reagent banks randomly inserted in each batch. Sample solutions were aspirated into a Perkin Elmer Elan 6000 ICP mass spectrometer. Limits of detection for arsenic were 0.5 mg kg^{-1}. One in 10 samples was sent in as duplicates while two certified soil reference materials (GBW07405, GBW 07402) were twice sent as controls. Comparison of the 8 duplicate analyses revealed an average difference of 2.7% in the arsenic concentration. The analysis of the four control samples showed an average error of 2.2% in the arsenic concentration.

Ure and Davidson (1995) state that the chemical form, the distribution within the soil/sediment phases, the mobility and the bioavailability of contaminants determine the risk. Bioavailability is mostly related to the water-soluble fraction of the accumulated chemical while the adsorbed or insoluble solid phase is generally not available for biological uptake (Stigliani, 1994). Hence, it is important to determine the speciation of the water-soluble (bioavailable) arsenic. Twenty samples from locations crossing the field were analysed in duplicate for the concentrations of arsenic species. The method for speciating water-soluble arsenic is as follows: a 0.1 g sample is weighed into an acid-washed digestion vessel containing 10 cm^3 of deionised water and shaken overnight. The solutions were passed through Watman 541 filter papers and diluted to 20 ml with deionised water before being analysed. Extracted samples were then analysed by a hyphenated High Performance Liquid Chromatography (HPLC), Hydride Generation (HG) and Atomic Fluorescence Spectroscopy (AFS) system. HPLC separates the arsenic species on a strong anion exchange column (Gomez-Ariza et al., 1998; Moreno et al., 2000; Le et al., 2000). The coupled HG-AFS was obtained from PS Analytical. The detection limit for total arsenic is 2 ppt. For speciation, the limit of detection is 0.2 ng cm^{-3}.

Water samples were analysed by HPLC-HG-AFS by South West Water using a standardized protocol: 20 ml of unacidifed sample was placed into a polypropylene screw capped container with 6 cm^3 of HCl (d_{20} 1.18) followed by heating to 80 °C for 30 min; after cooling, 50% KI/10% is added at a ratio of 50:1 sample KI/ascorbic acid solution and left to stand for 30 min before analysis.

All air-dried samples were tested for pH on soil pulps according to British Standard 1377 (1990). A 75 cm^3 of distilled water is added to 30 g of air-dried soil, stirred and left for 8 h. The suspension is stirred again before testing with a calibrated pH meter. Two or three readings are taken and these readings should agree to within 0.05 pH units before being accepted.

XRD analysis of the sized fractions was performed using a Siemens D5000X-ray diffractometer using CuKα radiation at 40 kV, 40 mA. Profiles were measured from 2–70° in step sizes of 0.02° per 1 s giving a total time of 56 min. Major and minor minerals that are greater than 3% were identified using the DEFRACT programme. Clay samples from 5E5N and 9E9N were characterised on the XRD by the following method: one smear slide was examined untreated, and again after being heated over glycerol in an enclosed vessel for 2–2.5 h at 110 °C. The other smear slide was heated for 2 h in a muffle furnace, first at 300 °C and then at 550 °C (De Kimpe, 1993). After each heating, the slide was cooled in a silica-gel dessicator and X-rayed. The diffractometer traces of each sample were then examined.

Automated mineral analysis was carried out using QemSCAN, a fully automated scanning electron microscope (SEM), which provides rapid automated fully quantitative mineral analyses. The instrument is based on a LEO 438VP SEM fitted with an array of three Gresham energy dispersive spectrometers. Samples were run using a QemSCAN automatic mineral analyser in particle mineralogical analysis mode (PMA). Up to 4000 individual particles were analysed in each sample. Arsenic-bearing minerals found automatically by QemSCAN were then investigated interactively, and EDS X-ray spectra collected for the main occurrences.

7. Results

7.1. Water samples

Water samples from locations indicated in Fig. 3, produced values below the recommended WHO values of 50 μg l^{-1}. The stream to the north had values from 1.3 μg l^{-1} (NM1) to 7.9 μg l^{-1} (NM2) and the one to the south 2.2 to 5.9 μg l^{-1} (NM4). In the Reens River running past the calciner site, the values ran from 11 μg l^{-1} (NM) upstream, 18 μg l^{-1} (NM6) adjacent to the calciner, to 21 μg l^{-1} (NM5) just downstream of the site.

