

**Microscopic and chemical studies of metal particulates in tree bark and attic dust:
evidence for historical atmospheric smelter emissions, Humberside, UK.**

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Abstract

Tree barks and attic dusts were examined as historical archives of smelter emissions, with the aim of elucidating the pathways of pollution associated with a plume of Sn and Pb contamination in top soils, found close to the former Capper Pass smelter, Humberside, UK. Samples were collected from three villages within the area of the contamination plume. Scanning Electron Microscopy (SEM) and bulk chemical analyses were used to assess particle type, number and deposition patterns. SEM analysis of dusts and bark revealed that Sn and Pb particles were present in samples from all three villages along with copper, zinc and iron particles. These were almost entirely $<10\ \mu\text{m}$ in diameter and occurred mostly as oxides, frequently forming clusters of sub-micron crystals. Samples further from the smelter contained considerably fewer particles. We present images of smelter derived Sn particles. Chemical assays of the barks and attic dusts demonstrated that concentrations of Sn, Pb, Cu, As, Sb and Cd diminished with increasing distance from the source. Strong positive correlations were found between Sn and Pb, As, Sb and Cd in the attic dusts. Enrichment Factors (EF) were calculated for these trace elements based on topsoil element concentrations obtained from the soil survey of the study area. Decreases in these trace element concentrations and EF values with distance away from the smelter are consistent with trends found in the soil survey for Sn and Pb and are typical of deposition patterns around smelter stacks. The study demonstrates that tree bark and attic dusts can be effective archives of metal particulates deposited from large static emission sources.

Introduction

A recent high-resolution soil geochemical survey across part of eastern England revealed unusually large concentrations of Pb and Sn in a plume extending up to 24 km north-east from the site of the former non-ferrous Capper Pass smelter ¹. It was situated on the north bank of the Humber Estuary and closed in 1991, four years before the soil survey samples were collected. This anomaly, when first presented as a conference poster ² produced considerable interest, particularly from groups concerned with public health issues in communities living close to the smelter during and after its operation ³. Topsoil (0-15 cm depth) Sn concentrations of ~100 mg kg⁻¹ within 1.5 km of the smelter are substantially larger than global mean soil Sn concentrations ⁴ of between 1 and 2 mg kg⁻¹. At distances of 8 km, in the direction of the dominant prevailing wind direction from the former Capper Pass smelter, soil Sn concentrations were between 10 and 30 mg kg⁻¹.

It is likely that the plume of Sn and Pb contamination reported in the soil survey was a result of smelter-related particulate deposition. However, on occasion, if emissions ceased many years ago and there are few or no documentary records, it may be necessary to gather additional evidence (e.g. the identification of particles specific to the smelting process) to clarify the pathway link in the source-pathway-receptor relationship. There are very few reports regarding pollution from Sn smelters in the literature. Some authors ^{1,5} have reported plumes and contamination in soils, whereas Mantell ⁶ stated simply that Sn smelter emissions consisted of 'fine particles of Sn and Sn oxide carried off with spent furnace gases' with no description of particle size, type or morphology.

In the initial phase of the study, Scanning Electron Microscopy (SEM) was used to analyse local soil samples to identify any smelter-derived particles. Despite finding Sn

particles this approach was considered flawed because the metal-bearing particulates in the soil may not have originated from atmospheric deposition, and those particles observed appeared to be altered by physical and chemical processes. Consequently, an atmospheric transport and deposition pathway could not be attributed unequivocally to these particles. This pathway would include both (i) direct deposition from smelter stack fallout and (ii) the re-suspension and transport of particles. This second route would have been active both when the smelter was operating and since closure. Therefore tree bark and attic dusts were collected from three villages at several distances and various directions from the former Capper Pass smelter and assessed for their use as historical archives that could help (i) clarify that smelter stack emissions were the source of the Sn and Pb plume found in the soil, (ii) enable the particles found to be characterised in terms of type and size and (iii) provide further information relating to deposition patterns.

Tree barks and attic dusts have often been used to identify contemporary and historical emissions from nearby smelters. Tree bark pockets (formed by the enclosure of surface bark by the trunk during growth and subsequently dated via the annual growth rings) have been used as time capsules of pollution^{7,8}. However, this method relies on the availability of felled trees containing suitable bark pockets. An alternative approach is to use exposed tree bark from living trees, because over long periods of time atmospheric particles can accumulate, providing a record of historical local deposition⁹. However, there are few reports of exposed bark being used to identify a pollution source so many years after emissions have ceased. Undisturbed attic dusts are another potential archive for atmospherically deposited particles and have been shown to be effective across urban areas and in the vicinity of smelters¹⁰⁻¹⁴. These have the additional benefit that they are protected from wash and aqueous alteration that may affect tree barks over long periods

of time. Although tree barks and attic dusts have been used regularly to provide information relating to pathways of contaminant deposition, it must be remembered that they represent a semi-quantitative record because of the vagaries of transport and capture efficiency.

In our study, microscopy techniques were used to identify and characterise heavy metal particles in exposed tree barks and attic dusts with respect to relative particle numbers, size, chemistry and morphology to determine whether they were likely to have been (i) emitted from a non-ferrous smelter stack or other smelter operations and (ii) aeri-ally transported. Chemical analyses of attic dusts and barks were used to calculate Enrichment Factors (EF) using local soil geochemical data for several elements. These were used to assess whether particulate abundance diminished with increasing distance from source as suggested by the soil survey.

Materials and Methods

Study region and sample collection

The Capper Pass smelter occupied ~28 ha of a 160 ha site on the north bank of the Humber estuary to the west of Hull (Figure 1). It was the world's largest producer of tin from secondary materials, including solder, drosses, non-ferrous slags, flue dusts and tin-based alloys and residues. At its peak in the early 1980s the plant produced about 90 000 tonnes of metal per year, including about 10 % of the world's output of tin. The smelter operated for 53 years from 1938 to 1991¹⁵. The original 61 m high chimney was replaced in 1971 by a chimney of ~183 m. Whilst predominantly a Sn smelter, it also processed many secondary materials containing potentially toxic elements including Pb, Sb, As, Cu, Ni, Zn and Cd¹⁵. Long-term data from the British Meteorological Office for a nearby

weather station and summarized in the form of a wind rose ¹⁶ show that the strongest winds in the region are from the south-west, which is also the dominant wind direction.

