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Environmental variables in a holistic evaluation of land contaminated by historic mine wastes: a study of multi-element mine wastes in West Devon, England using arsenic as an element of potential concern to human health

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Abstract

Unusual and unexpected concentrations of a number of elements were identified in samples of house dust, that indicated the presence of mine wastes in an area where they were not expected. In pursuing this matter, several other very unusual observations and practices, involving highly contaminated mine wastes, were also identified. Here, using an available, but not a custom-made database, the matter is pursued. In England and Wales, the usual framework within which hazards are assessed, starts with an identification of those levels of exposure to elements which are considered to be safe and acceptable. At the other extreme, levels that are considered to be hazardous are identified together with procedures for dealing with them for different situations; for example, the manner in which contaminated land is to be used. The level at which an identification of sites and their use rests with the Local Authority, such as District Councils. Although new legislation is pending; at present for the non-occupationally exposed population there are no firm values to define which levels are acceptable and those that are not acceptable. One of the elements in the samples is arsenic and, because of its well-known toxicity, this element is selected to be of prime concern. However, simultaneous exposure to the general public is from a number of other elements, such as copper, lead, zinc, antimony, molybdenum, tin, selenium and mercury which are present in the mine wastes. The collective impairment to human health, if it should occur, is far too complex to evaluate, hence a need to focus attention upon arsenic which by any standard is present in some samples at very high concentrations, for example > 1000 mg/kg. Irrespective of any changes in permitted levels of exposure to the general public in the study area, together with those that are occupationally exposed, it is the past exposure that will give rise to the present patterns of morbidity and mortality. Because of a latent period between exposure and effects for the induction of cancers, of between 5 and 20 years, past exposures cannot be ignored. They need to be evaluated before changes are made in legislation. In England and Wales, concern to health is, in practice, invoked when there is clinical evidence of harm.

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With the exception of a few accidents in the study area of SW England, this is not identified, hence it is accepted, in practice, to conclude that no harm accrues following acute or chronic exposure to the mine wastes. There are reasons for questioning this, but if eventually supported, then the current very high costs for remediation of land may not be necessary and brown field sites can be used for a number of purposes. The primary concern is the lack of adequate scientific and clinical data, in relation to exposure to the wastes for the past 100 years or so. For many elements, compounds and substances, the general public is being made aware of potential risks to health but often the levels are extremely low. Using basic geochemical data for any area, it is possible to evaluate the expected background levels for elements. They should serve to identify levels that are acceptable, i.e. it is impractical or uneconomic to reduce them. Within the environment, simple tests are also available that can be used to rank risks to fauna and flora. There are also well-structured clinical evaluations of harm to humans available, which can also be ranked. All three need to be considered in the establishment of safe levels of exposure. It may not be practical to identify universal levels for exposure, rather each site, area or region needs to be considered separately in order to rank the potential risks. For the study area the exposures can be extremely high; compared with the general population, the number who are exposed is probably small. It is surprising that no effects upon human health have been noted. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Contaminated land; Mine wastes; Elements; Arsenic; Health; Legislation

1. Introduction

At the start of the 3rd Millennium, it is opportune to reflect upon science, the manner in which it is implemented, the responses from the general public to contamination or pollution of the natural environment, and its influence upon the health and well being of humans. There is a need to evaluate whether or not existing ‘regulations’ mark a reasonable and acceptable balance between science and the manner in which it is presented and understood by the general public. In parallel with such deliberations, there is also the need to accommodate the requirements of industry; to evaluate the total costs and benefits, together with the impact that their wastes may have upon the environment and the quality of life. It is here that policy makers have the difficult task of satisfying the perceived needs of all parties. In ranking risks, first there is the protection of the total population together with small or local populations that are exposed to particular risks. At the other extreme are the concerns of individuals who may be exposed to hazards that are not obvious, if medical evidence is lacking; hence, in practice they do not exist. In the UK, at least, states of almost hysteria are generated by the media in pronouncing, almost weekly, the hazards that are associated with a large number of items that are not commonly associated with harm to health or the environment. For many, proper scientific evaluation is lacking, and when used, can be misleading or represent the views of interested parties for or against the exposure situations.

Here, in general terms, I consider some aspects that are related to contaminated land by examining the exposure of small groups of people to a large number of potentially toxic elements that are associated with many mine wastes. Within such groups, genetic make-up, an individuals susceptibility to disease and state of health present complex issues that may or may not be related to exposure to the wastes. Are current trends in relating cause and effect always acceptable? For example, are all skin cancers only caused by exposure to sunlight, do all wheezy chests indicate asthma and are all local clusters of disease always chance events that are related to events such as the immigration of people with respect to geography and their exposure to different viruses or dietary habits.

Those who have the responsibility of defining and administering acceptable levels of exposure of the elements of the Periodic Table to people, seem enchanted with the derivation of a single universal value for exposure, presumably because of simplicity and ease of use. Most certainly, as those who derive the permissible levels become more and more distant from the nuts and bolts of the science, so the temptation is to accept 'simple numbers' for use in models. So often these 'numbers' reflect theoretical states that are not supported with field evidence for a particular situation. The characteristic of the environment and nature itself is one of variability. For many situations, there is no scientific basis for establishing a single value for exposure (e.g. acceptable, one of possible concern, one of concern, one indicating a real hazard or one indicating serious and unacceptable harm). In relation to rocks and their overlying soils, single values for exposure may be realistic when the exposure is valid for large geographical areas where compositions are fairly constant. For example sediments of the Cretaceous Chalk of England and large limestone exposures, alluvial sediments of the N German Plain, the Deccan basic lava fields of peninsula India and the loess deposits of China. Often, it is not realised, or even understood, that the characteristics which describe the concentration and distribution of elements in igneous, metamorphic rocks and sediments have well-defined geological and geographical limits, i.e. geochemical provinces. Rocks which are similar with respect to appearance and bulk composition, can contain very different concentrations of trace elements that may be of concern, for example the differences between marine and non-marine shales. Despite the availability of average values for the concentration of elements in the environment, in relation to human, animal or plant health, the selected values for a site, area or region must be validated and should not be assumed. Today, it is unfortunate that past literature on the subject prior to approximately 1980 is poorly represented in currently available electronic disc data retrieval systems. It was in the period 1930–1970 that the foundations for the geochemical–clinical approach were established. Today, in the environmental field, there is a plethora of repetitive papers that describe similar geographical settings which do not advance our knowledge; they tend to restrict interdisciplinary studies and at the worst simply reinvent the wheel.

Ore deposits and the elements they contain represent the extreme fractionation of geologic processes. For any situation, initially there is a need to determine the total range of elements that are present at a site and then to select those of possible concern. From a consideration of the basic principles of geochemistry, the abundance ratio for pairs of elements is often of diagnostic value. For example, the Zn/Cd ratios for crustal rocks, shales and sandstones are approximately 350, 316, and 320, respectively; hence it serves no purpose to consider rocks that contain the minor element zinc to be free of the trace element cadmium, (see Ahrens, 1965; Cox, 1989). A diagnostic use of element ratios is when they differ from the average values with respect to sources, or an involvement with particular chemical processes. Ratios between elements can also be used to distinguish between contaminated, polluted and natural states. Once the characteristics of a source term are identified, it is then practical to predict the concentration of elements in other components of the environment, e.g. soil and water. In many environmental studies, this important diagnostic tool is rarely used, instead a single element or a geochemically disparate sequence of elements is selected. This is often dictated to by sensitivity or ease of analytical measurement, or simply because one element is identified as being of concern and attention is focussed upon it to the exclusion of all others. A further problem that besets many environmental studies is the absence of data for major and minor elements that so often control the abundance and behaviour of the trace elements. A holistic evaluation of elements is essential in relation to their chemical, physical and biological characteristics.

This paper considers some general aspects of the exposure of the general public to potentially harmful elements in relation to existing guidelines for acceptability and action. A number of elements are considered, among which arsenic is selected because of its acknowledged toxicity and where synergistic and antagonistic influences with other elements are minimal. It is essential that any harm that may accrue from existing policies is understood before any changes are made with respect to the degree of acceptability of risk. For arsenic, clinical expression of exposure is so diverse that diagnosis is not easy, various types of skin disorders can arise and are very difficult to identify, even if an exposure is known to have occurred. The need is to obtain reliable and focussed epidemiological data; present and past exposures dictate future incidences and patterns of mortality and morbidity.

At some concentration all elements of the Periodic Table are potentially hazardous to health. There seems to be a failure among many scientists and also the general public, to recognise that the human body contains all the elements of the Periodic Table, together with most of the radionuclides that originate from the nuclear industry, even plutonium. It is not merely the presence of an element or compound that is of concern, but rather how much is present, its toxicity, the amount ingested or inhaled, its bioavailability together with a consideration of dose–response relationships for individuals. In many parts of the world, very considerable amounts of money have been spent in order to evaluate risks to health from quite modest levels of cadmium. In places, the presence of cadmium and other elements in soil or crops is taken to indicate that harm to health occurs, often this is very far from the truth. For example, in Shipham, a village in Somerset, England, historic mining has contaminated the soils with cadmium at levels that are one order of magnitude higher than those which in Japan have been associated with the disease 'tai-itai' (Webb et al., 1978; Simms and Morgan, 1988). At Shipham, there were no signs of cadmium poisoning, there were no measurable effects on health for the population or individuals; sub-clinical changes were observed to be only slight and comparable to variations ordinarily found. As a safety measure residents were advised to reduce their intake of locally grown vegetables, hence there was no need for any large scale remediation procedures. For the exposure in Japan, rice contaminated by mine tailings was the principal cause of the disease. In relation to contaminated land it has to be accepted that despite the potential of technological knowledge to clean it up this is often totally unrealistic and uneconomic.

Mine wastes that contain a large number of elements of interest to which populations and individuals have been exposed for decades, offer an opportunity to evaluate whether or not there are causes for concern (Hester and Harrison, 1994). Can they be formalised in terms of clinical effects for specific elements, groups of elements or other site-related factors? More importantly, there is a need to consider the routes whereby populations and individuals are exposed and an evaluation of those risks. In an industrially developed part of the Arctic region, Moiseenko (1999) has considered priority pollutants from copper–nickle smelters; an integrated impact of toxicity (a toxicity index) is developed based upon concentrations of elements in lakes throughout the region. In this context, the chemical and physical forms of the element are of concern.

There is also the need to consider whether or not the element that may concentrate in parts of the human body is the prime cause of a disease or whether it reflects secondary processes. An impairment to cell transfer processes because of organic activated diseases, e.g. viruses, genetic states, etc., may result in the build-up of elements in specific organs and tissues. Bone remodelling with age is also a major process that influences levels of some elements in tissues and organs.

