The spatial distribution of arsenic in east Cornwall: geological and anthropogenic signatures

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Although the generalised picture of arsenic distribution in Cornwall and Devon has been established, detailed systematic investigation of most As problem areas has yet to begin. In particular little is known in detail of the spatial distribution of As in soils and waters. Understanding of geological control on As distribution is important in predicting natural As highs in soils and waters. Regional stream sediment and soil sampling demonstrate that highly anomalous geological As concentration is associated with specific phases of granite intrusion (particularly those with tungsten mineralisation, such as at Hemerdon and Castle-an-Dinas) and some main stage mineralised veins, as well as skarns. Analysis of major granite bodies shows that As concentrations are highly variable and highs are consistent with known mineralisation. Exclusion of granite areas during data analysis shows considerable variation with sedimentary lithologies and highlights lesser, although significant, anomalies in black shales in north Cornwall, especially near Port Isaac, and in west Devon.

More detailed work has focused on the area between the Lynher and Tamar rivers, around the granite ridge between Callington and Gunnislake, and adjoining the well studied Devon Great Consols hot spot. Available geochemical data were integrated with information on topography and known As production. In the west of the area, data from percussion drilling and soil sampling indicates that geological As anomalies are associated with known vein complexes (e.g. Redmoor) and hydrothermal leakage into surrounding lithologies at Haye. Impact from mining appears to be limited to mine waste and acid mine drainage. In the east of the area, the situation is different with significant airborne contamination around the Greenhill and Coombe refineries. These plumes appear to be up to 1.5 km downwind from the stacks. Stream water in much of the area exceeds 10 ppb although little is used for human consumption. Further definition of the plumes and their arsenic mineralogy is required.

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Introduction

Although the impact of arsenic (As) on the environment in S W England is significant (Farago *et al.,* 1997), the spatial distribution of As in the surface environment is not well understood in detail (Hamilton, 2000). The surface signature as mapped in the Wolfson Stream Sediment Atlas of England and Wales (Webb *et al*., 1978) shows inhomogeneous distribution with the areas of the Tamar Valley and west Cornwall being most affected (Abrahams and Thornton, 1987). Follow-up studies to the Wolfson Atlas and other work has demonstrated that the spatial patterns are a combination of primary As distribution and secondary re-working, especially as a result of mining, beneficiation and calcining (Nichol *et al.*, 1971; Colbourn *et al.,* 1975; Haswell, 1985; Abrahams and Thornton, 1987; Mitchell and Barr, 1995). This spatial distribution of As in the Wolfson Atlas correlates well on a regional basis with plots of As production (Burt *et al.*, 1984, 1987). However, a more detailed knowledge of surface As distribution would help focus investigations of the potential impact of As, which is becoming more urgent with the recognition of the risk to human health of low level leachable As and the proposed imposition of a 10 ppb As limit for drinking water in the USA (National Research Council, 2001).

The means of generating an improved knowledge of As distribution used in this study are the integration of available geological, geochemical and mine production information, as well as a higher precision regional survey of much of the relevant area of east Cornwall, within a GIS environment.

The area between the Lynher and Tamar rivers was selected for more detailed study as it was part of the Tamar Valley area that was known to be extensively contaminated and a large data set was available. Detailed information on this Cornish part of the area was largely lacking, in contrast to the detail available on the (Devon Great Consols) part of the area east of the Tamar in Devon (Thornton, 1995; Kavanagh, 1998; Hamilton, 2000).

In order to put the distribution of As in the area between the Lynher and Tamar rivers in context, the broader distribution of As in soils and stream sediments in east Cornwall is discussed, as are the production and dispersion of As.

Arsenic production and methods

Arsenic was produced in S W England up until the 1950s, either as a by-product of Sn and base metal mining or as a principal product during times of high As prices or declining by-product prices, notably during the 1870s and the First World War (Burt, 1988). The main mineral extracted was arsenopyite, often mixed with arsenian pyrite. Other As bearing minerals such as löllingite and As bearing sulphosalts were of lesser importance. Mining was largely underground with extraction of sulphides often made by hand labour and the sulphides were usually hand separated. Some re-mining of surface dumps also took place in the late nineteenth and early twentieth centuries (Dewey, 1920).

Arsenic oxide was produced by heating the arsenic-rich sulphides and subsequent cooling of the sublimates in long, labyrinthine cooling chambers (Toll, 1953; Earl, 1996). This production was of two types: a crude arsenic soot was formed at the mine site by calcining in rotary calciners, whereas the refining of the soot and calcination of transported ores in some cases took place in refineries in a central location (e.g. Roseworthy, Camborne) at a distance from the mines. Arsenic soot can also be recovered as a by-product of the smelting of other ores, notably tin, as is currently been undertaken at the Oruro tin smelter in Bolivia.

Production figures up to 1913 are available from the work of Burt *et al.* (1984, 1987) who digitised them from official figures. These 1913 figures have been updated by Dewey (1920) and Dines (1956). There is as yet no central database of the location of As calciners and refineries in SW England, although the work of Earl (1996) provides a good starting point, supplemented by data in Brown and Acton (1999) and surveys such as that at Gawton by Weddell and Pye (1989).

Dispersion and health impact

Dispersion of As from mining takes a number of forms: (1) leaching and airborne dispersion from waste rock, (2) leaching and dispersion from tailings after beneficiation, (3) leaching from mine workings into surface waters, from adits and pumping, often as acid mine drainage (AMD), (4) airborne dispersal from calciners and refineries, and (5) man made dispersion of waste rock and tailings for use in agriculture and building.

The signal of contamination can therefore be complex. On mine sites airborne dispersal from calcining can be mixed with contamination from the mining process or from AMD. The mineral form of As is important as it governs the bioavailability of the element and hence its toxicity. Investigation at Devon Great Consols by Kavanagh *et al.* (1997) showed that As in normal mineral soils was less labile than that of mine waste.

The calcination and refining process has long been known to cause problems to animal health. For example, Barton (1972) cites an early nineteenth century law suit in which the owners of the Perranarworthal refinery (formerly a tin smelter) were sued for the results of chimney discharge. In the Tamar Valley cattle were known to be poisoned by windblown dispersion of calcined arsenic (Gulworthy W.I., 2000) and more recently a dog, which habitually drank from a puddle on the football pitch at Gunnislake, was poisoned (Tavistock Times, 2000). Little is known of the sub-clinical impact on human health although attempts have been made to measure uptake at Gunnislake (Peach and Lane, 1998) and excretion (Kavanagh *et al.,* 1997).