Samples of tree bark and dusts were collected from three villages near the smelter (Figure 1). The first was North Ferriby approximately 300 m east of the site. We chose two further villages, Walkington (12 km north of Capper Pass) and South Cave (8 km north-west), on the margins of the plume of soil contamination, based on the soil survey data ¹. Given their locations and data on wind strength and direction, we would expect the magnitude of pollution to decrease in the order: North Ferriby >> Walkington > South Cave.

It was possible that there were other potential sources for the atmospheric deposition of metals in our study area, although it is predominantly an agricultural area. Both Walkington and North Ferriby are similar distances from the city of Kingston-upon-Hull, and therefore subject to similar urban, non-smelter-derived particulate pollution. A search of the UK Environment Agency's Pollution Index ¹⁷ showed that there were steelworks in Scunthorpe, situated ca. 15km to the South and a titanium-oxide manufacturing facility was also located in Grimsby, ca. 20 km to the south east of our study area.

Tree bark sampling

Metal concentrations in the outer part of the tree bark (surface) are determined largely by aerial deposition, since dissolved metals taken up from the soil are transported in the xylem cells which are separated from the bark by a layer of phloem and cambium ⁹. Fine particles adhere strongly to surfaces of vegetation and some are retained even after assiduous washing ¹⁸. The roughness of bark varies from species to species and

influences the quantity and type of particulates retained. Trees with rough bark may be better able to trap particles than ones with smooth bark. However, they also tend to shed bark from a relatively early age. By contrast, trees with smooth bark do not begin to shed until mature (~50 years). The original surface of smooth bark is retained in most places, although it tends to split as the tree gets larger. Thus, on a young smooth-barked tree, some of the bark surface will have been continuously exposed to the atmosphere from the beginning of the tree's life.

In March 2004, samples of bark were collected from several smooth-barked trees in each of the three villages, all in quiet residential areas where fewer particulates from local road-vehicle emissions were likely to have polluted the air. Smooth-barked trees such as cherry (*Prunus serrula*) and whitebeam (*Sorbus aria*) were sampled, because they retain their bark, as described earlier. On each tree, a 3 cm² piece of bark was removed with a stainless steel chisel. In each case, bark from the side of the tree facing the dominant wind direction (south-west) was chosen. A standard sampling height of 1.5 m above ground level was used to avoid areas where soil particles may splash the trunk. Tree ages were estimated by measuring the circumference at 1.5 m above the ground. Trees in the temperate zone of the UK, and in this environment, enlarge their girth by approximately 1 cm per year, so the circumference in cm divided by π gives an approximate age of the tree (P. Casey, *per comm*). The estimated ages of the trees were between 23 to 49 years. The estimated age for two of the trees, were confirmed to be accurate to within 1 year, by local residents. Table 3 lists the samples comprehensively. In addition, a bark scraping was taken from each tree with a stainless steel knife for subsequent chemical analysis. An area of 15 x 15 cm was scraped at a height of 1.5 m according to a method used by E. Schelle (*pers comm*). At each tree, the bark was scraped to a depth of approximately 1

mm and the scrapings placed in a plastic bag. The location of each tree was recorded to determine its distance from the former site of the smelter.

Attic dust sampling

Attic dust was sampled from municipal buildings of similar age, construction style and height. In North Ferriby, six dust samples were collected from two church buildings and a village hall. In Walkington, another sample of attic dust was taken from the Methodist church. We could not access any suitable buildings in South Cave. All the buildings were single-story brick buildings with slate or tiled roofs. They were built between 1850 and 1949 and so were present for the entire period when the smelter was operating. None of the attics had been disturbed since construction, and dust samples were collected from beams that would not have been affected by routine access. The dust samples were collected by brushing onto sheets of clean paper and then transferring it to a plastic sample bag. A new brush was used for each sample.

Microscopy methods

The surfaces of bark and attic dust samples were examined using Scanning Electron Microscopy (SEM). Bark surfaces were prepared by attaching the underside of the bark to an aluminium sample mount using 'Leit-C' carbon-based cement. Representative subsamples of attic dust were dispersed on sticky carbon tabs placed on aluminium sample mounts. All samples were coated with a thin (~20 - 30 nm) carbon film to prevent electric charge accumulating. The analysis was undertaken using a Leo 435VP Scanning Electron Microscope operated in both Secondary Electron Imaging (SEI) and Backscattered Electron Imaging (BSEI) modes. Semi-quantitative chemical analysis of individual particles was carried out using an ISIS300 Energy-Dispersive Spectrometer. As all the

samples were carbon-coated, the presence or absence of carbon in any particle could not be determined.

Images were taken of all tree bark sample surfaces under SEI mode at the same magnification ($\times 50$) to record the roughness and quantity of lichen on their surfaces. Samples were selected for further examination, based on similarity of species, estimated age and surface appearance. Two tree bark samples of the same species (Whitebeam) and similar age were chosen, one from North Ferriby (42 years old) and one from the more distant village of Walkington (49 years old), for systematic particle counting. In addition, two attic dust samples were chosen for particle counting; one from North Ferriby Village Hall and one from Walkington Methodist Church.

Particles were counted using the SEM in BSEI mode to scan across a pre-selected, fixed area of sample, while the brightness of the images was set so that only particles of a certain atomic density would be visible. This 'threshold' scanning method is a standard procedure used to characterise populations of environmental particles¹⁹. In this case, the threshold brightness was chosen to be equal to that of the Fe oxide particles that were present in every sample. This method was found to be effective in discriminating 'light' from 'heavy' particles. 'Heavy' particles in this context are taken to be those with average atomic density greater than that of the Fe oxides, and should include any particles where the chief constituent is a 'heavy' metal, such as lead and tin. Note that although Fe forms more than one oxide phase, all phases have similar atomic densities compared with heavy metal-bearing grains.