2. Materials and methods

2.1. Selection of elements

For the purpose of this paper, attention is focussed upon the chalcophilic elements in the ore minerals, i.e. those elements that are associated with sulfur (and selenium) as sulfides. This paper presents the outcome of an opportunistic study. The primary study, not considered here, is concerned with the data presented in Table 5, namely an investigation into elements and the occurrence of respiratory diseases with respect to indoor and outdoor air. These data identified an unusual occurrence of arsenic at a site where it was not expected. In pursuing the cause of this abnormality, a number of very unusual events and actions in relation to arsenic in the environment were identified. Many of the events seem in direct opposition to accepted practices and question the

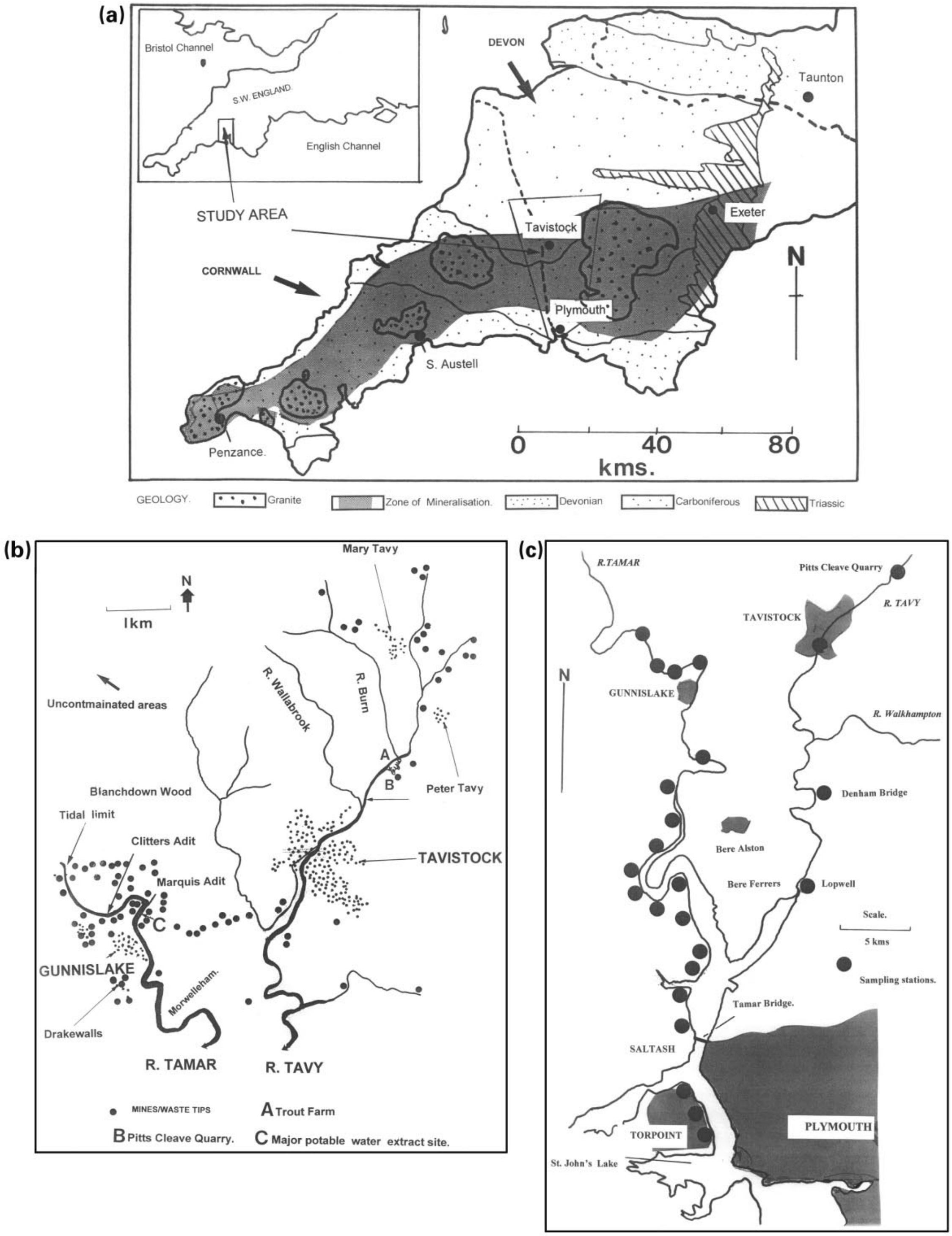

Fig. 1. (a) Study area, south-west England indicating the zone of mineralisation. (b) Mine waste sampling sites for the rivers Tamar and Tavy. (c) Sampling sites along the rivers Tamar and Tavey together with the estuarine area.

present system of risk assessment, at least in practice. In this paper, I pursue these observations by way of a general reconnaissance study and in order to do so I have made use of unpublished data that was not obtained specifically for this paper; hence it is not optimal, but it is

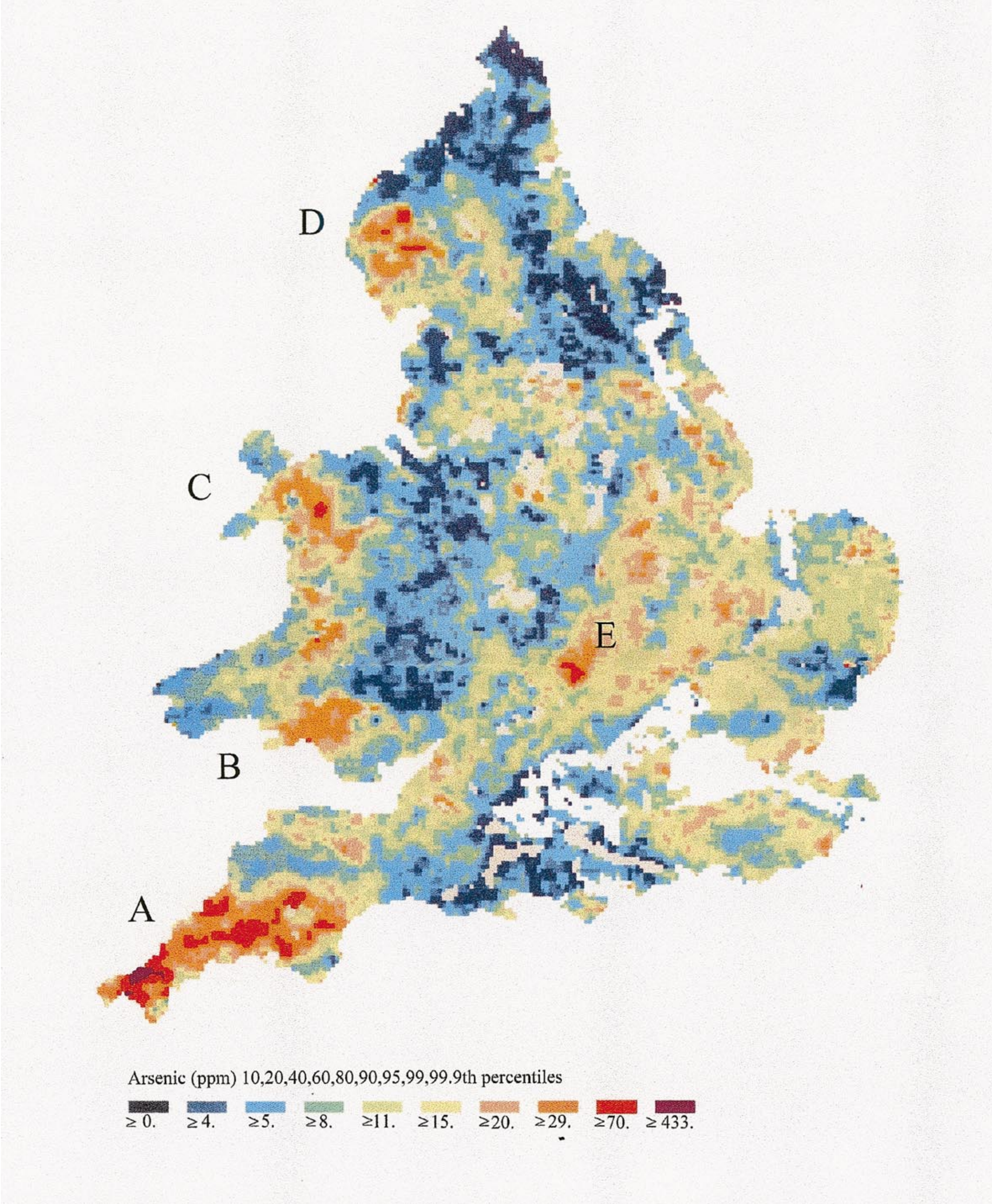

Fig. 2.

considered to be sufficient for the objectives of the paper.

2.2. Study area

The main study area is situated in W Devon, and adjoining regions in SW England which have been subject to intensive metal mining since pre-Roman times. Many of the areas adjacent to the mines are heavily contaminated with mine wastes. The main period of mining took place in the mid-1880s until approximately 1930. The ores occur along mineralised zones in slates and in granites. The principal ores contain copper, lead, tin, arsenic, zinc and silver, together with lesser amounts of uranium, radium, cobalt, tungsten, antimony, bismuth, tungsten, molybdenum and possibly thallium. A railway system was introduced into the region to export the ores and there is a close association between the mines and the exposed population that developed around the mining areas that is unique to the region (Barton, 1964). Historically, the processing of arsenic was associated with skin disorders and skin cancers. Today, the region is not noted for any significant diseases that can be related to exposure from the mine wastes, apart from some very rare types of exposure to individuals or occasionally those affecting cattle and horses. Within the region, molybdenum-induced copper toxicity occurs in cattle at a few sites. From an extrapolation of mine data there is also the generally accepted indoor air risk from exposure to radon and its daughter products for sites enriched in uranium.

The study area is illustrated in Fig. 1a–c. The high concentration of arsenic in SW England (counties of Cornwall and Devon) is illustrated in Fig. 2. Within the UK, this region contains the largest numbers of people in close proximity to sulfide ore mine wastes.

Today, many towns have been developed on mine wastes and some houses have even been built on highly contaminated arsenic sites, i.e. > 1000 mg/kg As. The reader is referred to Reid et al. (1911), Cantrill et al. (1919), HMSO London (1975), Richardson (1992) for a comprehensive description of mines and the processing of ores within the region. Mining in the region can be traced back at least to the Phoenicians who traded in tin ore, but it was not until the early 1800s that the main period of tin, copper and manganese with subsidiary amounts of iron, lead, zinc, tungsten, radium and uranium ore exploitation took place. By the early 1900s, the ores were depleted or were uneconomic to mine, although until 1998 tin was still mined, together with short periods when other diverse ores were also exploited. A feature of the region is the association of copper (chalcopyrite) with arsenic ores (arsenopyrites) (Thornton and Farago (1998), Xu and Thornton (1985).