Regional distribution of As

In order to understand the distribution of As around the mineralised areas between the Lynher and Tamar rivers, it is necessary to discount the effects of As variation caused by changes in background (geogene) concentration, related to changes in sedimentary lithology or intrusion of the different granite phases.

The regional distribution of As has been previously mapped by Webb *et al.* (1978). However, the methodology of the map production, smoothing using a window of 3 × 3 cells of 6.5 × 6.5 km, and the relatively poor (80%) precision of the modified Gutzeit analytical method do not allow detailed spatial analysis of the data by lithology. Smoothing can give rise to artefacts, in particular the As halo around the Bodmin Moor Granite could be a result of averaging very elevated values derived from mineralised centres. This distribution and a follow-up study by Aguilar (1974), led to the suggestion by Aguilar (1974), and supported by Colbourn *et al.* (1975), that As was not only concentrated in vein mineralisation but present disseminated within the metamorphic aureole, giving rise to a more general increase in background As. This possible enrichment within the metamorphic aureole, which has a major impact on any model, was tested on two datasets:

(1) a regional dataset of stream sediments (shown in Figure 1) collected by students at the University of Leicester over 1986-2001,

(2) a regional soil survey of the area to the north of the St. Austell Granite discussed in detail by Camm and Moon (2001)

Regional stream sediments

Stream sediment samples were collected by students at the University of Leicester on a systematic basis over much of east Cornwall and part of west Devon. The samples were sieved to –190 μm and analysed by ICP-ES for 23 elements using a nitric-perchloric digestion. Quality was controlled using duplicates and in-house reference materials, previously calibrated by

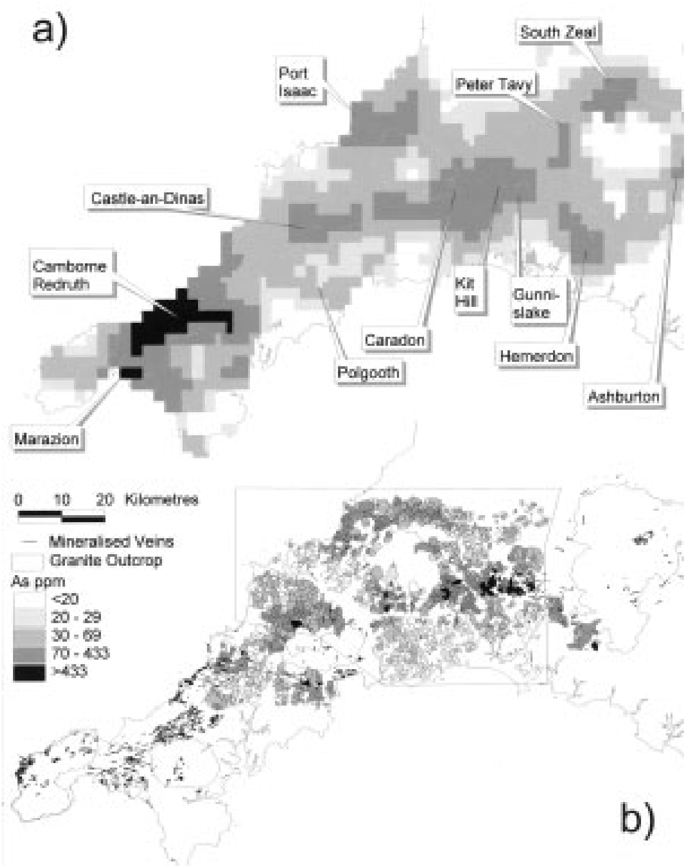

Figure 1. *Regional stream sediment geochemistry of As in Cornwall and W Devon. a) Grey scale grid of part of map from Webb et al. (1978). Analytical method: modified Gutzeit. Percentiles: 90, 95, 99, 99.9 of data for England and Wales. Arrowed locations are As highs. b) University of Leicester data (number of samples = 1305). Analytical method: ICP-ES following nitric-perchloric digestion. Subdivision as for map a). The box shows the area used for the catchment analysis, the results of which are shown in Figures 2 and 3.*

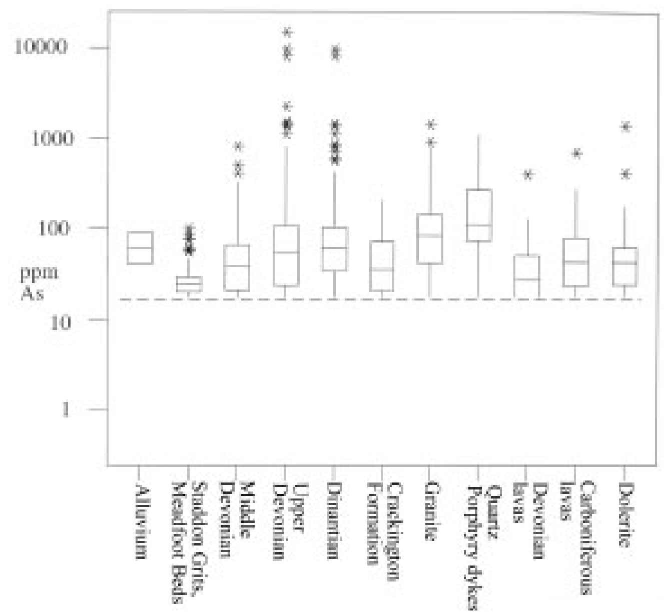

Figure 2*. Boxplot of As concentrations for known unmineralised catchments subdivided by lithology. Units based on B G S 1:250 000 sheets, Bristol Channel, Lands End, Lizard, Lundy, Portland (British Geological Survey 1988, 1985, 1983a, 1983b and 1983c). Dotted line is 20 ppm detection limit.*

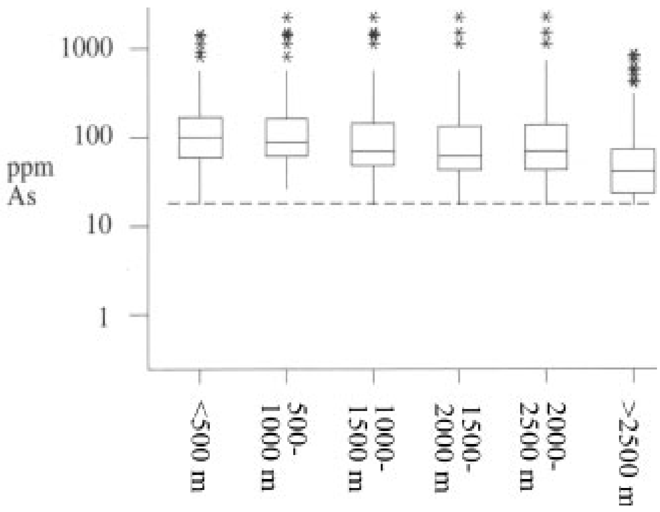

Figure 3. *Boxplot of As catchments (location shown in Figure 1) divided by distance from granite boundary. Dotted line is 20 ppm detection limit. Boxbottom is 25 percentile and top 75 percentile.*

international reference materials. The precision of As determinations is typically 20% at 50 ppm As, although the direct nebulisation method used has a relatively high detection limit of ~20 ppm As.