7.2. Soil mineralogy

Samples 5E5N, near the stack on the hillside, and 9E9N on the valley floor, were sized into the sand, silt and clay fractions. The XRD examination shows that the predominant mineralogy for both samples and size fractions is quartz, chlorite and muscovite minor illite and kaolinite in the clay fraction. The manganese mineral sergeevite ($Ca_2Mg_{11}(CO_3)_{13}\cdot 10H_2O$) was identified in the clay fraction of 5E5N and in sample 9E9N sand fraction, trace amounts of cassiterite (SnO_2) and rutile (TiO_2), and in the silt fraction of the same sample the manganese mineral pyrochrorite ($Mn(OH)_2$). The result of the clay XRD analysis are major quartz, illite, minor kaolinite, very minor chlorite, K feldspar and plagioclase.

The QemSCAN examination revealed arsenic-bearing minerals in most samples. Typically up to 10 arsenic-containing particles were found in each 30 mm polished block. The main arsenic species found were arsenic-oxide and iron-arsenic-oxide. These arsenic minerals were found in the following textural settings: inclusions in silicate-rich fragments, in-fills and rims associated with coke/fly ash fragments (Fig. 4), on the boundaries of silicate rock fragments, in the form of liberated arsenic-oxide grains and as inclusions in and on boundaries of liberated Fe-oxide particles.

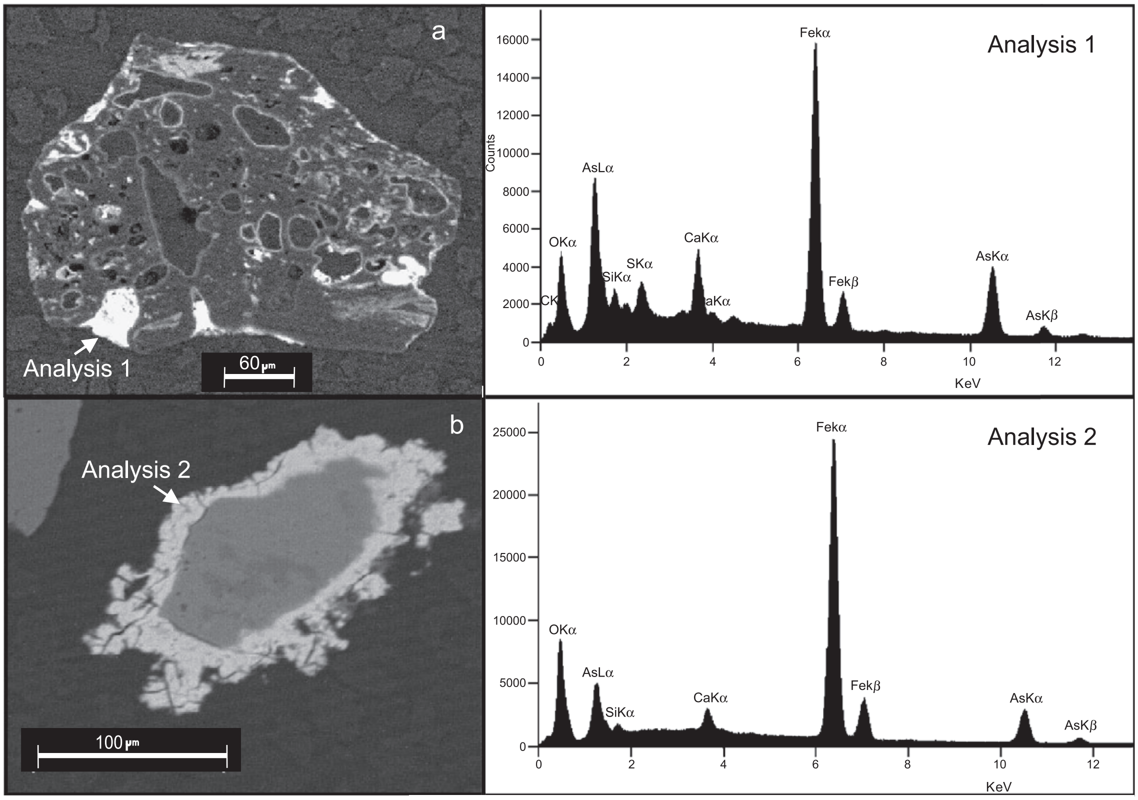

Fig. 4. Scanning electron microscope images of particulates and EDS profiles for the bright areas which are Fe–As-oxides. (a) Backscattered electron image showing Fe–As-oxide in coke/fly ash, (b) Backscattered electron image showing As–Fe-oxide rim around feldspar particle.