This study mainly considers one mine in West Devon, Great Devon Consols (GDC) which, between 1844 and 1909, was the richest copper and arsenic mine in the world. The main copper lode was approximately 12 m wide and was exploited by five large mines along the lode which extended to a depth of at least 540 m. The central lode consisted of exceptionally pure copper ore surrounded by a 2-m thick deposit of pure arsenopyrites; initially this was left in place as there

Fig. 2 The distribution of arsenic in stream sediments of England and Wales, after The Wolfson Geochemical Atlas of England and Wales (Webb et al., 1978). The pattern of element distributions in rocks and/or soils may be reflected to a degree in corresponding variations in the composition of the stream sediment. Although varying over the survey, sampling at tributary–road intersections gives a mean density of one sample/2.5 km^2. No samples were taken within conurbations; the total number of samples taken was 50 000. Composite samples (100 g) were dried, disaggregated and sieved to -200 μm. Of the elements presented in the Atlas, As, Mo, Cd and Zn were determined by atomic absorption spectrometric or colorimetric methods; Al, Ba, Co, Cr, Cu, Fe, Ga, Li, Mg, Mn, Ni, Pb, Sc, Si, Sr, Ti and V were determined by a direct reading ARL 29000B Quantimeter. (A) Mineralised region of south-west England. (B) South Wales Carboniferous coalfield and associated heavy industry. This area is not mineralised, apart from an association of chalcophilic elements in pyrite which is associated with the coal. (C) North Wales mineralised region. (D) Lake District Cumbria, mineralised region. (E) Jurassic sedimentary ironstone area. Permission to reproduce map 22 from the Wolfson Atlas by Professor I. Thornton is gratefully acknowledged.

was no market for arsenic. However, in the USA, for a short time in approximately 1870, the demand for arsenic as a cotton desiccant and to combat the cotton weevil (Carbonell et al., 1998; Murphy and Aucott, 1998). resulted in the region becoming the largest producer of arsenic in the world. At the mines, the arsenic ores were roasted and the evaporated arsenic sublimed in brick-built labyrinths and then purified by thermal methods. Waste products were exhausted via tall chimneys up wind of the mines as the toxicity of the extracts was well known to the miners. Today, the source of the arsenic is from the presence of large amounts of arsenopyrites in the waste tips, which rapidly weather to form low pH materials due to the production of sulfurous acids; this is the major source for the environmental transfer of the ore elements. Under dry conditions, an efflorescence forms on the surface of some tips enriched in arsenic which is then distributed by wind action. This can be important and over a long time may be significant in accounting for some observed levels of arsenic in agricultural soil adjacent to the mines. A second and important historic transfer route in the region concerns the distribution of highly toxic mine waste for use as land infill and for gravel drives throughout the area in order to provide a weed free surface.

For the purposes of this study the mining area in the vicinity of GDC and the adjoining mining area in E. Cornwall, together with the Peter Tavey mines in W Devon, are also considered. A general view of the GDC mine area today is illustrated in Fig. 3A,B. The waste tips and lagoons are devoid of vegetation, principally because of low pH (2.5–4) and they are poorly inhabited by animals and birds. However small, a few square metres of waste unmineralised soil that has been dumped in the area over the last 10 years is often calcareous and supports a vigorous growth of lime-tolerant plants as illustrated in Fig. 3D. These are frequented by insects and birds, testifying to the ease by which most of the site can be reclaimed. Indeed, the application of sewage sludge (organic matter) and under or topsoil is probably all that is required to return the area to one of biological diversity with respect to fauna and flora. The mines, associated buildings and railway systems offer an excellent opportunity for the tourist industry, which at present are poorly exploited and are deteriorating rapidly.

Three mine adits (Clitters, South Fanny Deep Adit and the Marquis Adit) are associated with ochreous discharge mine wastes directly into the river Tamar (see Fig. 1b) which, together with the river Tavy, dissect the mineralised area. Other routes of transfer to the rivers are through surface leaching and general run-off. The stability of the waste tips depends upon angle of rest and degree of binding by fine grained debris. Some tips are transected by gullies and the slopes are unstable; several tips, because of instability or topography are major sources of air-borne debris that can be seen to swirl across the site. One report prepared in 1990 indicated a pollution risk from the major Gunnislake freshwater intake for regional potable water and recommended that tree felling in the vicinity of the wastes should be restricted, vehicular access should be preferably avoided, and unauthorised removal of materials from the tips should be discouraged.

2.3. Sampling

Each sample of mine waste was obtained from five separate sites over an area of approximately 5 m^2, then sieved to pass through a 365-μm sieve; each aliquot was then quartered and passed through a 63-μm mesh from which a representative sample was extracted with a tube inserted into the powder, then ground in an agate mortar. This is considered to be sufficient in order to provide a reasonably representative sample of the wastes, albeit they can be very heterogeneous in composition. Furthermore, with respect to the total volume of a tip, it is difficult to determine the precise source term for the elements that are released into the environment through weathering. For mine wastes, the preliminary field survey is possibly the most important stage in any evaluation, in conjunction with a multi-element reconnaissance study, in order to identify the distribution of elements between individual tips and the area as a whole. This is often neglected or attention is focussed upon a few elements that are presumed to be the most harmful.

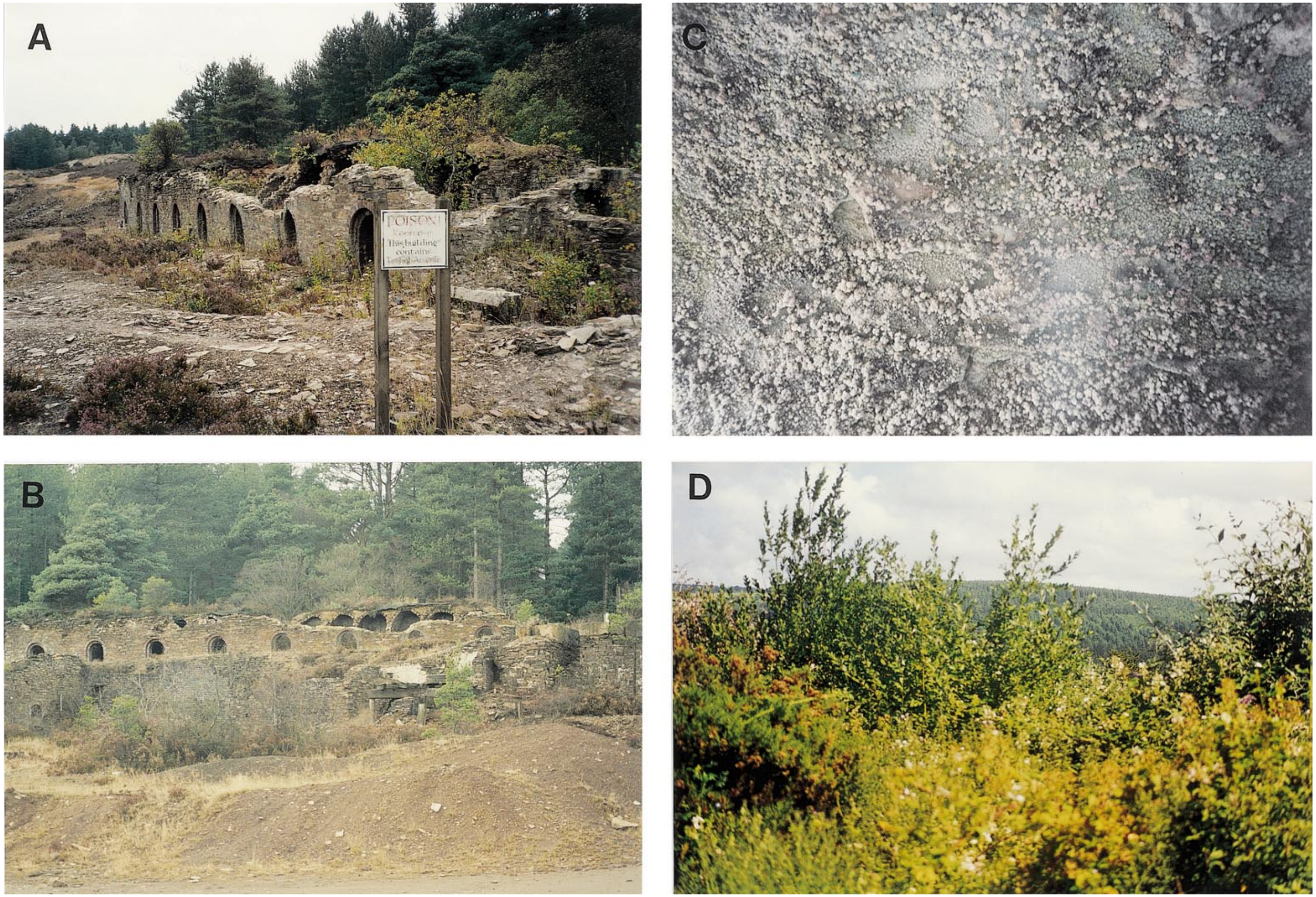

Fig. 3. (A) General view of the remains of the Great Devon Consols (see also Fig. 14A,B) arsenic labyrinth; each brick archway represents a condensation chamber. (B) View of the arsenic labyrinth and mine waster. Note the presence of coniferous forest to the rear of the labyrinth and non-coniferous shrubs close to the labyrinth that are seated in small patches of soil. The main areas of the mine wastes are not vegetated, apart from patches of grasses. (C) Inner walls of the arsenic labyrinth today illustrating the presence of crude arsenic sublimate which in places is coloured purple because of the presence of cobalt. (D) An example of the prolific plant growth that takes place on imported calcareous top and under soils amid the mine wastes.

2.4. Chemical analysis

Most of the preparatory procedures have been described by Hamilton (1979), Hamilton et al. (1979). All analyses, as far as practical, have been carried out in relation to Certified Reference Materials. However, it is inevitable that when dealing with such an extreme chemical composition as that presented by mine wastes, the absolute quality of the data cannot always be guaranteed because of the chemical matrixes of the samples. Nevertheless, for the purposes of this paper, the given values are believed to reflect rock, sediment and mine waste compositions. Where indicated, analyses are for either the total sample or acid leachates using 0.5 g of sample, the addition of 4–5 ml of 1:2:3 $HCl/HNO_3/H_2O$ and heating for 1 h at 80°C which will dissolve the main ore minerals present in the samples. For practical purposes, for the ore elements, there is little difference between total and leach analyses. Furthermore, the leach data reflects the extreme conditions whereby elements can be made available to biota, and their availability for aqueous transport during weathering of the deposits. Silicon has not been determined and for most samples the sum of all the elements that have not been determined is represented by silicon, i.e. quartz. Leach data are not presented for some elements, e.g. Zr and Bi because of difficulties in ensuring total removal of Zr from refractory zircons and instrumental problems for Bi, albeit the observed concentrations are compatible with the observed bismuth mineralisation. For some samples, analytical problems exist in the determination of Sb and As, such as interference of the arsenic signal by NaCl. Suspect ICP data were re-determined by atomic absorption with or without hydride generation or by neutron activation analysis.

2.5. Obtaining data and its interpretation

A holistic approach requires that all aspects of a study are carried out in an objective manner. Also, that the quality of the data or information that is obtained at each stage is defined in order that in the final evaluation the use of the data is realistic. For many types of contaminated land the real concentrations of contaminants are unknown, often approximations can be made based upon documented historical information. It is essential that, initially, observations are made at sites and that generalisations are not made at the onset. In many environmental studies the chemical and often physical composition of the main feature of a study, such as a soil or sediment, are not even described (Hamilton, 1993). A common practice is to refer to ‘the sediment’, without any qualification with regard to type or behaviour. This dispenses with a need to consider geological or geochemical facts, but results in the loss of valuable information in an assessment of the contamination.