This data set was used to test the possible lithological control on background As enrichment by subdividing the data by mapped lithology and distance from the granite outcrop. The methodology used was that of Bonham-Carter *et al.* (1987) and detailed by Moon (1999). Rather than representing samples as a point and contouring both up and down stream, a stream sediment sample is taken as being representative of its upstream catchment. In this study the catchments were generated using the Ordnance Survey 50 m Digital Elevation Model (Digimap, 2001) and the Basin1 extension to Arcview 3.2 (Basin1, 2000). The catchments are then linked after editing to the attribute data collected during geochemical analysis and the geochemistry of the catchment is derived by overlaying catchments on geology derived from geological coverages. At the time of writing, attributed 1:50 000 geology was not available for the area and lithology was based on sub-division of the 1:250 000 coverage (British Geological Survey, 1982, 1983a, b, c, 1985, 1988). Known mineralised catchments were removed by selecting only those catchments that did not contain known veins, as digitised from the 1:50 000 geological maps. The results provide a geochemical value for each geological sub-division of the catchment and the results can be interpreted by examining the overall distribution of elemental concentration by lithology (Figure 2). A similar approach is used to plot As concentration against distance from granite by overlaying catchments on 500 m buffer zones around the selected granites (Figure 3). The area used was that surrounding the Bodmin Moor Granite (Figure 1) and includes both known mineralised and non-mineralised areas. In general the data set presented here shows a very strong correlation with that of Webb *et al.* (1978) as shown in Figure 1.

The lithological analysis of the stream sediments (Figure 2) shows that the Upper Devonian and Lower Carboniferous units are significantly enriched compared to the Meadfoot Beds, Staddon Grits and Culm. Examination of Figure 1 shows that the major area of enhanced As background is between St. Teath and Port Issac. Although this area is known to carry veins with Sb and As sulphosalts (Clayton *et al.,* 1990) soil sampling by Major (1985) shows that As enrichment is not directly related to known mineralisation and is probably related to the occurrence of metal-enriched shales, although this needs to be confirmed. A study by the author shows that the area to the north of St. Teath is strongly enriched, probably as the result of the movement of mineralising fluids along low angle faults (Figure 4) and possible re-use of mineralised material in building. This As-rich unit extends eastwards towards Dartmoor and the metalliferous unit contains a number of black shale-hosted zinc prospects. In the area on the NW of Dartmoor, on the strike continuation of these units, As-rich skarns have been investigated for possible base metal and tin potential (Dearman and El-Sharkawi, 1965).

The median values of granites and, particularly, the co-magmatic quartz porphyry dykes (elvans) are also enriched although they show considerable variation and the central areas of the granite plutons are lower. For example the Bodmin Moor Granite is enriched at its contact in the Caradon and Millpool

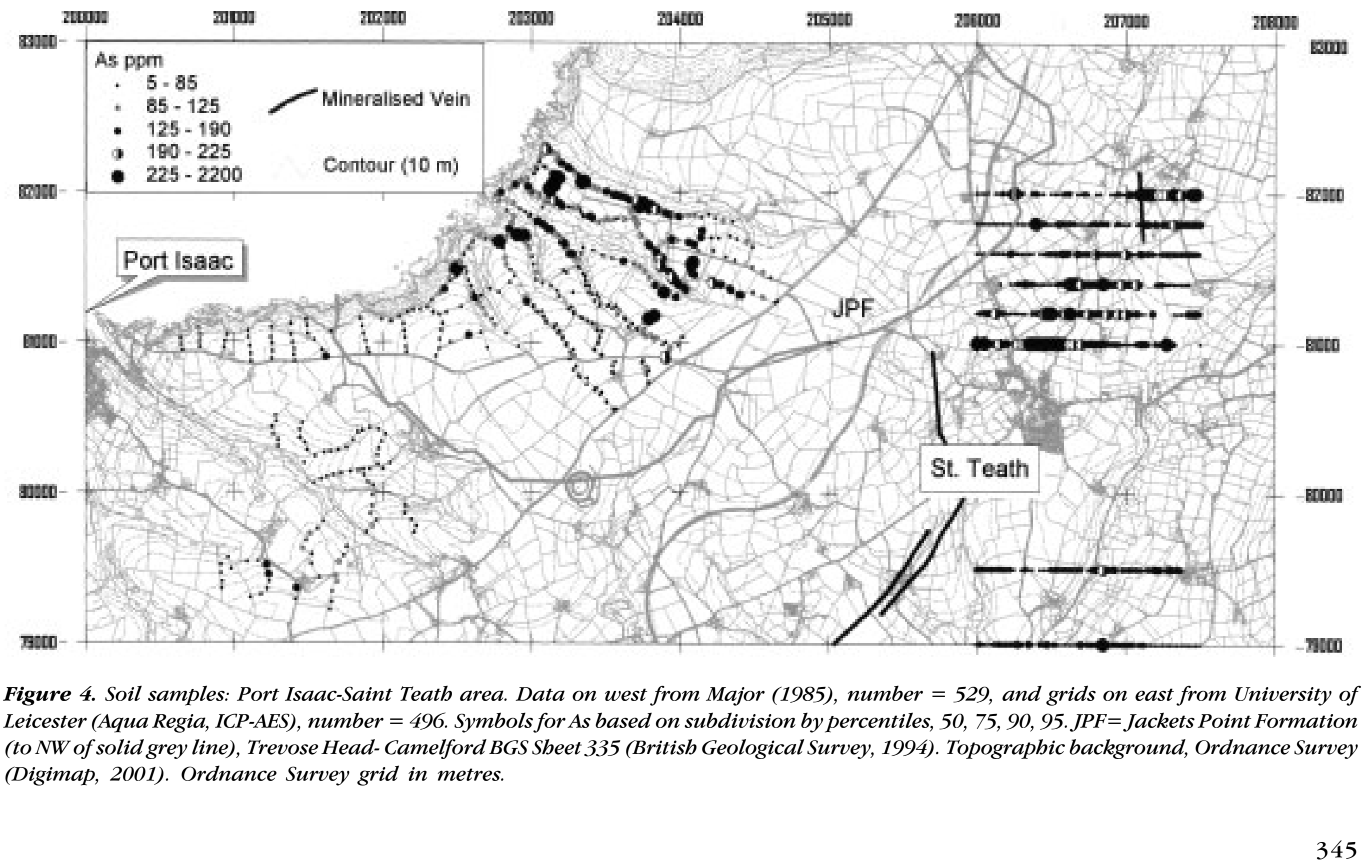

Figure 4. *Soil samples: Port Isaac-Saint Teath area. Data on west from Major (1985), number = 529, and grids on east from University of Leicester (Aqua Regia, ICP-AES), number = 496. Symbols for As based on subdivision by percentiles, 50, 75, 90, 95. JPF=Jackets Point Formation (to NW of solid grey line), Trevose Head- Camelford BGS Sheet 335 (British Geological Survey, 1994). Topographic background, Ordnance Survey (Digimap, 2001). Ordnance Survey grid in metres.*