7.3. Soil geochemical values

Background values for arsenic from sedimentary rocks ranges from 5 to 10 mg kg^{-1} (Webster, 1999) or for Cornwall between 22 and 28 mg kg^{-1} (K. Reid pers. comm.). Background values for soils from uncontaminated areas in Cornwall range from 26 to 67 mg kg^{-1} (Elghali, 1994) with values of 63, 40, 84 mg kg^{-1} for histols, fluvisols and gleysols, respectively, for England (Ferguson, 1990). Soils in Cornwall have an average of 90 mg kg^{-1} arsenic (DoE, 1980) but can range up to 750 mg kg^{-1} in contaminated areas such as the land around Camborne/Redruth/Hayle (Abrahams and Thornton, 1987). Contamination from atmospheric dispersal from aerosols and dusts sources can be grouped into three classes; continuous point sources, such as stacks; area sources such as waste tips or industrial activity; and line sources, such as the roads that the raw or refined material was transported along (Davies, 1983).

According to the criteria above, the area of New Mill is severely contaminated by arsenic from the calciner stack, a point source; the calciner furnace site, an area source; and transported material spills, a line source. The spatial distribution of arsenic in the soil is shown in Fig. 5. Values of up to 4466 mg kg^{-1} were obtained from soils in the valley bottom downwind of the calciner and 456 mg kg^{-1} just downwind of the stack. High values of up to 1830 mg kg^{-1} to the southeast, and slightly elevated values up to 218 mg kg^{-1} to the southwest of the site, are interpreted as spills, or a line source, from either the transportation of the raw feed or refined product. High values of arsenic were found in samples close to tracks to the site and in the valley adjacent to the calciner site. This is attributed to fugitive dust from the calciner waste dump and industrial activity at the site. Samples from

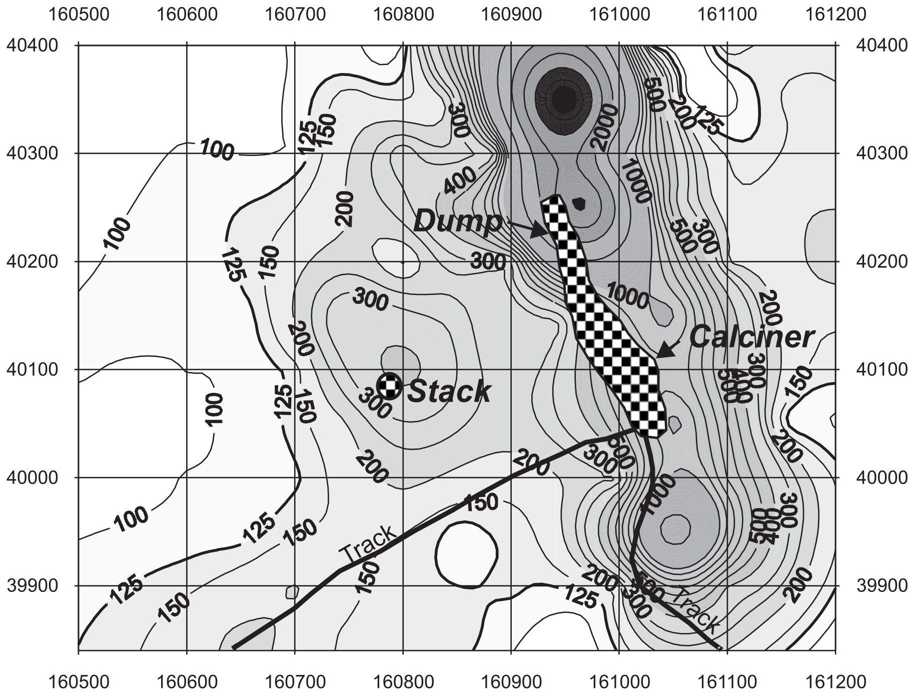

Fig. 5. Spatial distribution of As values (mg kg^{-1}) shown as a contour plot.