Particles were mapped at a magnification sufficiently high to identify bright particles as small as 0.1 μm in diameter. The area was scanned at a magnification that gave a field of view of approximately 80 μm^2 . The total area scanned was 0.2 mm^2 of each tree bark sample and 0.1 mm^2 of each stub-mounted dispersion of attic dust. Once identified, the ‘heavy’ particles were classified according to their composition and size. Qualitative examinations were also performed on these and other samples in which Sn and/or Pb-bearing particles were characterised in more detail in terms of their chemistry, size and morphology. Table 1 lists the samples analysed.

Analytical Methods

Tree bark scrapings were milled before microwave digestion in a mixture of HNO_3 and H_2O_2 with a small amount of HF acid added. Attic dust samples were sieved to pass < 0.63 μm , to remove a few brick and plaster fragments within the sample, and then digested on an automated heating block with an HF- HClO_4 - HNO_3 attack. The digests from both attic dust and tree bark were analysed by ICP-MS (VG Elemental PQ ExCell) and ICP-AES (Fisons ARL 3580) for a suite of 19 major and trace elements (Al, Ca, Fe, K, Mg, Mn, Na, P, S, Ti, Cr, Ni, Cu, Zn, As, Cd, Sn, Sb, Pb) and results are expressed on a dry-weight basis.

Calculation of enrichment factors

To determine whether element concentrations in the tree bark and attic dust were large, Enrichment Factors (EF) were calculated. These relate the concentration of an element, X, to a crustal element (e.g. Ti, Al, Sc) in the particulate deposition, and this ratio is then normalised to the ratio of those elements in the Earth’s crust. Both Bellis *et al.*²⁰ and

Ketterer *et al.*²¹ adopted this methodology for assessing atmospheric deposition and enrichment on tree barks, in soil and in air.

For the calculation of EF in tree barks the following assumptions were made: (i) elements are concentrated at the bark surface and (ii) elements are accumulated to a comparable degree. If these conditions are met the ratio of elements in the bark will be independent of the efficiency of the accumulation and the depth of sampling²⁰. In addition, Bellis *et al.*²⁰ suggested that the EF factor in bark should equal the time-averaged EF in air, assuming that the contributions via the soil solution are insignificant compared with airborne inputs. The major non-anthropogenic input of particulate deposition from the air is soil dust, hence the use of crustal values²⁰. However, data from a geochemical survey for topsoil throughout this region of eastern England shown in Figure 1 were available²². These data, in place of average crustal values, provide a more accurate and local ratio of elements against which to normalise the data. Enrichment factors using Equation (1) were calculated for all elements analysed in the tree bark and attic dust, using Al as the reference element:

$$EF = \frac{X_a}{Al_a} \times \frac{Al_s}{X_s} \quad (1)$$

where X_a and Al_a are concentrations of metal and Al in dust or bark, and Al_s and X_s are their median concentrations from the soil survey.

Results and discussion

SEM results - particle counting

Table 1 describes the samples that were analysed by SEM. Particle counting was performed on two tree barks and two attic dusts, one each from the villages of North Ferriby and Walkington. A summary of counted particles in the tree bark and attic dust is reported in Table 2. Particles were identified by the thresholding method and have been characterised as ‘A’, ‘B’, and ‘C’ type. All particles of atomic density equal to or greater than Fe oxide, are categorised as ‘A’ type. Those particles with a greater density than that of Fe oxide are identified as ‘B’ particles, and are a sub-set of ‘A’, and those which contain Sn and/or Pb are identified as ‘C’ particles, a sub-set of ‘A’ and ‘B’.

Most of the particles characterised as ‘A’ are Fe oxide particles (a common constituent of soils) with some Fe oxide fly ash particles. For the two bark samples, equal areas have similar numbers of total ‘A’ particles, approximately 300 over the area mapped for each sample, or 7,500 per mm². In the attic dusts, there were similar numbers of estimated ‘A’ particles per unit area in both samples, suggesting a similar density of distribution on the prepared sample mounts from the two villages.

The percentage of counted particles containing Sn and/or Pb (i.e. C as a percentage of A) varies widely amongst the samples, with the North Ferriby samples (both bark and attic dust) having higher concentrations (7 and 34%) than the Walkington samples (0 and 2%) (Table 2). Although only four samples were analysed by this technique, the difference in Sn and Pb particle concentrations between samples from the two villages is considerable. Apart from those containing Sn and Pb, the ‘B’ particles comprised various ferrous metals and occasional other phases such as zircon and barite (see Figure 2). Table 2 gives more details of the Sn and Pb particles, both by composition and size. In terms of particle size, the overwhelming majority (97 %) of these particles are less than 10 µm in diameter.

This size class is much smaller than that of the attic dusts as a whole, based on qualitative observation. In addition, around two thirds (63 %) of the Sn and Pb particles observed are even finer-grained (i.e. $< 1 \mu\text{m}$ in diameter). These grain sizes are consistent both with an airborne depositional pathway and with a smelter emission origin²³⁻²⁵. It is the PM_{10} ($< 10 \mu\text{m}$) particulate that is the inhalable fraction of dust, and $\text{PM}_{2.5}$ that can penetrate the alveolar regions of the lung, is thought to be the fraction most hazardous to health²⁶.