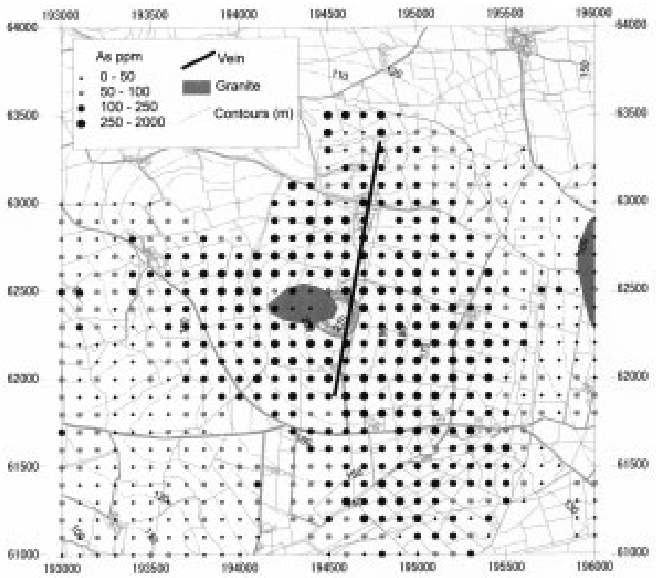

Figure 5. Soil samples, Castle-an-Dinas, 100 m grid, number of samples = 647. Arsenic rounded percentiles, 50, 75, 95 of whole data set. Topographic background, Ordnance Survey (Digimap, 2001). Ordnance Survey grid in metres, 10 m contour interval. Geology from BGS Bodmin sheet 347 (British Geological Survey, 1982).

areas, known to be mineralised respectively in copper and tungsten, but the western contact appears to have low As concentrations. There is no systematic variation with distance from the Bodmin Moor Granite (Figure 3) although broadly the area within 2.5 km of the granite has a higher median As concentration than that outside this distance.

Regional soil survey north of the St. Austell Granite

This regional sampling campaign was undertaken as part of a commercial programme and the details have been discussed in Camm and Moon (2001). All samples were collected within the metamorphic aureole of the St. Austell Granite. The results around Castle-an-Dinas (Figure 5) showed that As enrichment is spatially related to the tungsten vein and relatively late intrusion of the Castle-an-Dinas Granite (Dines, 1956). Although there is a good correlation between As and W in the main vein, As also appears to form a halo around the Castle-an-Dinas Granite. A similar effect was observed in a study at the Hemerdon W-Sn deposit (Woodham, 1985). A maximum As content (up to 3000 ppm As) was observed within the metasediments 150-200 m from the granite contact. Elsewhere within the regional soil sampling, As was generally low with the exception of a small area to the west of the St. Austell Granite.