the calciner dump residues adjacent to the arable land in the valley, returned values up to 15% arsenic. Elevated values of tungsten, antimony, bismuth, uranium, lead, and copper are probably due to fugitive dust contamination in the adjacent field and the area interpreted as a spill further up the valley. This geochemical signature would indicate that the majority of the feedstock for the calciner came from the Camborne–Redruth polymetallic orefield some 6 km away. When the logarithmically transformed As values are plotted on a cumulative frequency plot (Fig. 6), several populations can be discerned with a background value of up to 125 mg kg^{-1} at the first inflection point and the next at 450 mg kg^{-1}, and others probably reflecting the fugitive dust and spills. Within the high values there appears to be a subpopulation where the lower end is interpreted as general dust or runoff from the calciner site due to general industrial activity and the higher levels from dust from the calciner residues when being discarded onto a dump. Background values therefore would indicate that (a) the area is contaminated or that (b) the background values for soils in this area are elevated. Spills and general surface contamination have probably been dispersed by ploughing enlarging the area of contamination. The extent of the contamination extends to the northeast, beyond the area examined, and is probably derived from the stack plume. The ground pattern around stacks is generally in the form of an ellipse, with the major axis trending along the direction of the prevailing wind (Davies, 1983), but at the New Mill site it is more dispersed. The fugitive dusts from the waste dump, however, are confined to the valley base due to topographic effects. Other contamination is probably from the stack aerosols.

Soil samples taken at 5E5N (near the stack) and 9E9N (near the calciner) were sized into sand, silt and clay fractions. When grain size and arsenic distribution (Fig. 7) are compared, the arsenic occurs in all sizes in roughly proportional amounts. In both samples, the sand and silt fractions accounted for 98.3% of the total arsenic, with the clay fractions constituting the remaining 1.7%. The sand fractions in 9E9N and 5E5N contained 63.2% and 44.6% of the total arsenic.

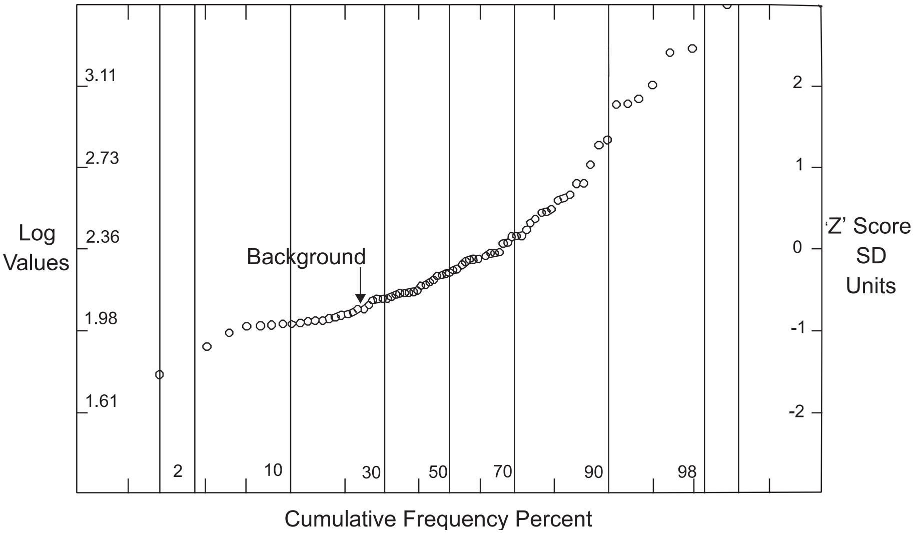

Fig. 6. Cumulative frequency plot of log transformed As values showing inflection points and background value.

This is probably a reflection of the particulate contamination in both soils, which was identified by the QemSCAN analysis. Sectioning of the soil profile to a depth of 30 cm in 10 cm sections revealed that there was no increase in arsenic values in depth. Values were similar in the three sections down-profile ranging from 228 to 252 mg kg^{-1} in sample 5E5N, and 2844 to 3029 mg kg^{-1} in sample 9E9N. These results are in good agreement with compare with Li and Thornton (1993).

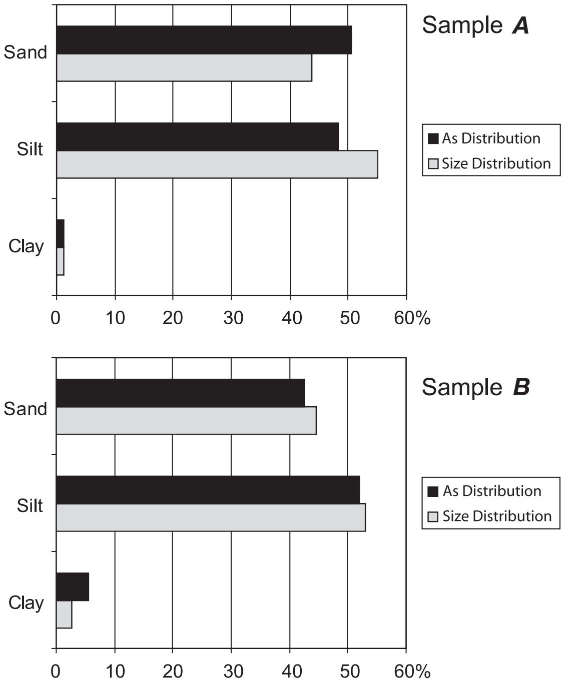

Fig. 7. Arsenic/particle size distributions in (A) sample 5E5N and (B) sample 9E9N.