A major problem with chemical and physical analysis of the elements of the Periodic Table concerns those restraints that are imposed by the method of analysis. For example, often important major and minor elements are not determined, albeit they have well characterised associations with particular trace elements and control those distributions. The development of analytical chemistry also has a bearing upon the manner in which elements have been selected for analysis, for example, sensitivity of detection which has also had an influence on the public’s perception of which elements are of concern. In risk assessment, a single element should not be considered in isolation to the chemical and physical matrix in which it occurs.

When presented with data for a large number of elements, databases become cumbersome to handle with respect to interpretation. Here, multi-element spider diagrams are used in order to obtain a holistic overview of the spatial and temporal distribution of elements in mine wastes.

2.5.1. Spider diagrams

Spider diagrams (x–y plot of normalised multi-element diagrams) are useful tools in order to identify the provenance of materials by means of characteristic associations or trends for the elements. The diagrams have been developed in petrology and geochemistry in order to depict the chemical characteristic of materials (Rollinson, 1993). The x-axis consists of an element listing arranged in a particular manner, the *y*-axis is a normalised value for each element. Here, I use the average composition of the North American Shale Composite (NASC), (Gromet et al., 1984) and where NASC values are missing they are supplemented by a few values from Hamilton et al. (1979). The NASC may be considered as representing the composition of a global fine-grained mudstone (slate, shale) that reflects the decomposition of average crustal rocks and deposition of weathering products in aqueous environments. It is also similar in gross composition to the rocks into which the SW England ore lodes have been emplaced. Choice of the NASC is reasonable as it represents a very common sediment that has been intimately associated with the process of organic evolution, hence, cannot be considered as a matrix of overt toxicity to life forms. The NASC represents a sediment that has not been affected by contamination or pollution. A normalised value of > 1 indicates relative enrichment with respect to the NASC. The NASC contains 28 mg/kg of arsenic which may be compared to the ICRCL soil trigger value of 10 mg As/kg (see Table 11) for domestic gardens and allotments. Transfer factors for inorganic arsenic from soil to edible crops that develop on shales tend to be low, together with a decrease in toxicity as a consequence of alteration of toxic inorganic arsenic to the relatively non-toxic organic forms.

For present purposes, as illustrated in Fig. 4a,b, the elements are arranged along the *x*-axis in groups that reflect their position, hence, chemical characteristics in the Periodic Table of Elements. Various groupings of elements can be made depending upon the purpose for which the diagrams are to be used. Spider diagrams can also provide information on how the overall element composition varies from site to site with respect to particular components; this is useful when considering leaching profiles and element import–export budgets. Here, for the spider diagrams, the distribution of elements from the left to right along the *x*-axis, are the alkali metals that are useful when considering leaching processes; alkaline earth and phosphorous to reflect the presence of calcareous rocks or building debris such as concrete; aluminium, scandium, gallium and the REE's, etc., for the presence of aluminosilicates and clay minerals; silicon for sand and also to identify the presence of resistate heavy minerals, such as zircon (Zr, Hf), rutile (Ti Fe), sphene (Tl, REE, U, Th), monazite, and apatite (P, Ba, REE, U, Th). Next, Ge to Ag the chalcophilic elements that are associated with sulfur and selenium in sulfide minerals. Vanadium and nickel for organic associations, especially with oils; chromium and tungsten are present as oxides while the halogens indicate the presence of saline conditions or fluorine mineralisation. It is also practical to consider the presence of contaminants and pollutants from particular sources, for example, Cr from tanneries, Pb–Br from car exhausts, Fe–Ni–Co for particular types of steel, V–Ni in oil and B together with P from detergents.

For the W Devon study, interest is focussed upon the distribution of the chalcophilic ore minerals, sphalerite (ZnS), galena (PbS), chalcopyrite ($Cu_2S \cdot Fe_2S_3$), arsenopyrite (FeAsS), bismuthinite (Bi_2S_3), molybdenite (MoS_2), cassiterite (SnO) and schellite ($CaWO_4$), both individually and collectively to identify the characteristic group of elements that are present in the mine wastes. Although not discussed here, the distribution of elements with respect to volatility can also be used to identify thermal processes, for example the enrichment of arsenic, antimony and thallium in soils with respect to deposition from thermal sources, e.g. smelters or chimneys.

2.6. Validation of the NASC normalisation procedure

The natural composition of shales can vary greatly for different source rock regions (i.e. geochemical provinces) with respect to chemical composition and mineralogy. Having selected the NASC, in order to compare multi-element associations for similar rocks, e.g. SW England shales and slates into which the ore minerals were emplaced in association with intrusion of granites some 275 million years ago, there is a need to identify the extent to which the NASC differs in composition from the regional rocks. There is a common tendency today to compare environmental materials, such as sediments and soils, from different geographical areas that are totally dif-

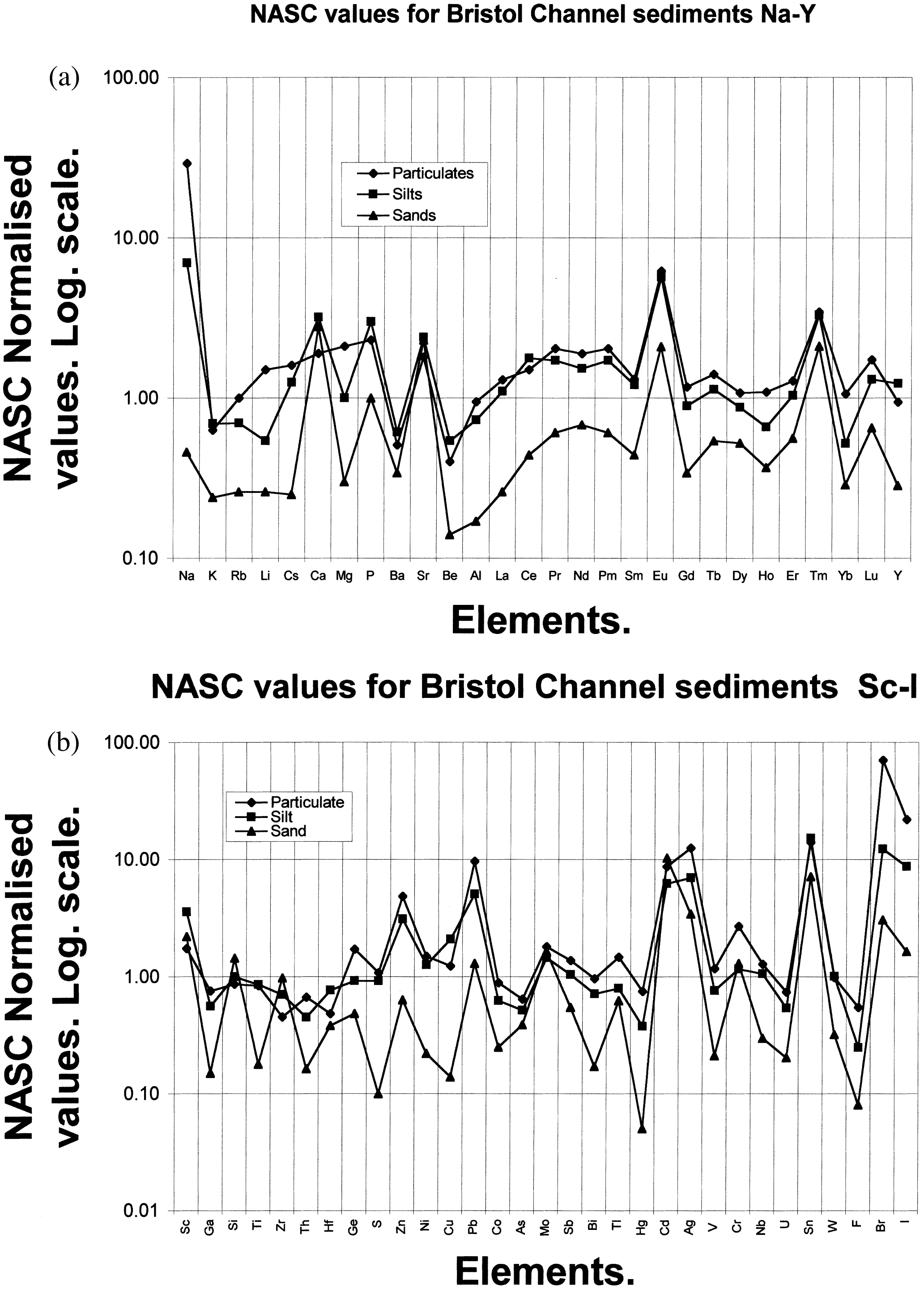

Fig. 4. North American Shale Composite (NASC) normalised values for suspended particulate matter, deposited silts and sands from the Bristol Channel estuary (Hamilton et al., 1979) illustrating similarities between the composition of the NASC (particulates and silts) sample and shale like sediments from a different part of the world. Note the similarities in the distribution pattern for many elements in all samples. The lower normalised values for sand simply reflects the dilution effect of the quart in such sediments.

Table 1
The concentration (mg/kg dry wt.) of the elements in global averages for crustal rocks, shale (NASC) and sandstone compared with suspended particulates, silts and sands from the Bristol Channel, SW England[a]