SEM results - qualitative observations

Detailed, qualitative observations were made of many of the Sn and Pb-bearing particles from several samples of the bark and attic dust from both North Ferriby and Walkington to assess their composition, morphology and size. Many of the particles were sub-micrometric in size, and it was therefore difficult to obtain SEM images showing morphological detail or to obtain chemical analyses uncontaminated by surrounding material. However, larger particles (i.e. 1 to $10 \mu\text{m}$) were more successfully characterised for their chemical composition. For particles in this size range the chemical analyses by SEM tend to include contributions from the material surrounding or underlying the heavy metal particles. On the barks this was generally the organic substrate containing carbon and oxygen. In the attic dusts, the 1- $10 \mu\text{m}$ heavy particles were frequently resting on or mixed with alumino-silicates or calcium sulphate (plaster) grains. In addition, as the samples were coated with carbon, the presence of carbon in the particles could not be reliably determined. Despite these limitations, on several occasions we could determine the qualitative composition and phase type of a particle. Individual particles were found to consist of mixtures of metal and oxide forms, including Sn metal, Sn oxide, Pb oxide, Sn-Pb metal and Sn-Pb oxide, with or without small amounts of Cu, Fe or Zn. Pure Sn and Sn oxide were the most common forms, whilst Pb metal was rarely seen. Sn and Pb

can form many types of oxide phase, depending on the oxidation state (i.e. co-ordination number) of the metal. The SEM chemical analyses were not fully quantitative, so the oxide phase of the metal could not be determined exactly. However, the Sn oxide is likely to be cassiterite (SnO_2), a tetragonal phase that is the only natural oxide of pure tin²⁷ and one that forms after heating pure Sn in oxygen⁶. This particle assemblage is representative of the secondary processing of Sn and other metals at the Capper Pass smelter. Metal sulphate and sulphide particles are commonly found where primary sulphide ore materials containing Pb, Zn and Cu are smelted^{23-25,28} and their apparent absence is perhaps indicative that Capper Pass was primarily a reprocessing smelter. This observation appears to be borne out by the chemical analyses. No apparent trend was found in concentrations of S in the tree barks between the three villages and in the attic dusts it is probable that the CaSO_4 from gypsum plaster was probably one of the major determinants of S concentration (Table 3).

Many of the larger particles of Sn were found to consist of loose aggregates of micrometric to sub-micrometric, apparently crystalline grains (Plates 1). These aggregates consist of mixtures of metals and oxides. The individual crystalline grains often appeared equant and possibly even pseudo-cubic. The combination of metals and metal oxides in loose, ultra-fine grained aggregates strongly suggests a smelter, rather than a primary ore, origin. Aragón-Piña et al.²⁴ reported similar clusters of sub-micrometric Pb-bearing particles near metallurgical works in Mexico. Large concentrations of fly-ash particles and spherical Fe oxide or Fe silicate particles were identified in all attic dust samples and some barks. In particular, the spherical Fe oxide particles are typical of high temperature furnaces²⁴ and such particles are typically emitted from smelters, steelworks and power stations. It is likely that these emitted Fe

particulates came from the active steelworks in Scunthorpe. However, Sn and Pb particles were frequently seen to be closely associated with these fly-ash particles, and in some cases to be intimately mixed with them (e.g. Plate 2).

Chemical analysis of tree barks and attic dusts

SEM analysis has demonstrated that particles found on the tree barks and attic dusts were likely to be smelter derived. Chemical analysis of the tree barks and attic dusts can give more information regarding the spatial distribution of the smelter particulates. Table 4 lists the results of chemical analysis of the attic dusts and tree barks. For barks, there are large variations and no apparent trends in the composition of the major elements, either within or between the three villages. Some of these variations might be due to the variation in the composition of the soil or its parent material, as well as a multitude of anthropogenic sources. The concentrations of some trace metals (Pb, Sb, Sn, Cd, As and Cu) associated with smelting are higher in North Ferriby, the closest of the villages to the smelter. However, not all the trees sampled in North Ferriby exhibit large concentrations of metals. This suggests that other factors such as species, age, the relative roughness of their bark, and the location of tree within the built environment might influence the efficacy of the bark to act as a collector of metal-enriched particles.

Elements in the attic dusts come from both atmospheric sources and construction materials in the attic itself. Major elements were found to have greater concentrations in attic dust than tree bark. We found both plasterboard (gypsum) and brick dusts in the attics during sampling, and these are likely to have contributed to the observed concentrations of Al, Ca, Fe, K, Na, Ti, Mg and S. There were only small differences in major element concentrations between the North Ferriby and the Walkington attic dusts.

However, some trace elements (Pb, Sb, Sn, Cd, As, Zn) had noticeably larger concentrations in samples from North Ferriby than in those from Walkington (Table 3). Although there were too few samples to test statistical significance, the mean concentrations of these five elements in the North Ferriby attic dusts are between 4 and 10 times greater than the values in the single Walkington attic dust. A correlation matrix for the chemical elements was computed and scatter diagrams drew to display relationships. Those elements with the closest relationships ($r > 0.68$ for tree barks and $r > 0.89$ for attic dusts) are listed in Table 4. The strongest correlations with Sn were for Cd, Sb and Pb, suggesting that they have a common source. Figure 3 shows the positive correlations between Sn and As, Sb, Cd and Pb. Table 3 lists the attic dust data with values from other published sources, collected in urban areas with no specific point source of pollution^{11,13}. For some elements (Fe, As, Cd, Sn, Sb and Pb) the concentrations found in the attic dust samples collected from North Ferriby and Walkington were larger than the published data for large urban areas where many sources of pollution are found. Therefore, the large concentrations of trace elements found in the attic dusts sampled from rural areas that we assayed in this study suggest a local emission source, such as the Capper Pass smelter.