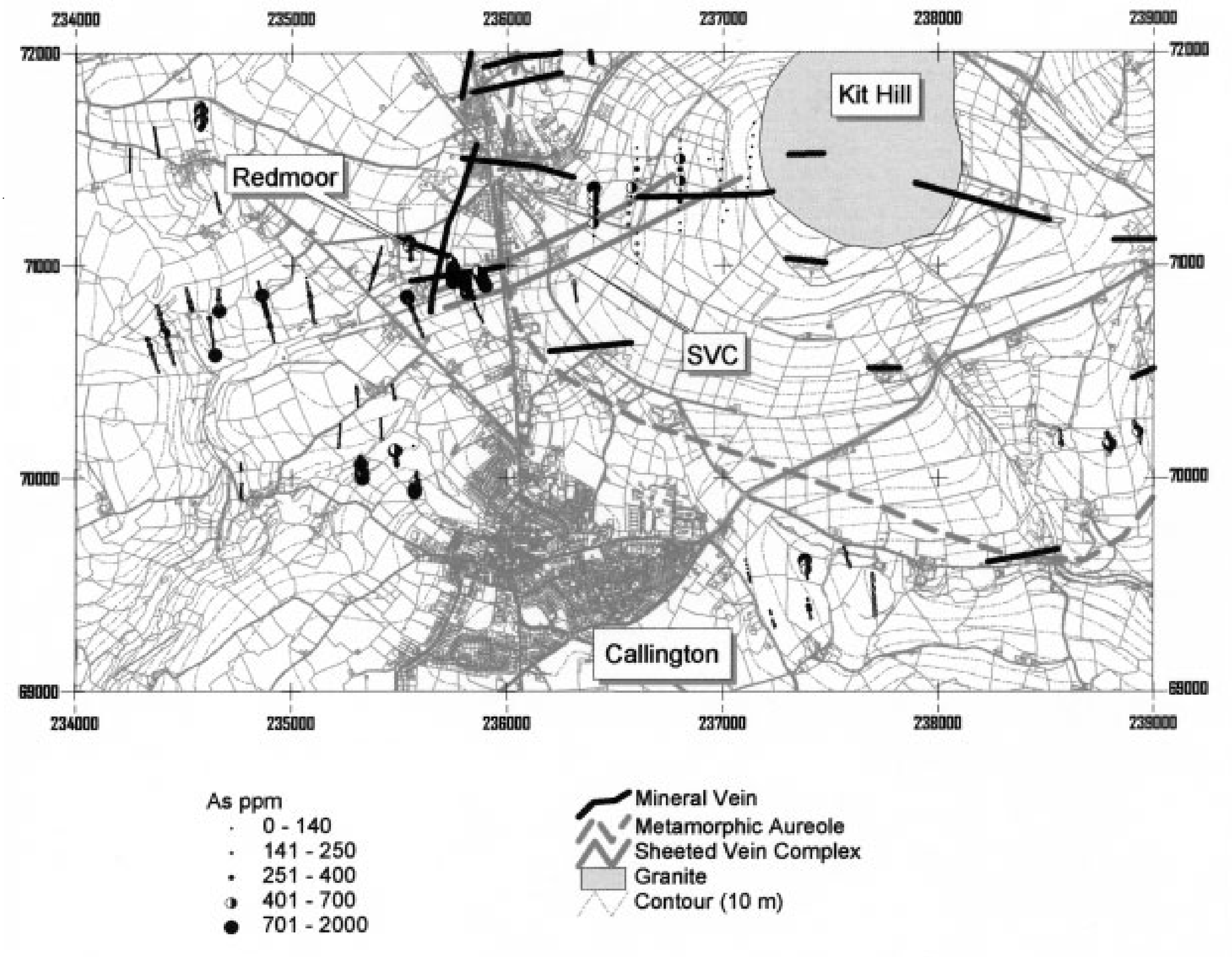

Figure 6. Top of bedrock samples, Callington. Data sources: auger drilling, Boswell and Harrison (1978), Redmoor and Kit Hill percussion (Newall, 1991). Number of samples = 531, subdivision by percentiles: 50, 75, 90, 95. Geological data: BGS Tavistock Sheet 337 (British Geological Survey, 1993), SVC= sheeted vein complex, Newall and Newall (1989). Topographic background, Ordnance Survey (Digimap, 2001). Ordnance Survey grid in metres, 10 m contour interval.

East Cornwall study

The detailed study included the mining area east of the River Lynher and west of the Tamar River. The area was divided into two because the contamination in the western part is almost entirely caused by mining whereas in the eastern part there has additionally been extensive calcining and refining, notably at Coombe and Greenhill. Some comparison of the distribution of leachable As between the two sub-regions can be made from the work of Knott (1990) who undertook a stream water and sediment sampling study of the whole area.

Western area

Although considerable (>26000 t) As has been mined in this western area, particularly from the Holmbush and Redmoor mines, most As was calcined and refined at the Greenhill refinery (Toll, 1953). The basis for mapping As distribution in detail is the exploration programme of South West Minerals plc in the late 1970s and early 1980s, as well as soil sampling by the author. The company collected soil, auger and percussion drill samples to define deeper drilling targets for Sn and tungsten exploration (Newall and Newall, 1989; Boswell and Harrison, 1978). Four styles of mineralisation were initially recognised in the Kelly Bray area (Newall and Newall, 1989):

(1) Greisen bordered veins, generally occurring as swarms within the Kit Hill Granite and carrying arsenopyrite and löllingite in association with cassiterite and wolframite.

(2) East- west trending veins of a few cm to 3 m in width that were the target of most 19th century mining and which contain arsenopyrite with other sulphides.

(3) The Redmoor sheeted vein complex with a NE-trending strike of >1 km length and width ~100 m hosted in thermally metamorphosed slates overlying a steep sided granitic dyke. The sheeted vein complex has a complex paragenesis with greisen style mineralisation overprinted by later sulphides. Arsenopyrite is present in all stages and löllingite is in the greisen style mineralisation.

(4) Cross course mineralisation striking N-S and over 1 km in strike. This has mainly been mined for lead and silver, although sphalerite and arsenopyrite are present.

Weathered rock samples

Plots of the auger and near surface percussion drilling samples, effectively weathered rock, show that there is inhomogeneity both within and outside the metamorphic aureole (Figure 6). Newall and Newall (1989) showed that As is strongly enriched in the sheeted vein complex, south of Kelly Bray, particularly in the hanging wall (N) contact with metasediments. This hanging-wall enrichment is also seen in Sn, W and Zn, indicating that it is a general mineralising factor. Sampling to the east of Haye, shows significant enrichment in As and was investigated by soil sampling, as discussed below. Other areas of enrichment were detected to the east of Callington and are probably on the extension of known veins.

Soil sampling

The digitised plot of Aguilar's (1974) traverse across Kit Hill shows the considerable variation both inside and outside the metamorphic aureole. When plotted against the published geology and topography (Figure 7) most As highs correlate with the known subcrop of veins, with the exception of the area to the south of the metamorphic aureole and that to the N of the Kit Hill Granite.

A soil sampling survey in the Haye area (on a 200 × 25 m grid) demonstrates strong As enrichment around Haye House. Very oxidised sub-economic Pb-Zn-Cu-Ag mineralisation was

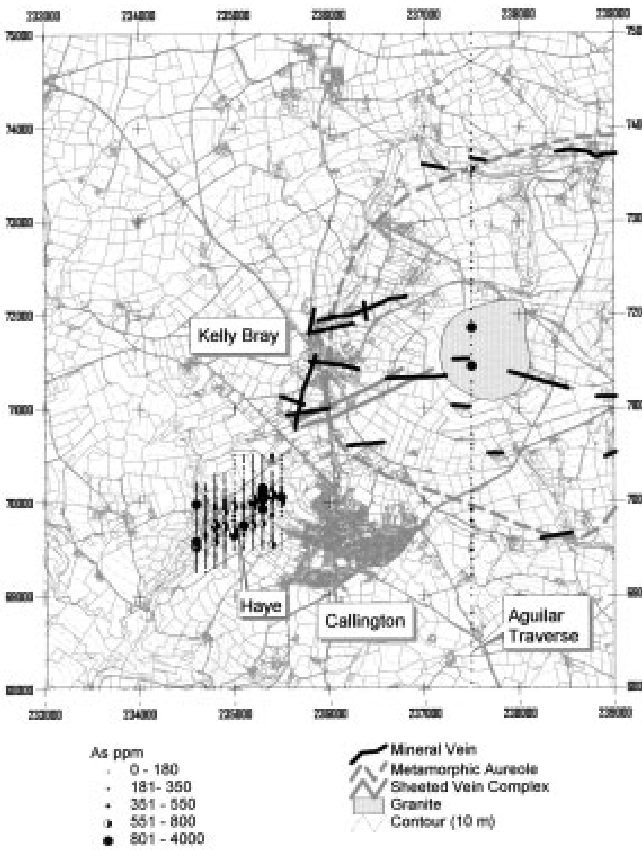

Figure 7. *Soil samples, Callington. Data sources: Haye area, University of Leicester, Aguilar Traverse, Aguilar (1974). Number of samples = 346, subdivision by percentiles: 50, 75, 90, 95. Geological data: BGS Tavistock Sheet 337 (British Geological Survey, 1993), SVC= sheeted vein complex (Newall and Newall, 1989). Topographic background, Ordnance Survey: (Digimap, 2001). Ordnance Survey grid in metres, 10 m contour interval.*