Element	Global values			Bristol Channel					
	Crust	Shale	Sandstone	Suspended particulates ($n = 21$)	*N*	Silts ($n = 18$)	*N*	Sands ($n = 16$)	*N*
Na	28 200.00	7479.00	3300.00	218 000.00	29.20	52 000.00	7.00	34 000.00	0.46
K	27 400.00	31 546.00	10 700.00	20 000.00	0.63	21 600.00	0.69	7700.00	0.24
Rb	90.00	125.00	60.00	125.80	1.00	86.90	0.70	32.20	0.26
Li	20.00	66.00	15.00	99.40	1.50	35.45	0.54	19.68	0.26
Cs	3.70	5.16	1.00	8.14	1.60	6.47	1.25	1.31	0.25
Ca	25 000.00	24 303.00	39 100.00	45 900.00	1.90	76 700.00	3.20	66 900.00	2.80
Mg	19 500.00	15 000.00	7000.00	31 300.00	2.10	15 500.00	1.00	7100.00	0.30
P	1050.00	700.00	170.00	1600.00	2.30	2100.00	3.00	672.00	1.00
Ba	700.00	636.00	350.00	325.50	0.51	386.30	0.61	218.30	0.34
Sr	350.00	142.00	40.00	252.70	1.80	340.30	2.40	331.30	2.30
Be	2.80	3.00	0.50	1.23	0.40	1.63	0.54	0.41	0.14
Al	84 700.00	89 471.00	2647.00	85 000.00	0.95	65 200.00	0.73	15 000.00	0.17
La	30.00	31.10	30.00	40.35	1.30	35.72	1.10	7.99	0.26
Ce	64.00	66.70	92.00	104.10	1.50	118.50	1.78	29.09	0.44
Pr	8.20	5.60	3.00	11.40	2.04	9.60	1.71	3.40	0.61
Nd	26.00	27.40	20.00	51.76	1.89	41.90	1.53	18.62	0.68
Pm	8.20	5.60	3.00	11.40	2.04	9.60	1.71	3.40	0.61
Sm	4.50	5.59	3.00	7.34	1.31	6.73	1.20	2.47	0.44
Eu	0.88	1.18	3.00	7.34	6.22	6.73	5.70	2.47	2.09
Gd	5.40	6.40	2.00	7.53	1.18	5.73	0.90	2.18	0.34
Tb	0.64	0.85	1.60	1.20	1.41	0.96	1.13	0.46	0.54
Dy	3.00	4.60	7.20	4.96	1.08	4.02	0.87	2.40	0.52
Ho	1.20	1.20	2.00	1.31	1.09	0.79	0.66	0.44	0.37
Er	2.80	2.50	4.00	3.20	1.28	2.60	1.04	1.40	0.56
Tm	0.50	0.20	0.30	0.69	3.45	0.66	3.30	0.42	2.10
Yb	2.20	3.06	4.00	3.25	1.06	1.59	0.52	0.88	0.29
Lu	0.32	0.46	1.20	0.80	1.74	0.60	1.30	0.30	0.65
Y	22.00	26.00	5.00	24.45	0.94	32.04	1.23	7.37	0.28
Sc	10.00	14.90	1.00	25.85	1.73	53.03	3.56	32.82	2.20
Ga	15.00	19.00	12.00	14.35	0.76	10.63	0.56	2.84	0.15
Si	282 000.00	265 555.00	346 800.00	228 300.00	0.86	264 100.00	0.99	380 600.00	1.43
Ti	3600.00	4676.00	1499.00	3900.00	0.83	4000.00	0.86	835.30	0.18
Zr	2400.00	200.00	200.00	90.09	0.45	139.76	0.70	194.78	0.97
Th	10.50	12.30	3.00	8.18	0.67	5.51	0.45	2.00	0.16
Hf	5.80	6.30	3.50	3.03	0.48	4.82	0.77	2.41	0.38
Ge	1.50	1.60	0.80	2.74	1.71	1.47	0.92	0.77	0.48
S	260.00	2400.00	240.00	2600.00	1.08	2200.00	0.92	240.00	0.10
Zn	70.00	95.00	16.00	461.00	4.85	295.60	3.11	60.06	0.63
Ni	20.00	58.00	5.00	86.35	1.49	73.00	1.26	12.75	0.22
Cu	55.00	45.00	5.00	55.38	1.23	93.72	2.08	6.25	0.14
Pb	15.00	20.00	7.00	192.80	9.64	101.30	5.07	26.00	1.30
Co	10.00	25.70	1.50	22.75	0.89	16.00	0.62	6.39	0.25
As	1.80	28.40	1.00	18.22	0.64	14.62	0.51	10.99	0.39
Mo	1.50	2.60	0.20	4.69	1.80	3.76	1.45	4.23	1.63
Sb	0.20	2.09	0.05	2.88	1.38	2.17	1.04	1.14	0.55
Bi	0.17	1.00	0.30	0.96	0.96	0.71	0.71	0.17	0.17
Tl	0.45	1.40	0.82	2.05	1.46	1.11	0.79	0.87	0.62

Table 1 (*Continued*)

Element	Global values			Bristol Channel					
	Crust	Shale	Sandstone	Suspended particulates ($n = 21$)	*N*	Silts ($n = 18$)	*N*	Sands ($n = 16$)	*N*
Hg	0.00	0.40	0.03	0.30	0.75	0.15	0.38	0.02	0.05
Cd	0.20	0.30	0.05	2.61	8.70	1.86	6.20	3.10	10.33
Ag	0.07	0.07	0.05	0.88	12.57	0.49	7.00	0.24	3.43
V	60.00	130.00	10.00	152.60	1.17	98.46	0.76	27.46	0.21
Cr	35.00	124.50	30.00	335.30	2.69	144.80	1.16	162.00	1.30
Nb	25.00	11.00	20.00	14.09	1.28	11.65	1.06	3.26	0.30
U	2.50	2.66	0.45	1.96	0.74	1.43	0.54	0.54	0.20
Sn	2.00	6.00	0.50	84.43	14.07	91.14	15.19	42.91	7.15
W	1.50	2.10	1.60	2.06	0.98	2.11	1.00	0.67	0.32
F	625.00	740.00	270.00	404.80	0.55	183.40	0.25	59.30	0.08
Br	2.50	4.00	1.00	282.40	70.60	49.31	12.33	12.25	3.06
I	0.50	2.20	1.70	48.10	21.86	19.24	8.75	3.61	1.64

[a] *N*-values normalised against the NASC. (Bristol Channel data by SSMS, XRF and AA analysis) Average crust values, see Hamilton et al. (1979); Taylor and McLennan (1981, 1985). Bristol Channel data, see Hamilton et al. (1979).

ferent in origin and composition, hence the comparisons are of little value. Table 1 presents global values for average crustal rock, shale and sandstone which have been derived from large scale geochemical compilations, but that may have limited value for particular sites.

For purposes of validating the approach, especially with respect to sensitivity for the presence of particular materials, I have selected silts (silts = shales) and sands from the adjacent SW region of the Bristol Channel area that are of similar geological age and provenance (see Fig. 1a). Normalised values, for suspended particulates and silts and sands to NASC values are also given in Table 1. For present purposes, and ignoring the halogen elements and REE anomalies, the elements Zn, Pb, Cd, Ag, Cr, Sn and Br are enriched relative to the NASC. For the silts, the enrichment is noticeable for Zn, Pb, Cd and Ag reflecting their presence in wastes from industrial effluents common to the region; for example, Zn and Cd from a smelter and Sn from tin plating. Values for Na, Ca, P, Sr, Br and I reflect the association of the fresh Bristol Channel sediments with seawater; there is no enrichment in arsenic. For the purposes of this paper elements have been grouped along the *x*-axis in order to identify the presence of the chalcophilic elements that are a feature of ore mineralisation in SW England. The Bristol Channel survey was carried out between 1973 and 1975, since when there has been a major decline in industrial activity for the region coupled with legislation to reduce or terminate significant inputs of pollutants. A similar survey today will probably indicate a closer similarity of element abundances with the NASC.

3. Results and discussion

3.1. Mine wastes

3.1.1. GDC mine wastes

Data for the composition of some typical mine waste materials are given in Table 2. In Fig. 5, data are presented for the wastes normalised against NASC. The chalcophilic elements Cu and As are especially enriched relative to the shale composition, iron is only slightly enriched despite the brown–orange colour of the wastes which is principally caused by surfical staining, while manganese is significantly enriched. Samples 144–147 are mine soil-dusts that represent the principle source term for GDC materials into the environment following atmospheric weathering and transport by aerial and aqueous routes.

Table 2
NASC element concentrations and NASC normalised values for the Great Devon Consols samples [see text for a description of samples (analysis by ICP and AA for leachates)]

Element	NASC	NASC-normalised values								
		Sample 144	Sample 145	Sample 146	Sample 147	Sample 150	Sample 148	Sample 266	Sample 265	Sample 264
Al[a]	16.88	2.96	2.07	3.04	1.51	10.77	2.82	2.88	2.11	1.6
Li	66	72	52	71	19	29	64	5	11	7
K[a]	3.8	0.15	0.05	0.12	0.2	0.1	0.17	0.01	0.02	0.01
Mg[a]	2.5	0.35	0.4	0.35	0.17	0.26	0.44	0.06	0.16	0.11
Ca[a]	3.4	2.17	1.03	1.77	2	0.24	1.81	0.05	0.04	0.04
P[a]	1.59	0.47	0.15	0.44	0.14	0.19	0.37	0.04	0.07	0.05
Sr	142	242	22	242	23	15	121	2	3	3
Y	26	25	7	22	11	111	17	32	35	19
Ba	636	200	17	205	45	48	143	9	24	24
La	92	15	9	14	12	103	17	30	42	21
Ce	59	20	13	22	18	93	27	25	30	19
V	130	28	24	33	31	26	31	6	13	10
Cr	124.5	19	16	18	16	22	20	6	14	8
Fe[a]	5.65	11.91	10.2	15.09	20.54	7.58	9	1.98	3.63	3.71
Mn	4646	404	488	376	1166	601	515	112	148	105
Cu	45	1343	1008	1532	957	8120	1769	3041	3909	1810
Pb	20	205	67	242	130	159	197	47	97	164
Sb	2.09	84	81	98	169	43	96	15	44	36
As	28.4	9782	9668	11 335	9308	3011	10 426	693	769	3852
Zn	95	44	32	45	329	970	71	208	347	160
Cd	0.3	16	12	16	29	10	16	3	7	5
Co	25.7	17	19	14	80	29	19	6	13	5
Ni	58	17	16	19	46	90	21	23	43	18

[a] Elements measured as %. All other elements in mg/kg.

Samples 150, 148, 266, 264, and 151 (see NASC normalised data in Fig. 5), were opportunistic and were taken from the floor of a small potable water reservoir fed by springs, that had been exposed during a rare period of a prolonged drought, approximately 500 m beyond the mine boundary in a NE direction and protected from the wastes by a band of deciduous and coniferous trees. The exposed floor of the reservoir consisted mainly of decaying leaf litter and even at a depth of 25 cm the deposit was clearly rich in organic matter and anaerobic. Because of the presence of large amounts of decaying organic matter the reservoir is unsuitable as a source of historic data. Nevertheless, the overall composition of the leachate is similar to that obtained on farmland (e.g. As 150–280 mg/kg) to the NE of GDC and probably reflects aerial transport of material from the GDC site. It seems highly probable that within the reduced environment of the black decaying leaf debris, biomethylation of some of the arsenic takes place and possibly the generation of small amounts of the highly toxic arsine gas. Allowing for the inherent problems of adequate sampling and analytical problems that are associated with the matrix of the samples, the GDC ore signal can be characterised at the site and is recognised beyond the perimeter of the mine.