Enrichment factors

Reimann and Caritat^{29, 30} criticized many uses of Enrichment Factors based on average crustal or deep (profile) soil concentrations, especially in calculating deposition rates because of: (i) the variable composition of real rocks, (ii) the natural fractionation of elements that occurs during near-surface processes, (iii) the differential solubility of minerals in weak chemical digestions and (iv) the common disregard for the importance of biogeochemical processes for element concentrations as observed at the Earth's

surface. However, EFs were not used in this study to calculate deposition rates, but to examine whether a trend in contamination is analogous to the one found in the soil survey data¹. Median surface soil concentrations (n=6549) from a geochemical survey of the Humber Trent region¹ were used to provide a local estimate of topsoil geochemistry in Equation (1). Graphs of \log_{10} EF were plotted for several elements from both tree barks and attic dusts against distance from the smelter to assess patterns of contamination (Figure 3). Tin (Sn), Cd, Pb and Sb all show greatest enrichment in the tree and attic dusts near the smelter and these EF values generally decrease rapidly with increasing distance. In comparison, an EF of ~ 1 was obtained for Ti. A potential source of Ti emissions exists from a TiO factory in Grimsby. However, our calculated EF of ~ 1 for these two elements, suggests that the likely provenance of both elements is the clay fraction in soil. Therefore it is likely that any enrichment of Sn, Cd, Pb, and Sb is from non-soil sources. The EF values found for the trace elements at 12 km from the smelter are all between 10 and 100 times greater than background demonstrating that particulates travelled considerable distances from the smelter site. Values for the EFs for Sn and Pb decreasing with increasing distance from the smelter are analogous to the patterns reported for their concentrations in the soil survey data¹.

Conclusions

A combination of microscopy and chemical assays were used to clarify the pathway responsible for a plume of soil Sn and Pb contamination near the Capper Pass smelter. Attic dusts and tree barks provided evidence, fifteen years after emissions ceased, that aerial deposition of particles (mainly $< 10\mu\text{m}$), were responsible for the soil contamination plume. The Sn and Pb particles were mainly oxides, although some pure or mixed metal particles were also found. Chemical analysis of the bark and attic dusts

and the use of EFs demonstrated that concentrations decreased with distance away from the smelter, analogous to the soil survey, and typical of smelter stack deposition.

Acknowledgements

This study was partly funded by Towells solicitors (Wakefield) as an investigation of the impact of the former Capper Pass smelter on the surrounding land. The authors would like to thank Paul Casey, tree officer for East Riding County Council for his help and advice concerning sampling methods for tree barks, the Rev. Antony Bash the Rev. Liz Allison and Rev. Mark Street for providing access to their attics. This paper is published with permission of the Director of the British Geological Survey. We would like to thank Professor R Webster (Rothamsted Research) for comments on an earlier draft of the manuscript.

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Figure and Plate Headings

Fig 1: The study region in Eastern England showing the villages in which samples of bark and dust were collected in relation to the site of the former Capper Pass smelter. Coordinates are metres of the British National Grid

Fig 2: Relationship between Sn and other PTEs in attic dusts collected from buildings in two villages near the Capper Pass site.

Fig 3: Enrichment factors in tree barks and house dusts sampled from the villages of North Ferriby, South Cave and Walkington, England.

Plate 1: North Ferriby Methodist Church attic dust, imaged by SEM in Back-Scattered Electron mode, showing an aggregate of ultra-fine metal-bearing particles whose compositions include Sn metal, Sn oxide, Sn + minor Cu (metal and oxide), Sn-Pb-Cu oxide.

Plate 2: Walkington Methodist church attic dust, imaged by SEM in Back-Scattered Electron mode, showing an aggregate of particles consisting of spheres of silicate fly ash mixed with ultra-fine metal-bearing particles (appearing as bright regions). The metal-bearing particles include Sn oxide, Sn-Pb metal, Sn-Pb oxide, Pb oxide, Fe oxide.

Table 1: Summary of tree bark and attic dust samples analysed by SEM and collected from three villages close to the former Capper Pass Sn smelter.

<i>Sample description</i>	<i>Estimated age (years)</i>	Location	<i>SEM heavy particle counting?</i>
Tree bark: Whitebeam	42	North Ferriby	Yes
Tree bark: Lime	27	North Ferriby	-
Tree bark: Sycamore	48	North Ferriby	-
Tree bark: Whitebeam	49	Walkington	Yes
Attic dust: Village Hall	55	North Ferriby	Yes
Attic dust: Methodist Church	126	North Ferriby	-
Attic dust: Methodist Church	154	Walkington	Yes

Table 2: Numbers and characteristics of heavy particles in tree barks and attic dusts collected from three villages close to the former Copper Pass Sn smelter and identified by SEM particle counting.

	<i>N Ferriby Whitebeam</i>	<i>Walkington Whitebeam</i>	<i>N Ferriby Village Hall</i>	<i>Walkington church</i>		
Area mapped (mm ²)	0.2	0.2	0.1	0.1		
A Estimated number of particles ≥ Fe oxide in density	334	287	128	145		
B Number of particles > Fe oxide in density	38	5	49	16		
(as % of A)	(11)	(2)	(38)	(11)		
C Number of particles with Sn and/or Pb	25	0	43	3		
(as % of A)	(7)	(0)	(34)	(2)		
(as % of B)	(66)	(0)	(88)	(19)		
<i>Breakdown of 'C' particle numbers by element type:</i>						
	<i>Particle size (µm)</i>	<i>N Ferriby Whitebeam</i>	<i>Walkington Whitebeam</i>	<i>N Ferriby Village Hall</i>	<i>Walkington church</i>	<i>Total</i>
Pb (± V)	0.1 - 1	1		5		6
	1 - 10	3		9		12
	10 - 50			1		1
Pb, Sn (± Zn)	0.1 - 1	3		3		6
	1 - 10			3		3
	10 - 50			1		1
Sn (± Zn, Cu, Ni, Fe)	0.1 - 1	18		14	1	33
	1 - 10			7	2	9
	10 - 50					0
Total Pb and/or Sn, PM1	0.1 - 1	22	0	22	1	45
Total Pb and/or Sn, PM10	0.1 - 10	25	0	41	3	69
Total Pb and/or Sn, PM50	0.1 - 50	25	0	43	3	71
<i>Remaining 'B' particle numbers by element type:</i>						
Metallic Fe ± Cr, Mn, Ni, Zn, Ca	0.1 - 50	10	5	3	8	26
Other	0.1 - 50	3	0	3	5	11
Total 'B' particles, PM50	0.1 - 50	38	5	49	16	108

*B is a subset of A

**C is a subset of B

± in the table means 'with or without the presence of...'