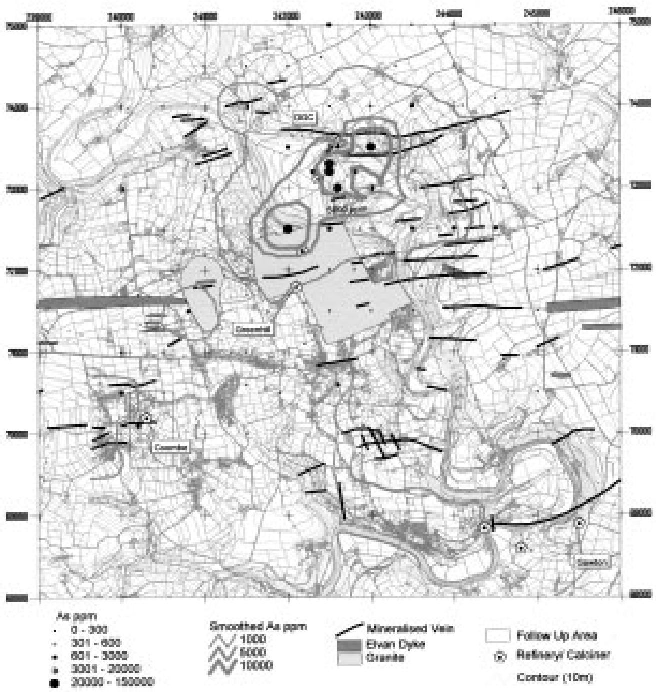

Figure 8. *Regional soil As data, digitised from Kavanagh (1998). Contours generated using 250 m grid, 1000 m window, 1/d² weighting and excluding samples > 50 000 ppm As. Percentiles: 50, 75, 90, 95, number of samples = 94. Geological data: BGS Tavistock Sheet 337 (British Geological Survey, 1993). Topographic background, Ordnance Survey: (Digimap, 2001). Ordnance Survey grid in metres, 10 m contour interval.*

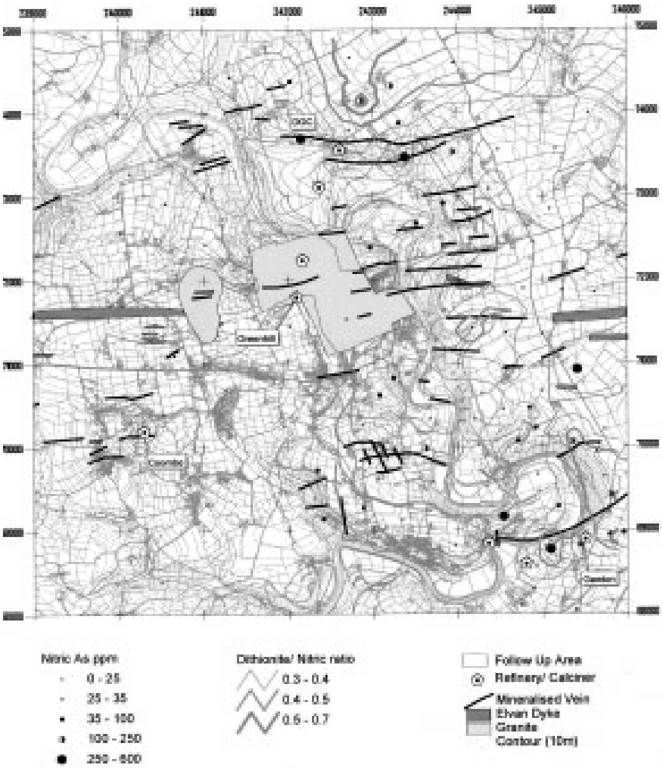

Figure 9. *Regional soil As data, nitric acid digestion, digitised from Haswell (1985). Dithionite/nitric contours generated using 250 m grid, 1000 m window, 1/d² weighting. Percentiles: 50, 75, 90, 95, number of samples = 128. Geological data: BGS Tavistock Sheet 337 (British Geological Survey, 1993). Topographic background, Ordnance Survey: (Digimap, 2001). Ordnance Survey grid in metres, 10 m contour interval.*

encountered in a drillhole which cut 12 m of 1.1% As hosted by tuffs, cherts and breccias and at the contact of an acid porphyry that may have ponded mineralisation at its lower contact (Newall, 1982). The drainage from the Redmoor adit also causes high As values on this soil grid.

Eastern area (Gunnislake)

In contrast to the western area, few percussion drill data are available, although there have been public domain soil surveys, carried out by Haswell (1985) and Kavanagh (1998). These mainly cover the area around the Tamar River, both on the Cornish and Devon banks (Figures 8 and 9). In addition the author has supervised smaller surveys in the area around the Coombe and Greenhill refineries (Figures 10 and 11).

Arsenic data from the Kavanagh (1998) soil survey shown in Figure 8 have been smoothed using a 1 km window. The smoothed data show the broad, ~ 4 × 2 km, As high over the Devon Great Consols area with an area averaging >0.5% As around the refineries. Other smaller areas with >1000 ppm As are present on the Cornish side of the area, where a notable feature is the relative low over the village of Gunnislake, to the SE of the Greenhill refinery. There is little evidence of the distinction between highland and lowland areas proposed by Colbourn *et al.* (1975) although the Tamar alluvial area is not well sampled in this survey. While the data in Kavanagh (1998) provide a good broad picture of the area, it is not possible to differentiate the impact of calciners from that of mining.

Such a differentiation is possible in data from Haswell (1985). He collected regional soil samples (Figure 9) over an area that partly overlaps with that of Kavanagh (1998) and analysed the samples using both a hot nitric and sodium dithionite digestion. The ratio of As extracted by sodium dithionite to that extracted by hot nitric acid provides a measure of the amount of arsenic