3.1.2. Mary Tavy, Peter Tavy mines W Devon

Similar to the GDC mining area, the ores at Mary Tavy, W Devon (Wheal Friendship) and Peter Tavey (Devon United) are emplaced into Lower and Upper Carboniferous shales and are associated with chert, pillow lava and sandstones. Although at a similar altitude to the GDC site, the SW granite slopes of Dartmoor are open to the weather, trees are sparse and leaching and

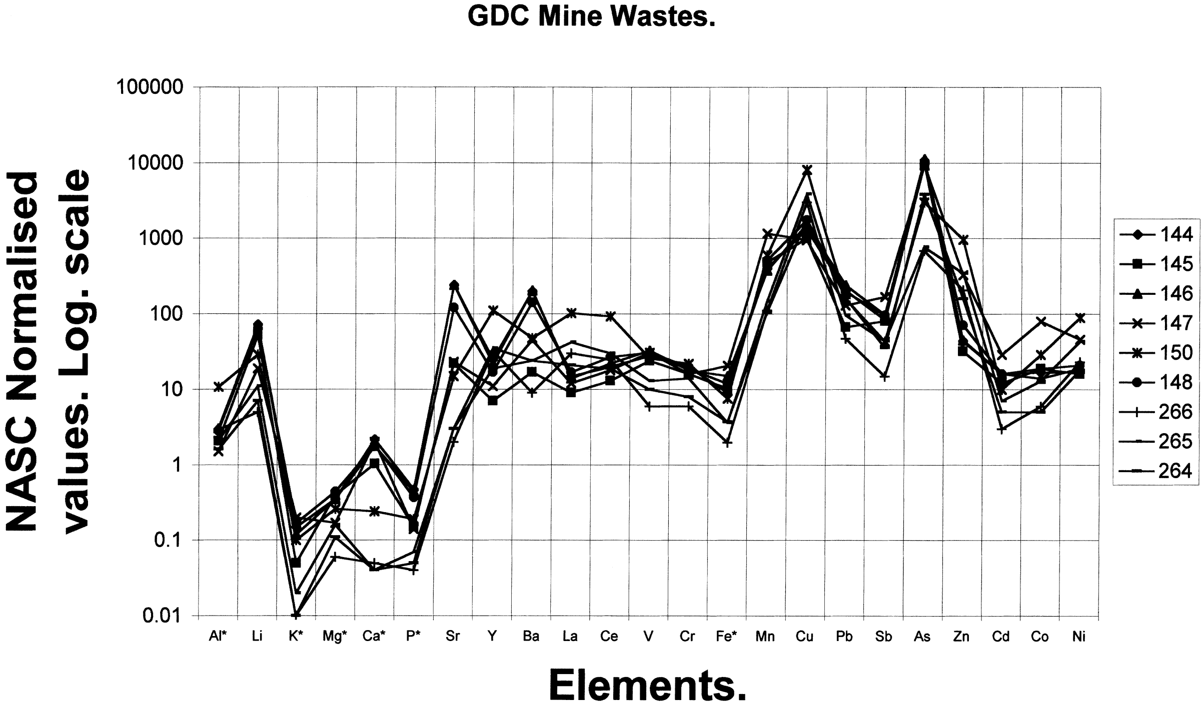

Fig. 5. NASC normalised values for Great Devon Consols (GDC) mine wastes, near Tavistock, W Devon. Note maximum relative enrichment for the characteristic chalcophilic mine elements Mn, Cu, Pb, As and Zn. The relative enrichment in REEs, Sr and Ba seems to be a regional geochemical characteristic of the area.

transport of mine wastes takes place through surface processes via the small upper catchment tributaries of the River Tavy (see Fig. 1) Until the 1870s, the main ores mined were tin, lead, silver, zinc and tungsten. Between 1870 and the arsenic slump in 1925, arsenic was the main ore mined; in the area there are several large arsenic calciners and the associated condensing chambers. At Peter Tavy (see Fig. 1b) and along a 5-km stretch of the east bank of the river Tavy, several large mines occur together with addits draining into the river. Mining ceased by around 1922 and today, with the exception of some waste tips, most of the sites are covered by dense vegetation. Approximately 6 km downstream from the mines is the town of Tavistock with a population of approximately 45 000.

Data are given in Table 3 and Fig. 6 illustrates the NASC normalised values for samples from the Tavy mining area, through the town of Tavistock to the tidal limit of the Tavy at Lopwell dam (see Fig. 1b). Samples 253–254 were taken from mineral processing tips at the Wheal Betsy mine just above Tavistock. Samples 600 and 612 were taken at the northern outskirts of Tavistock from the banks of the Tavy and reflect the fluvatile transfer of mine debris down the Tavy. Sample 716 was taken from the bank of the river Tavy within the town of Tavistock at the West Bridge. It should be noted that within a public recreation park in the same area, levels of arsenic have dropped to between 15 and 25 mg/kg, illustrating the retention of the mine wastes between the river banks. Samples 718 and 721 were from a domestic building site in Tavistock that was being developed in the close proximity to mine wastes. Sample 1013, downstream of Tavistock at Denham Bridge, and sample 1014 at Lopwell, the tidal limit of the Tamar–Tavy estuary. At the confluence of the Tamar and Tavy, at the Bere

Table 3
NASC-normalised values for samples taken from the Mary Tavy–Peter Tavy mining area, Devon, through the town of Tavistock to the tidal limit of the Tavy at Lopwell[a]

Sample:	253	254	600	601	601	716	718	721	1013	1014
Element										
Li	1.00	1.00	74.00	83.00	83.00	76.00	53.00	0.83	62	0.76
K[b]	0.05	0.12	0.01	0.14	0.14	0.11	0.05	0.01	0.08	0.01
Al[b]	0.29	0.17	3.25	3.25	3.25	3.42	2.90	0.16	2.91	0.15
Mg[b]	0.02	0.08	1.43	1.61	1.61	1.78	0.63	0.31	1.31	0.40
Ca[b]	0.04	0.03	0.38	0.26	0.26	0.50	0.24	0.05	0.44	0.08
P[b]	0.25	0.17	0.13	0.12	0.12	0.15	0.12	0.04	0.17	0.11
Sr	3.00	7.00	13.00	11.00	11.00	15.00	7.00	0.06	13	0.15
Y	7.00	2.00	13.00	12.00	12.00	9.00	5.00	0.19	10	0.23
Ba	7.00	6.00	46.00	44.00	44.00	41.00	34.00	0.05	32	0.03
La	35.00	24.00	24.00	24.00	24.00	25.00	15.00	0.51	23	0.55
Ce	69.00	44.00	50.00	50.00	50.00	50.00	27.00	0.46	37	0.42
V	15.00	9.00	58.00	57.00	57.00	55.00	24.00	0.17	39	0.26
Cr	5.00	58.00	57.00	66.00	66.00	49.00	23.00	0.19	47	0.27
Fe[b]	27.70	12.34	5.72	6.01	6.01	6.96	5.14	0.73	5.96	1.08
Mn	72.00	41.00	1346.00	2513.00	2513.00	1905.00	602.00	0.07	1202	0.09
Cu	6296.00	613.00	371.00	288.00	288.00	308.00	97.00	0.71	344	4.69
Pb	18 930.00	946.00	569.00	703.00	703.00	71.00	51.00	2.85	278	8.70
Sb	1276.00	304.00	41.00	42.00	42.00	14.00	53.00	24.88	48	80.40
As	13 750.00	6340.00	1050.00	1380.00	1380.00	1356.00	612.00	2.11	1018	1.69
Zn	4145.00	4145.00	354.00	277.00	277.00	260.00	114.00	0.8	222	2.95
Cd	14.30	3.40	0.90	0.90	0.90	1.30	6.00	16.8	1.2	3.00
Co	9.00	6.00	42.00	39.00	39.00	46.00	12.00	0.43	25	0.66
Ni	14.00	10	60	64	64	71.00	23.00	0.57	48	0.78

[a] See text for a description of samples and sampling localities in Fig. 1c (analysis by ICP and AA for leachates).

[b] Elements measured as %. All other elements in mg/kg.

Ferrers Peninsula, low-lying flood plain sediments are contaminated by the ore minerals that are transported to the area by both rivers. These soils contain the characteristic signal of the mine wastes.

3.2. Examples of contamination to land related to the dispersion of the W Devon mine wastes by commercial and recreational activities

3.2.1. Pitts Cleave Quarry, Tavistock Devon

In 1996, the disused Pitts Cleave Quarry, adjacent to the river Tavy on the outskirts of Tavistock, was developed by the local Council as an industrial building site; the site also contains an area of special scientific interest. The site had been derelict since 1992 following the closure of a ready mix concrete works. Since the closure, it has been used as a general dump and its contents are unknown. The site has been identified by independent consultants as being contaminated and requiring defined working practices in its development. In a recent development of the site, the land was levelled and roads and drains were installed. In this process, and as a consequence of levelling the various piles of waste, the surface of the area was raised to approximately 1m above the new road surface, thus permitting the transport of any leachates directly into the Tavy via road drainage routes. Towards the end of September 1996, just before a new landfill tax was introduced, the surface of the site was lowered and approximately 1500 t of contaminated waste were removed in uncovered lorries. While it proved impossible to adequately sample the site, NASC normalised values for leach data for localities within the quarry are illustrated in Fig. 7. The

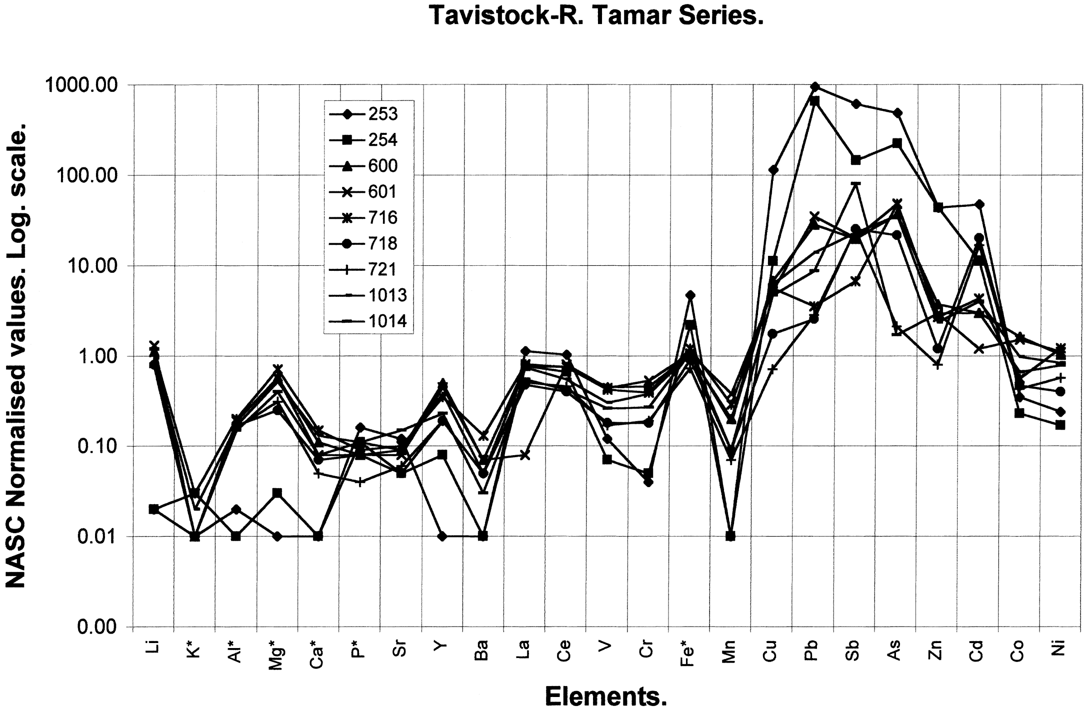

Fig. 6. Illustrating the chalcophilic enriched elements, characteristic of the mines wastes, in the river Tamar and Tavey fluvatile deposits. Samples 253 and 254 were sampled at the mine site upstream of the town of Tavistock, W Devon.

wastes contain concrete rubble mixed in with other materials; the elements Cu, Pb, Sb, As, and Zn are enriched relative to the NASC values and reflect the presence of the ore minerals. There is a significant depletion of K and Mn relative to NASC values which may reflect the loss of these soluble elements by leaching. The general composition of the contaminated site reflects the presence of river-borne mine wastes. A few metres downstream of the site, a large commercial trout fishery has been in existence for some time. Despite its proximity, any leachates that arise from the site, or from upstream mine wastes, do not appear to affect the health of the fish. It should also be noted that the River Tavy supports a large number of water fowl and the river is noted as a salmon run. Most aquatic organisms have a well-developed biochemistry to deal with many potentially toxic elements and inorganic arsenic in particular.