Table 3: Chemical composition of tree bark and attic dust samples collected from three villages (units mg kg⁻¹) close to the former Sn smelter at Capper Pass.

Village (Tree / Building)	Al	Ca	Fe	K	Mg	Mn	Na	P	S	Ti	Cr	Ni	Cu	Zn	As	Cd	Sn	Sb	Pb
-----Tree Barks (mg kg ⁻¹)-----																			
Walkington (Horse Chestnut)	1610	8160	1300	2340	501	55	279	547	1200	155	3	3	18	28	<2	0.6	2.7	0.8	20
Walkington (Lime)	1190	13500	1220	3390	614	123	257	1020	1890	83	4	3	14	37	<2	0.4	0.8	0.6	32
Walkington (Cherry)	616	13400	681	<1250	563	303	<420	703	1210	64	<5	<30	34	24	<30	3	<3	<3	14
Walkington (Sorbus)	1940	2020	2780	1310	446	30	354	650	1610	138	8	5	20	25	<2	0.4	9.6	3.4	60
South Cave (Cherry)	2790	2860	4310	1380	550	53	402	896	2540	180	14	12	23	54	2	0.4	6.4	2.3	49
South Cave (Silver Birch)	660	1850	1200	620	257	18	149	394	1070	43	4	4	11	49	<2	0.2	1.3	0.6	14
South Cave (White Beam)	1120	5240	2040	879	366	28	163	676	1610	75	5	5	14	20	<2	0.3	3.9	0.9	24
South Cave (Beech)	2310	4450	2850	2830	615	48	640	1100	2620	135	10	7	19	34	<2	0.3	2.2	1.6	34
North Ferriby (Lime)	530	6090	967	1230	312	22	<92	958	2400	122	4	<6	17	21	<6	0.6	2.8	0.7	21
North Ferriby (Sycamore)	931	13500	2390	1830	581	104	261	1400	2100	69	5	10	63	54	21	8.5	252	129	1430
North Ferriby (White Beam)	437	11250	1190	1010	740	111	79	936	930	34	4	7	52	54	5	2.6	442	7.9	414
North Ferriby (Beech 1)	825	7640	2240	1980	468	246	238	452	1390	42	7	10	50	54	11	5.6	128	22	989
North Ferriby (Beech 2)	686	21510	2780	1120	770	221	284	497	1230	45	8	8	146	130	19	12	99	29	2100
-----Attic Dusts (mg kg ⁻¹)-----																			
North Ferriby (Methodist Church 1)	33200	111000	32180	9190	17410	563	3730	840	71400	1960	44	48	129	266	127	8	139	34	546
North Ferriby (Methodist Church 2)	34100	100600	34500	10400	13900	566	4980	1200	71700	1660	51	80	297	548	175	24	408	74	1180
North Ferriby (Methodist Church 3)	32700	104000	41460	9470	8680	675	4170	1090	74000	2010	61	74	352	437	181	18	342	63	1160
North Ferriby (Parish Church)	45400	46800	60680	12100	9620	742	7220	2070	38500	2080	83	81	1400	3110	128	39	877	40	3370
North Ferriby (Village Hall 1)	40400	110900	47670	10680	8550	1070	5560	1330	34100	2800	66	99	758	501	171	23	566	84	3370
North Ferriby (Village Hall 2)	40800	107800	50490	10870	8420	1020	5430	1420	35700	2840	66	111	884	526	193	27	682	120	3650
Walkington (Methodist Church)	30600	79200	30700	8850	14800	683	5900	978	55500	2160	59	36	121	203	46	3	48	13	270
Published values																			
¹ Ambient Urban Attic Dusts	26000		27000			580	4000			1600	83	55	125	1620	28	3.9	20	7.4	646
² Ambient Urban Attic Dusts						459					37		81	860	12	2.4	9.9	5.6	860

¹Sajn (2003); ²Cizdziel & Hodge (2000)

< values reported on the basis of 3x SD of the blank

Table 4: Correlations ($r > 0.70$) of elements in tree bark and attic dusts collected from three villages close to the former Capper Pass Sn smelter

Attic Dusts	Tree Barks
Al – Fe (0.74)	Al – Na (0.81)
Al – Na (0.80)	Al – Ti (0.83)
Fe – Cr (0.95)	Fe – Cr (0.95)
Fe – Ni (0.71)	Cu – Cd (0.94)
Na – S (0.79)	Cd – Sn (0.80)
Na – Cr (0.71)	Cd – Pb (0.97)
Sn – Cd (0.80)	Sn – Sb (0.94)
Sn – Sb (0.94)	Sn – Pb (0.79)
Sn – Pb (0.80)	
Cu – Cd (0.94)	
Cu – Pb (0.94)	
Zn – Cd (0.81)	
Zn – Pb (0.85)	
As – Cd (0.92)	
As – Sb (0.79)	
As – Pb (0.92)	
Cd – Pb (0.98)	

Fig 1:

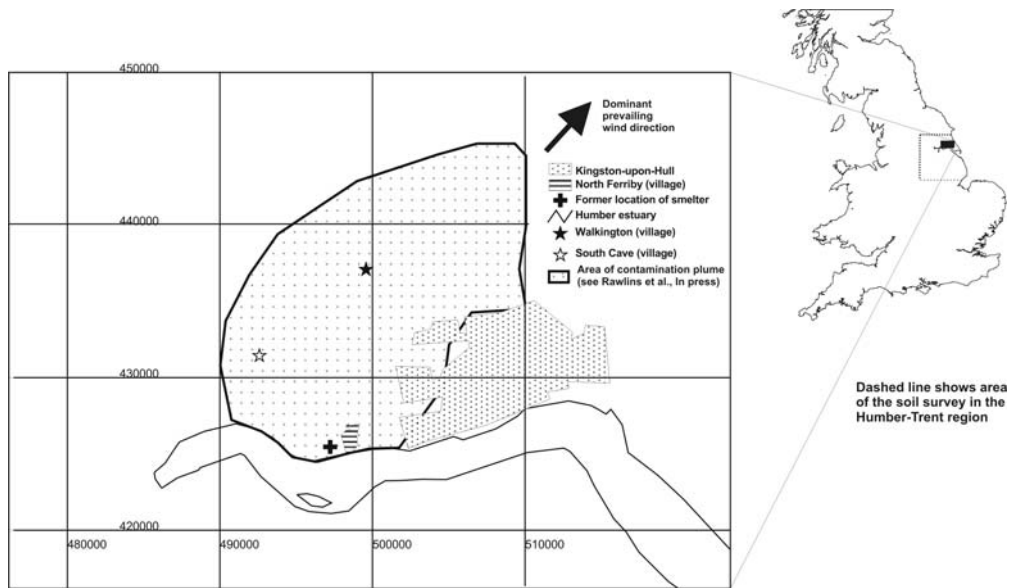


Fig 2:

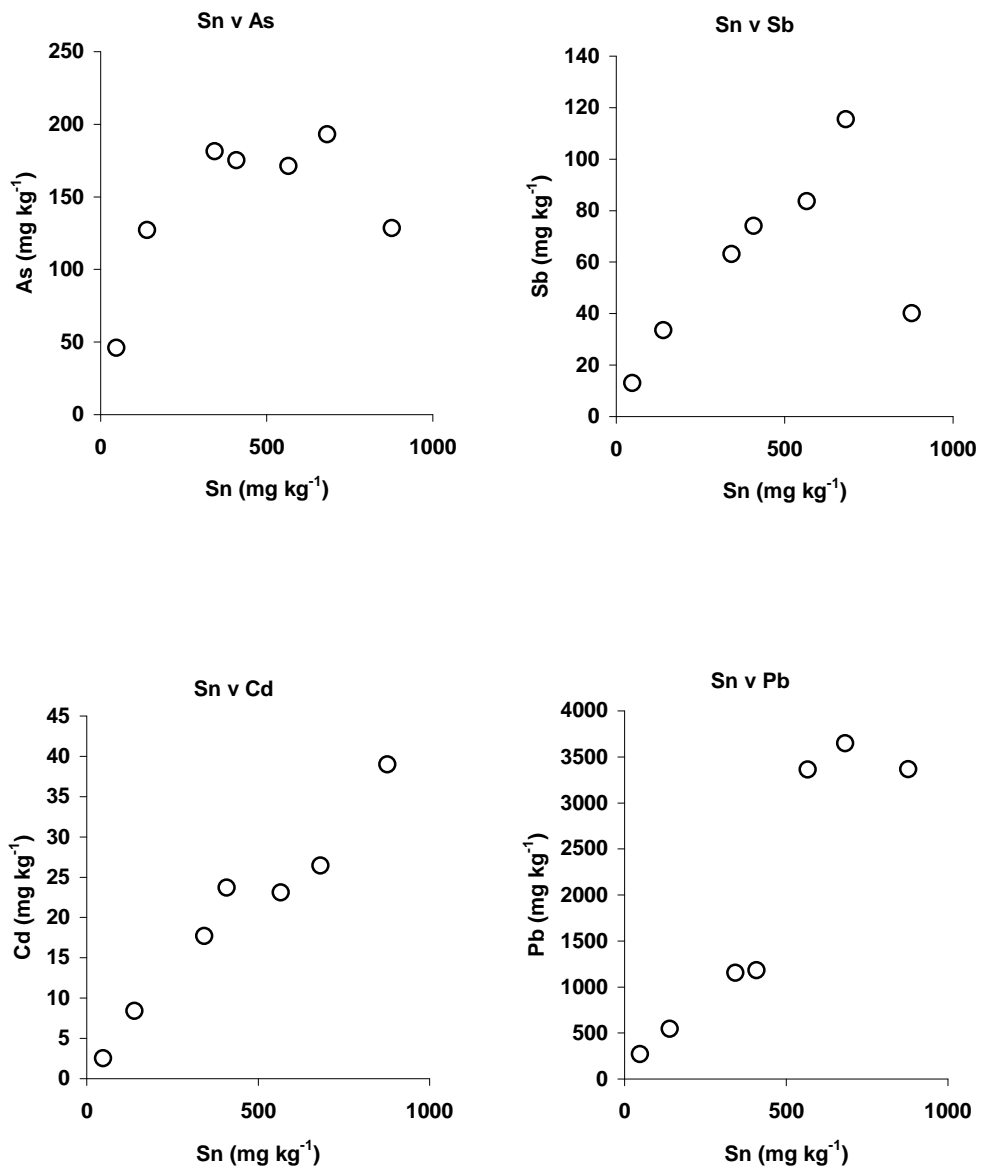


Fig 3:

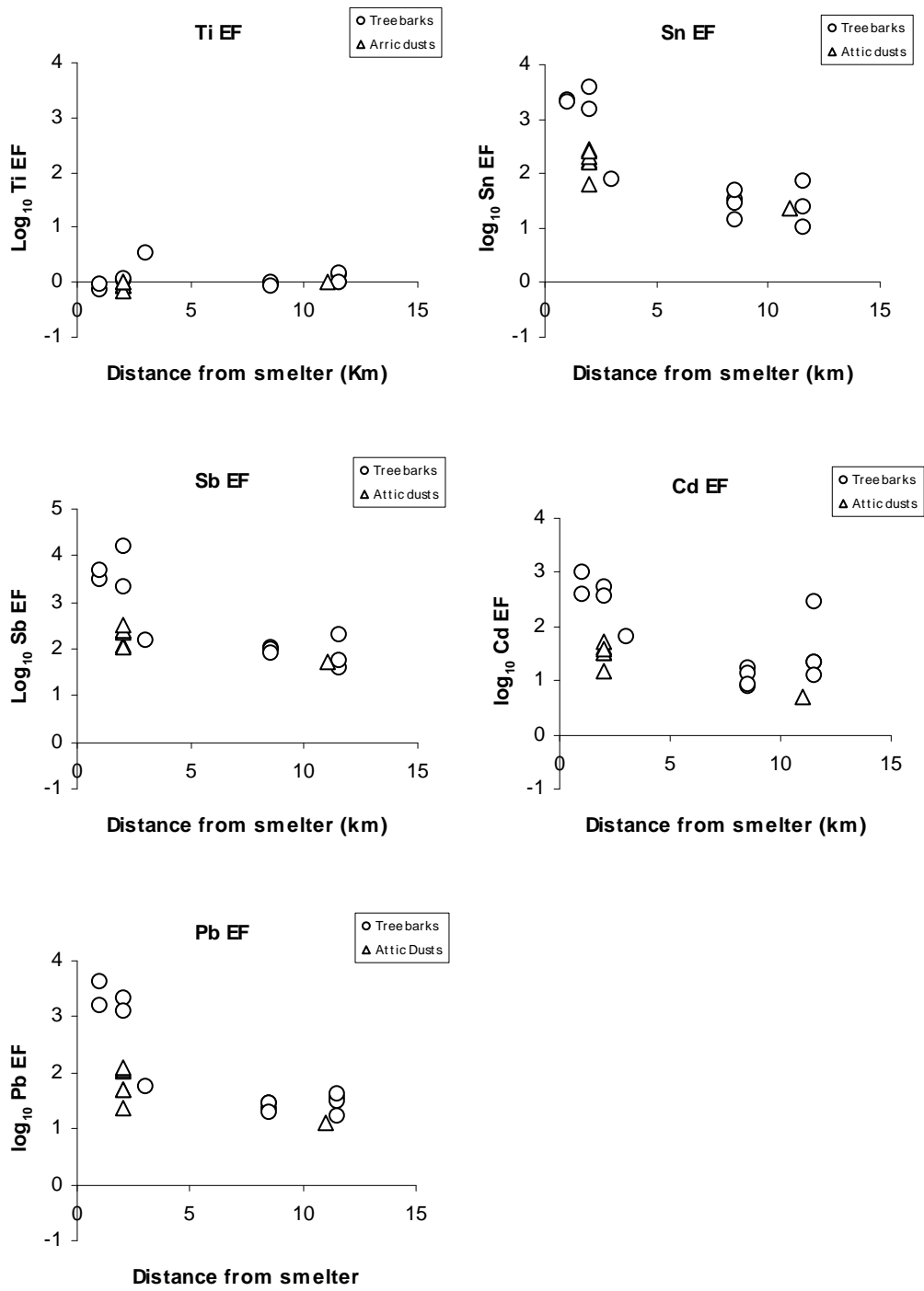


Plate 1.

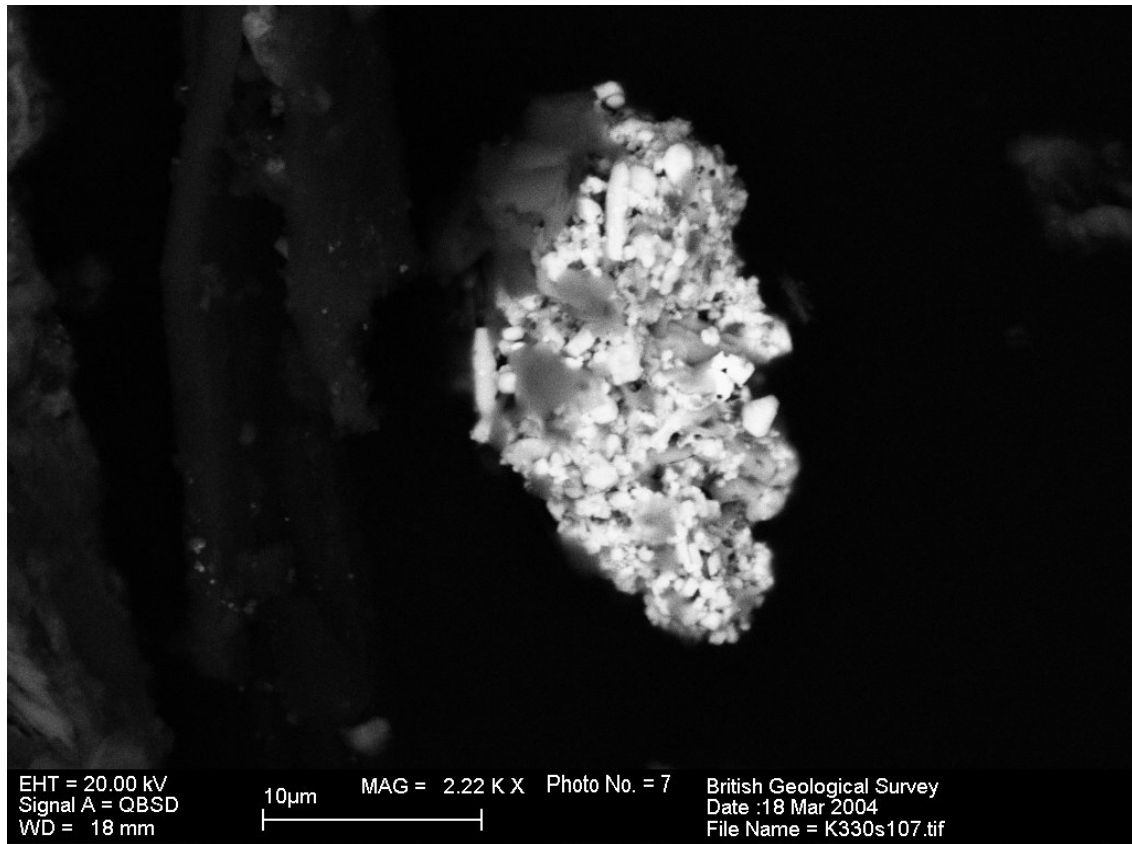


Plate 2.