7.4. Water-soluble speciation

To investigate arsenic speciation, two transects were taken across the area of interest in the shape of a cross covering both a variation in total arsenic values, pH, land use and topography. One transect runs from the south west to north east (2E2N to 12E12N), and the other from north west to south east (3E11N to 12E2N). Total water-soluble arsenic values ranged from 0.185 to 36.161 mg kg^{-1} and accounted for between 0.32% and 1.73% of the total arsenic in the samples. The results are graphically illustrated for each transect in Fig. 8. In the first transect, arsenate values rise gently peaking at sample 9E9N adjacent to the calciner residue dump where 33.6 mg kg^{-1} are recorded, and gently falling to the northeast. Arsenite values peak at this point also at 2.5 mg kg^{-1}. In the north west to south east transect, there is an increase in the available arsenite at 5E9N of 1.6 mg kg^{-1} in the woodland, where the pH is acidic at 4.8, and a high value of 11.2 mg kg^{-1} at 11E3N. The

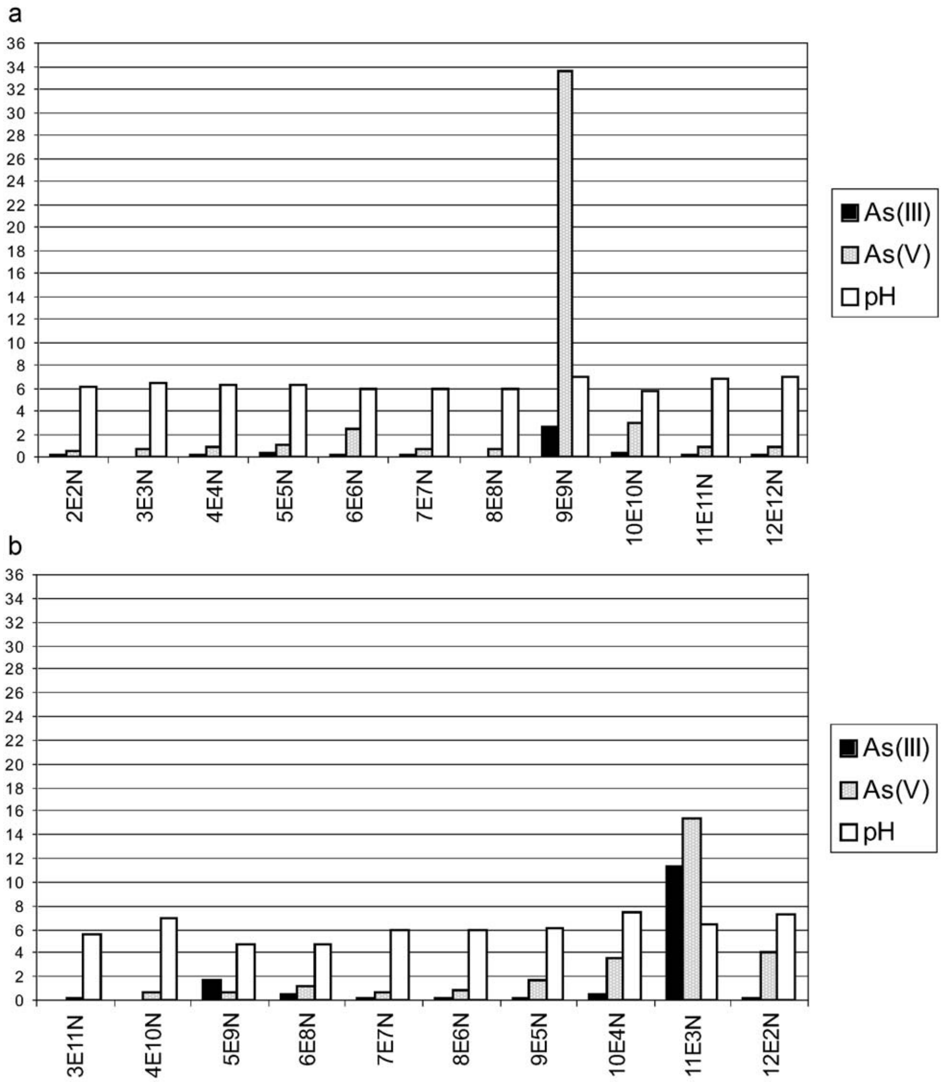

Fig. 8. Speciated water soluble As values (a) transect SW–NE and (b) transect NW–SE. Arsenic values in mg kg^{-1}.