3.2.2. *Morwellham Quay*

Approximately 4 km to the south of GDC, Morwellham Quay on the banks of the River Tamar was used to export ores from the local mines. It is now disused and has silted up; in its heyday it could accommodate ships up to 300 tons. In April 1995, a chance visit to the site, which receives approximately 160 000 visitors annually, clearly indicated that the most contaminated GDC mine waste had been used to cover pedestrian areas. The NASC leached values and chemical data are given in Table 4 and illustrated in Fig. 8. Fig. 9A illustrates the use of the GDC mine wastes at Morwellham to represent piles of ore along the wharves. The use of the sand–gravel sized mine wastes at Morwellham represents contamination of fairly clean land and the potential loss of leachates to the adjacent Tamar. Evidence of very extensive removal of fine and coarse grain mine wastes at the GDC is shown by the truncated rock piles and the extensive areas of excavation (see Fig. 9B). In the 1960s, the site from where the wastes had been removed contained thin horizons of very high-purity arsenic wastes,

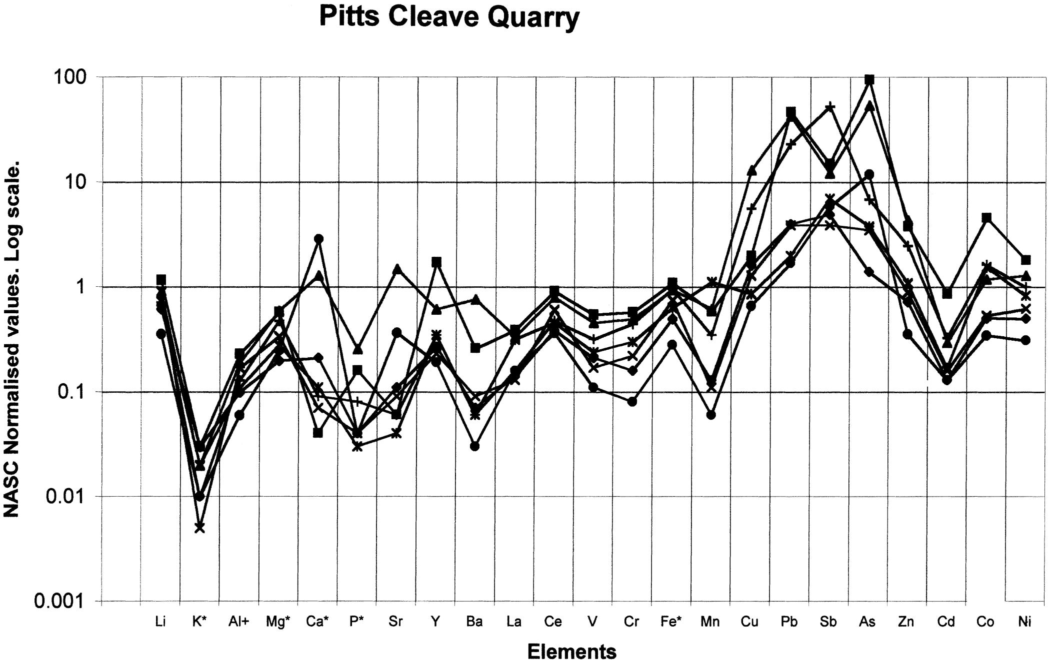

Fig. 7. NASC normalised values for Tamar fluvatile deposits from the floor of the Pitts Cleave Quarry, Tavistock, Devon illustrating an enrichment in mine waste elements for some samples. The floor of the area contains a variety of types of debris of diverse compositions. However, in areas many samples clearly contain mine wastes whose presence throughout the area is supported by independent consultant reports.

possibly derived from slime ponds and wastes from the condensation labyrinths and arsenic purification plants. At Morwellham, in active demonstrations of mineral processing in which the public can participate, rather than using a copper ore, high-purity samples of arsenopyrites are commonly used. There is no evidence of staff working at the site or from visitors that exposure to high concentrations of the mine wastes has given rise to any illnesses. However, this is very difficult to document.

3.2.3. Commercial and domestic transfer of mine wastes

In SW England, a common and long-standing practice is the use of arsenical mine waste for use on garden drives, pathways, car parking areas or other open spaces to provide cover and in order to discourage the growth of weeds. There is little doubt that this practice has existed over the last 100 years or so and has resulted in the contamination of large areas of uncontaminated land throughout the region, albeit once more no detriment to human health is known. In the 1900s, before the availability of building sand from a local source the arsenical, low pH GDC sands were used for normal domestic building mortar. Indeed, even today it is common knowledge that houses in which wastes have been used require special paints to prevent them peeling away. Other uses of the cheap waste are for building infill and in soakaways, but here a graded ‘stone’ fraction is favoured (see Fig. 9B). However, this phase can contain considerable amounts of ore minerals as discrete blocks or disseminated throughout the ‘stones’. Because of the cost of removing the material and transport charges the practice is restricted to a radius of approximately 15–30 kms around the mine sites. This practice can give rise to three potential hazards: first, heavy contamination at the removal site due to disturbance of the wastes and the generation of dusts; second, contamination at the site of deposition; and third, long-term leaching of the wastes and transfer of

Table 4
Morwellham Quay, River Tamar (the concentration of elements in contaminated mine wastes used to surface paths at the site, together with NASC-normalised values (analysis by ICP and AA. for leachates)

Element	Concentration				NASC value			
	136	137	135	138	136	137	135	138
Li	48.00	63.00	65.00	87.00	0.73	0.95	0.98	1.32
K[a]	0.11	0.05	0.10	0.30	0.03	0.01	0.03	0.08
Al[a]	2.50	3.02	11.02	3.06	0.15	0.18	0.15	0.18
Mg[a]	0.46	0.70	0.48	0.29	0.18	0.28	0.19	0.12
Ca[a]	0.97	0.19	1.22	3.22	0.29	0.06	0.36	0.95
P[a]	0.20	0.07	0.17	0.24	0.13	0.04	0.11	0.15
Sr	36.00	101.00	27.00	131.00	0.25	0.71	0.19	0.92
Y	10.00	10.00	7.00	18.00	0.38	0.38	0.27	0.69
Ba	50.00	123.00	79.00	75.00	0.08	0.19	0.12	0.12
La	14.00	12.00	11.00	15.00	0.15	0.13	0.12	0.16
Ce	23.00	20.00	48.00	18.00	0.39	0.34	0.81	0.31
V	26.00	24.00	33.00	26.00	0.20	0.18	0.25	0.20
Cr	18.00	16.00	23.00	15.00	0.14	0.13	0.18	0.12
Fe[a]	11.87	9.48	11.02	9.87	2.10	1.68	1.95	1.75
Mn	794.00	500.00	618.00	295.00	0.17	0.11	0.13	0.06
Cu	1731.00	2283.00	620.00	1628.00	38.47	50.73	13.78	36.18
Pb	107.00	132.00	71.00	151.00	5.35	6.60	3.55	7.55
Sb	82.00	76.00	81.00	79.00	39.23	36.36	38.76	37.80
As	9652.00	9795.00	1874.00	13 054.00	339.86	344.89	65.99	459.65
Zn	69.00	239.00	57.00	49.00	0.73	2.52	0.60	0.52
Cd	13.00	11.00	12.00	12.00	43.33	36.67	40.00	40.00
Co	12.00	17.00	16.00	14.00	0.47	0.66	0.62	0.54
Ni	18.00	22.00	30.00	15.00	0.31	0.38	0.52	0.26

[a] Oxides %. Other elements in mg/kg dry wt.

elements to water courses. For none of these operations is there any recorded incidence of mortality or morbidity to the local population or workers, neither is there any record of where the wastes have been used.

In order to pursue the transfer of GDC wastes onto private uncontaminated land, a study was initiated at one site, assumed to be uncontaminated. A series of unusual circumstances that follow illustrate quite clearly the nature of the problem. In 1993, a number of elements had been determined for indoor and outdoor dust composition by neutron activation analysis; the selection of elements was governed by the choice of analytical method which was free from problems of sample contamination and interferences as a consequence of matrix effects. The data were originally acquired in relation to a larger study in which the concentration of elements and organic compounds in indoor and outdoor air were to be studied in relation to respiratory disorders and asthma in particular.

The data are given in Table 5 and illustrated in Fig. 10 for the concentration of a few elements in indoor and outdoor air, together with NASC normalised values for the site. The outdoor air is enriched with caesium (reflecting the abundance of aluminium and clay minerals) silver, arsenic antimony, and zinc. The indoor air is enriched in scandium (alumino-silicates), silver, antimony, zinc and mercury. The overall pattern of element abundances is similar for the two samples. For both samples, the levels of mercury are unexpected, but may be related to a regional source from Lower Carboniferous volcanic activity from which the manganese ores were derived. Within the region, numerous houses are constructed of lava blocks, often containing crystals of pyrites, and it is possible that elements such as arsenic, antimony and mercury may be derived from

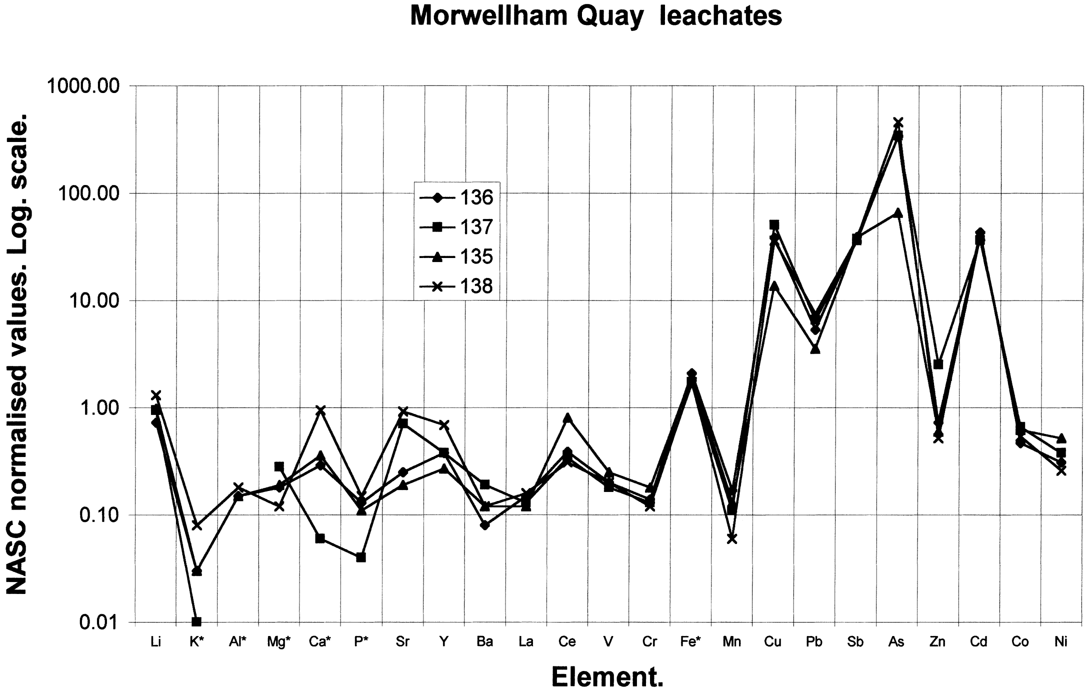

Fig. 8. NASC normalised values for materials used to cover the tourist site of Morwelleham Quay, Tavistock, W Devon. Element abundances are fairly similar for all samples hence, as the material is distributed throughout the pedestrian areas, the contamination is widespread.

weathering products and hence penetrate into buildings and their surroundings. In relation to the known history of the building, there is no reason to consider that the mercury may have been derived from an internal domestic source such as a broken thermometer. Concentrations of arsenic for indoor and outdoor air were significantly higher than expected for an uncontaminated site, i.e. 15–25 mg/kg. The source of the arsenic, iron and REEs was identified as originating from weathered concrete that, in the past, had been used to cover a courtyard and contained mine waste together with other local rocks as an aggregate. The area was subsequently covered with asphalt and the source of the contamination was removed. A similar procedure had been adopted in Tavistock in order to immobilise mine wastes that had been used for a car park.