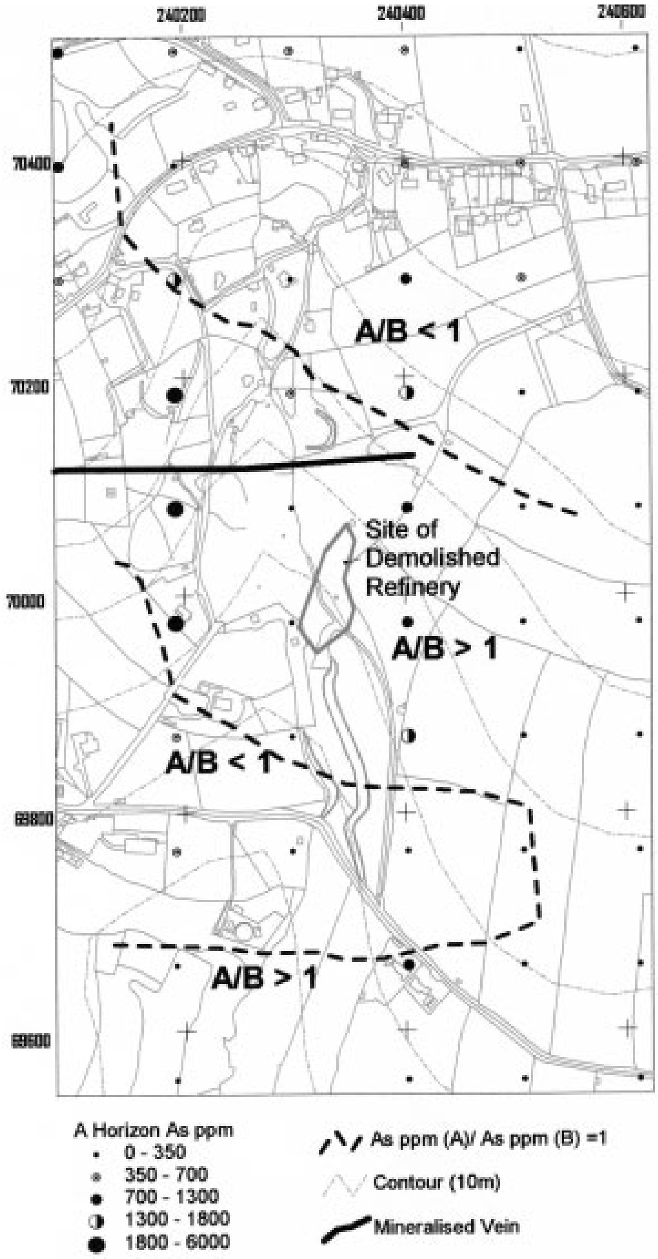

Figure 10. *Soil sampling, Coombe area by R. Ainsworth. Contours of As in A horizon/ As in B horizon superimposed on A horizon As ppm. Percentiles: 50,75,90,95, number of samples = 67. Geological data: BGS Tavistock Sheet 337 (British Geological Survey, 1993). Topographic background, Ordnance Survey: (Digimap, 2001). Ordnance Survey grid in metres, 10 m contour interval.*

weakly bound to iron versus total arsenic. Although the absolute As levels in Haswell (1985) are much lower than other surveys, the patterns of the nitric digestion are similar to Kavanagh (1998) and appear reliable. Haswell (1985) sampled the area around the Gawton mine and calciner, which forms a discrete As high in the nitric data. This area also shows a 1 × 0.5 km high in the contour dithionite plot around this area, which is known from contemporary photographs to have suffered deforestation from As calcining when the calciners were active (Jenkin, 1974). A similar but broader dithionite/nitric high is present to the NE of Devon Great Consols, as is a much smaller high at 244200E 71500N. It seems probable that the Gawton and Devon Great Consols dithionite/nitric highs indicate airborne contamination. Samples around Coombe and Greenhill are too sparse to detect any similar signal.

A detailed survey of the area was undertaken around the Coombe refinery although the site has been partly remediated by

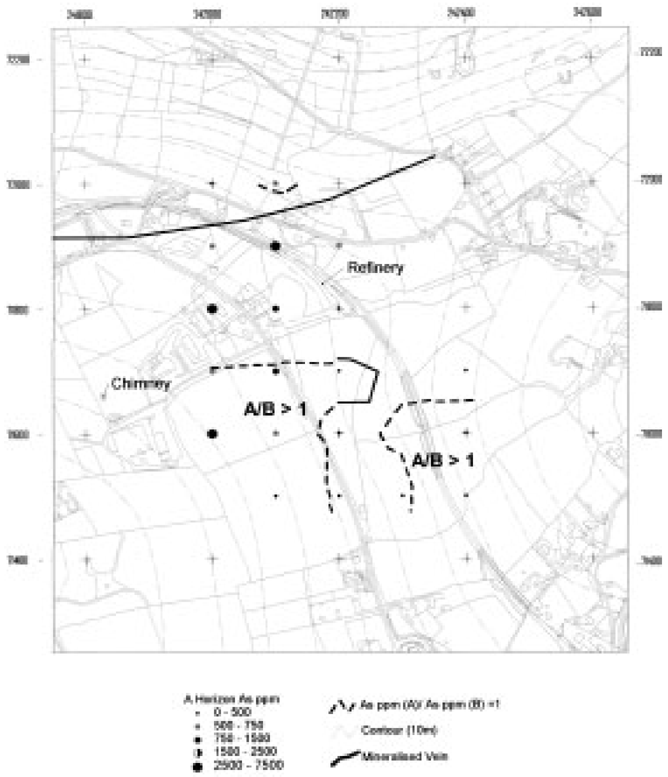

Figure 11. *Soil sampling, Greenhill area by R. Ainsworth. Contours of As in A horizon/ As in B horizon superimposed on A horizon As ppm. Percentiles: 50,75,90,95, number of samples = 20. Topographic background, Ordnance Survey: (Digimap, 2001). Ordnance Survey grid in metres, 10 m contour interval.*

soil removal and overlies a mineralised area (Figure 10). In this survey A and B horizon soils were collected and analysed for As (and other elements) using an aqua regia attack. An A/B ratio map gives coherent areas with a central high over and to the south of the known mineralised vein, including the area of the refinery. The low on line 240300 reflects the soil remediation. The extreme S of the survey area also shows high A/B As values, although absolute As values are lower, probably reflecting airborne dispersion.

A smaller 20 sample trial survey around the Greenhill refinery (Figure 11) on a 100 m grid showed maximum As values of ~8000 ppm with coherent A/B ratio greater than 1 to the south of the area to the SE of the still standing high chimney from the flue. The area around the calciner showed very strong enrichment in the B horizon with a maximum of 24000 ppm As and an associated Cu high

East Cornwall: regional water samples

The distribution of As in regional samples collected by Knott (1990) was examined for some indication of present day As bioavailability. Knott (1990) collected a series of 44 samples from streams draining the two sub-areas discussed above (Figure 12). The results are broadly similar to the stream sediments with Devon Great Consols and a broad area draining the Kit Hill ridge having >25 μg/l As. The highest values (> 500 μg/l As) all correlate with low pH water, mainly emanating from mine adits, suggesting that the main source of As is via AMD. However, lower, but still enhanced, As levels may be derived from surface runoff. Knott (1990) also measured As levels in the Lynher and Tamar rivers and found levels of <10 μg/l in the Lynher but 15 μg/l in the Tamar. A broader survey of Aston *et al.* (1975) showed similar results with a broad (4 km wide) zone of >50 μg/l As stretching from Dartmoor through Callington to Caradon.