latter is interpreted as the result of a historic spillage of arsenic soot feedstock for refining. This area is near a watercourse and is generally wet. Hence, the higher arsenite values are attributed to a more reducing environment. It should be noted that changes in oxidation state may have an important effect on the degree of bioavailability of the various phases (Stoppler, 1992). Soil textural characteristics may influence available arsenic. In the case of the New Mill soil it appears to be coarse textured. The distribution of iron oxide coatings on other soil minerals can cause locally very high concentrations of arsenic (Walchope, 1975; Lombi et al., 2000).

8. Discussion and conclusions

Soil sampling has clearly identified the calciner site through the residual contamination from the metalloid halo. At the New Mill site, the arsenic concentrations in the soil range up to 4466 mg kg^{-1} and at the calciner site waste dump up to 15%, indicating that this is a highly contaminated site. The major contamination within the site was derived from fugitive dusts from the calciner waste dump rather than from the calciner stack. However, the lower contamination levels from aerosol dispersion stack contamination would appear to be more widespread and has not been constrained in this survey. Agricultural disturbance by ploughing and leaching down-slope has probably dispersed the contamination, especially in the valley floor. QemSCAN results highlight the importance of coal/coke/fly ash as a significant carrier of arsenic contamination in addition to locked and liberated particles associated with silicates and oxides. Most of the arsenic phases appear to be in the form of oxides. The study has also shown that "hot spots" can occur along access tracks to the processing site and are probably due to either spills of the raw material, or refined product, and any investigation of a similar site should take this possibility into consideration.

Speciation of the water-soluble component in the soil samples was undertaken because the most important water-soluble inorganic species in soil are compounds of As^{3+} and As^{5+} (Vaughan, 1993). The capacity of soils and sediments to store arsenic depends on intrinsic chemical properties such as pH and on the chemical form or speciation (Stigliani, 1994). As^{5+} is the predominant species observed in free-draining agricultural soils where oxidising conditions prevail. Values of water-soluble arsenic, between 0.3% and 1.7% of the total arsenic, are higher than those reported by Kavanagh et al. (1997), who studied both agricultural soils and mine wastes in the Tamar Valley, north Cornwall. However, they are slightly lower than the maximum of 2.78% found by Xu and Thornton (1985) in garden soils in Cornwall. In making an assessment of the level of contamination, total arsenic values should be differentiated from that which is bioavailable.

The water-soluble fraction of arsenic between 0.3% and 1.7% is low for such a contaminated site, suggesting that the arsenic is bound to a solid-phase. Onken and Adriano (1997) made this observation on soil spiked with sodium arsenite and arsenate, where the water-soluble or bioavailable fraction was lowered in time. The low water-soluble arsenic values in the soils also indicate that the majority of the arsenic contamination is immobile. This is supported by the point water samples taken in the area of interest. Perhaps surprising for a highly contaminated site, they are all below 50 $\mu g\ l^{-1}$ arsenic, the WHO standard. Arsenic bound to iron oxides is relatively immobile, particularly under oxidising conditions (Smedley and Kinniburgh, 2002). This has been observed in the mineralogical examination in rims around particles of fly ash/coal and silicates. Solid phase precipitation and adsorption are the main processes that may control metalloid partitioning between the solid phase and mobile solution phase (Evans, 1989).

The highest arsenic values lie within the valley floor and, although the water-soluble component is low, any change in the pH or oxidation state could potentially release of arsenic into the Reens River. A change of pH to more alkaline conditions due to the addition of amendments such as lime or calcareous sands could also lead to increased arsenic solubility (Masscheleyn et al., 1991). While there may be diagenetic alteration of the phases over a period of time, iron arsenates are the predominant form of arsenic in the soil within the area of interest. Field redox conditions, which can influence the mobility of arsenic (Robertson, 1989), were not measured in this characterisation study and therefore require further work. In addition, constraining the high values in the valley floor and from the stack plume requires further sampling in the area.

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