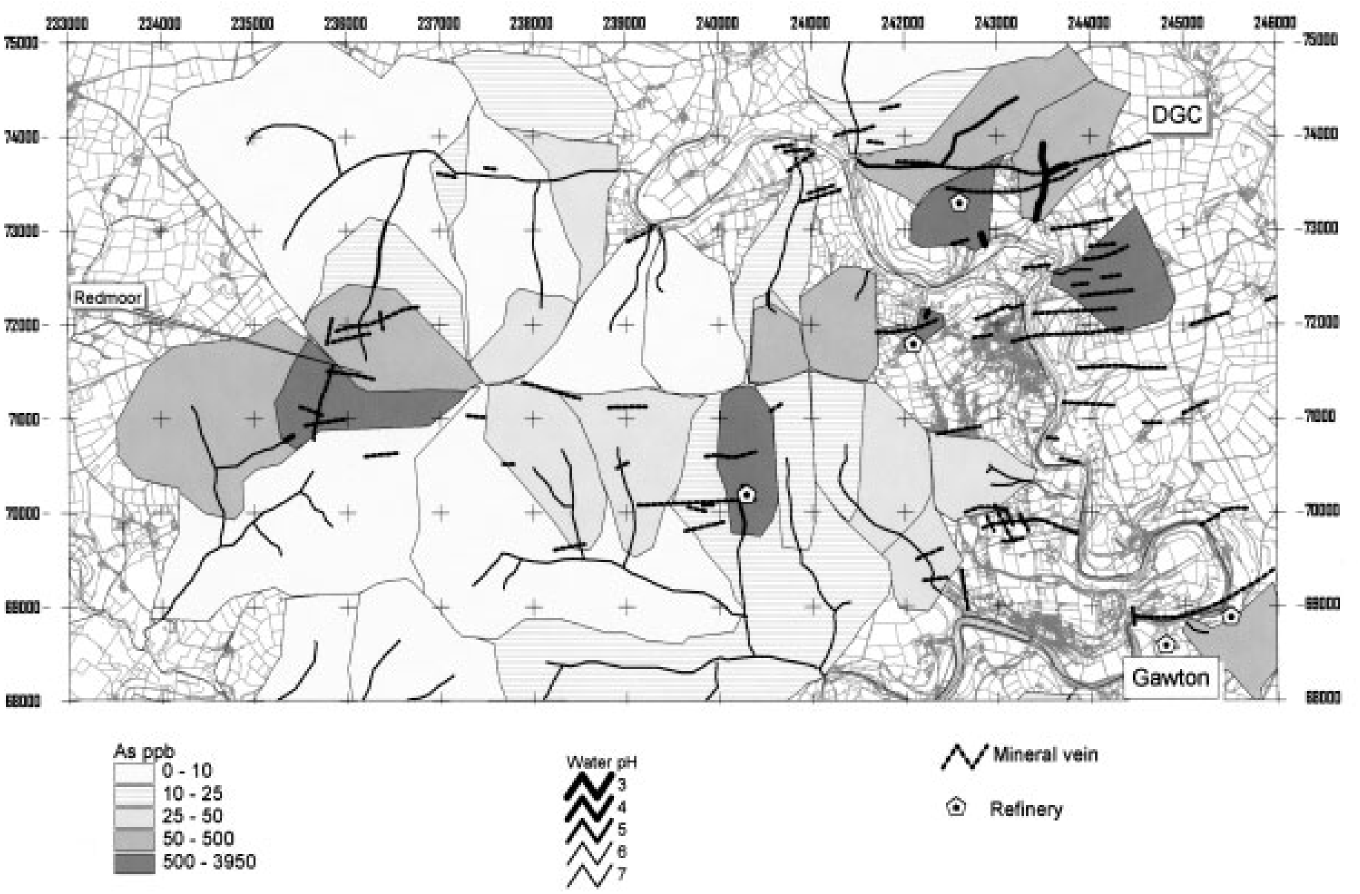

Figure 12*. Regional stream water As, plotted as catchments. Analytical data from Knott (1990). Number of samples = 44, Analytical method hydride generation AAS. Topographic background, Ordnance Survey: Digimap, University of Edinburgh. Grid in metres, 10 m contour interval.*

Discussion and conclusions

The regional studies confirm the inhomogeneity of As distribution. Part of the stratigraphy in the upper Devonian-lower Carboniferous sediments is enriched in As although it is not clear what the exact controls are. Selwood *et al.* (1998) suggest that As mineralisation is a multi-stage process even in pre-granite times, with enrichment in the sediments and by thrusting. Although As is enriched in a wide variety of base metal, Sn and tungsten mineralisation, this study has failed to recognise a general enrichment in As associated with granite intrusion, as suggested by Aguilar (1974). Areas of broad As enrichment at Hemerdon, Redmoor and Castle-an-Dinas appear to be associated with late stage granitic dykes and cupolas that are associated with tungsten mineralisation, or where As-rich sedimentary lithologies, mainly black shales and cherts, have been metamorphosed. The background within the aureoles of the large granite bodies appears to be much lower where they consist of mid-Devonian lithologies. Metamorphosed dolerites and limestones (skarns) are also enriched within some parts of the metamorphic aureole (e.g. the NW flank of Dartmoor) and these may reflect granite related processes.

The auger and percussion drilling studies at Callington show that As enrichment within most of the metamorphic aureole is spatially associated with vein mineralisation. This enrichment is not confined to the aureole and can, as at Haye, extend outside it. The bioavailability of As from areas of As enrichment and from undisturbed mineralisation will be governed by its mineralogy and this requires further investigation. A study comparing the results from Port Isaac and Castle-an-Dinas would be useful.

The studies in the Gunnislake area confirm that contamination is spatially related to a combination of mining, calcining and refining. Data in Kavanagh (1998) and Haswell (1995) indicate that the Cornish part of the area is less contaminated than west Devon. The worst case appears to be at Devon Great Consols where plumes may be up to 1 by 1.5 km. The data in Haswell (1985) show that there appears to be a similar plume around the Gawton complex. Studies of soil and animals at Gawton by Erry *et al.* (1999a, 1999b) confirm high levels in soil, voles and kestrels. Further soil sampling studies of the order of 100 x 100 m spacing are required to define other plumes. The bioavailability of As deposited from these plumes needs to be established, as does the current flux of As from these plumes. It may well be that most of the available As has already been leached.

The studies by Knott (1990) and Aston *et al.* (1975) suggest that much of the surface water in the area contaminated by mining or refining will be in excess of the new US drinking water standard. Although most drinking water is now from piped supplies, wells and surface water abstraction points need to be tested for As within refinery plumes and downstream from mine waste. There is considerable scope for further work on sub-clinical impact on human and animal health once these plumes have been identified.

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