Because of the problems of not being able to identify natural- vs. man-contaminated sites, an attempt was then made to determine the probable concentration of arsenic and other elements at the site that may reflect general background levels, uncontaminated by GDC wastes. Because of the variety of sedimentary rocks in the area, abundances of the elements will vary considerably. Within a single rock type such as shale or slate, there are arenaceous and calcareous bands of varying thickness that contain several characteristic elements, for example sandy bands enriched in resistate minerals such as zircon (Zr, Hf, U, Th), sphene (Ti, Ba, REE, U, Th) and calcareous deposits (Ca, Sr, Ba). Data are illustrated in Fig. 11 for a number of selected samples that are not likely to be significantly contaminated by ore minerals. Sample 715 was taken from the main recreation ground in Tavistock and reflects average values for the area; here, the lead values may be influenced by the adjacent main road. Sample 717 was taken from the WDBC offices car park; once more the lead and possibly the zinc levels reflect the use of the area for parking cars. Both these samples illustrate some of the confounding factors when evaluating the concentration of ele-

Fig. 9. (A) Piles of mines wastes, believed to be derived from Great Devon Consols waste piles used at Morwelleham Quay in order to simulate piles of ore awaiting transfer to ships. The materials used seem to have been derived from the most highly contaminated areas of GDC. (B) Illustrating the excavation, today, of coarse mine wastes for use in soakaways and building developments. Many of these blocks of stone contain large amounts of arsenopyrites and copper ore.

ments in soils. Samples 256 and 263 were taken from a bore hole at a soakaway site (see below and Table 5 and Fig. 9) at depths of 10 and 45 m, respectively. Here, lead is present in significant amounts together with copper, antimony, zinc and nickel. These samples were obtained from sediments that act as aquifers, hence they represent a complex system of elements in, adsorbed onto, or precipitated between, minerals of the sediment. It should also be noted that the sediments of this area are influenced by a different mineralisation from that present at GDC and where lead and zinc are more abundant. However, within these sediments copper tends to be more mobile and, therefore, may be derived from more distant sources. Sample 141 is of topsoil taken at a soakaway site (see below) and is not believed to be contaminated. However, sample 140 was taken in an adjacent field and there is no obvious reason for the enrichment in lead for this sample. While

Table 5
NASC composition compared to indoor and outdoor air for a domestic site together with NASC normalised values (analysis by INAA, XRF total concentrations)

Element	NASC (mg/kg)	Indoors		Outdoors	
		Sample 373 (mg/kg)	*N* 373	Sample 367 (mg/kg)	*N* 367
Na	7479	5000	0.96	3000	0.4
Rb	125	47	0.38	320	2.56
Cs	5.2	3.5	0.67	20.1	3.87
Sc	14.9	53.8	3.6	32.5	2.18
Ba	636	540	0.85	650	1.02
La	31.1	10	0.32	35	1.13
Ce	66.7	21.5	0.32	140	2.1
Nd	27.4	5	0.18	25	0.91
Sm	5.59	0.8	0.14	4.7	0.84
Eu	1.18	0.4	0.34	1.2	1.02
Lu	0.46	0.1	0.22	0.25	0.54
Fe	39 565	32 567	0.82	100 120	2.53
Ag	0.88	4.2	4.77	0.5	0.57
As	28.4	44	1.55	84	3
Sb	2.09	7	3.3	5.7	2.73
Zn	95	945	9.95	660	6.95
Hg	0.4	3.7	9.2	2.2	5.5
Cr	124.5	168	1.6	388	3.12
Ta	1.12	1.4	2.3	1.25	1.12
Th	12.3	7.75	0.63	29.5	2.4
U	2.66	2.35	0.88	4.5	1.69
W	2.1	3.6	1.71	1.1	0.52
Hf	6.3	1.5	0.24	2.1	0.33

it is possible to evaluate the background levels of elements in the region that are free from mine wastes, other confounding factors are introduced that make it unrealistic to recognise a single regional value for most elements. Following Pleistocene fluvatile glacial events, redistribution of surface materials, aerial transport of wastes over the centuries and the influence of local practices have resulted in a redistribution of the elements in soils. In recent years, prolonged periods of drought have resulted in the loss of fine grained topsoil to roadways, following episodes of intense rainfall which is an additional mechanism for the redistribution of elements within the region.

By chance, during the drought of 1995, a pit approximately 6 m^3, was dug adjacent to a house in rural settings to provide a soakaway for sewage. The pit was filled with some 30 tons of highly contaminated GDC mine wastes that gave rise to the expulsion of a dense brown cloud of dust that covered adjacent properties when it was emptied into the pit and which contained significant amounts of arsenic and antimony. The uncontrolled use of such wastes is hardly in keeping with improving the quality of the environment.

Fig. 12 illustrates the influence of the tipping upon adjacent land. Sample 143 and sample 175 were obtained for topsoil some 10 m up and downwind from the pit before the wastes were discharged. Samples 139 and 142 for soil from the same sites after the tip had been filled with the mine wastes. These samples now contain the characteristic GDC mine waste signal; the dust was spread over an area of approximately 100 m^2, and enveloped a domestic premises. Once the pit was filled and covered with topsoil the characteristic GDC signal remained in the soils for approximately 10 months.

Because of the drought and an absence of any appreciable wind at that time, the soakaway dusts penetrated the nearby house (20 m), hence, a limited study was undertaken for the composition of the indoor dust 3 h after the discharge; the data are given in Table 6 and illustrated in Fig. 13. Sample 544 is for bedroom floor dust, 545 lounge dust, 546 for stair carpet dust and 252 curtain dust. The chalcophilic signal (Cu, Pb, Sb, As, Zn) of the mine wastes is apparent and took approximately 1 year before it decreased in intensity to a normal range of values. It is clear that uncontrolled discharge of mine waste in the region can contaminate residential property and also result in uncontaminated land becoming contaminated. With respect to the site, the stream draining the soakaway is a tributary of the River Tamar, but any discharges into the Tamar are negligible; that contained within the soakaway is likely to be retained and is not likely to constitute any hazard albeit anaerobic conditions may exist, thus, enhancing the solution of the ore minerals.

A further and final example of how the unacceptable and uncontrolled use of mine waste sites can give rise to a concern for human and animal health is illustrated by the GDC site itself. On 1 May 1994, during a particularly dry spell of weather, a pale brown cloud was seen over the

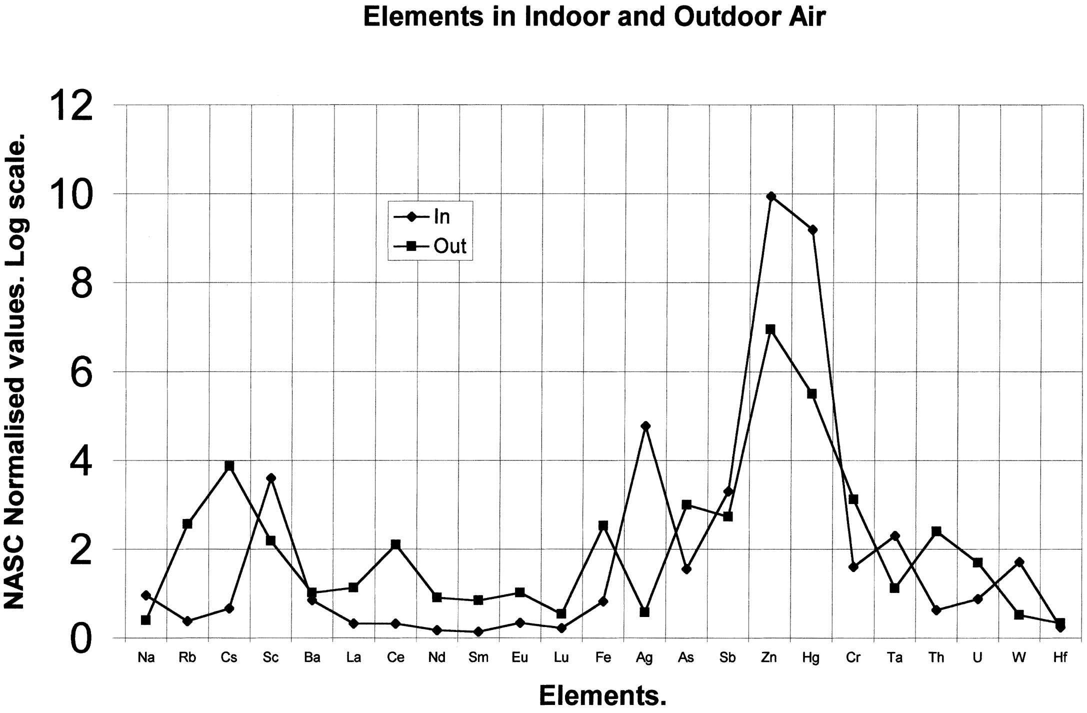

Fig. 10. NASC normalised values for the abundance of some elements in indoor and outdoor air for a domestic building site. The site was not considered to be contaminated prior to the analysis of samples. The abundance of As, Sb and Zn is related to historic use of mine wastes near the site, Ag from internal domestic sources and Hg, probably a regional geochemical characteristic.

site. The cloud, as illustrated in Fig. 14a,b was generated from the most highly contaminated mine spoil dusts and was caused by the site being used for a four-wheel car rally. Revving of engines buried the wheels into the wastes and churned up large amounts of dust which reached a visible height of > 100 m. On this occasion, between 150 and 200 participants and onlookers at the rally, together with approximately 40 local residents, were exposed to the dusts for approximately 10 h.

The history of the site as a rally vehicle test circuit is long and is not documented. In February 1990, the West Devon Borough Council (WDBC, 1990) approved the use of an existing rally vehicle test circuit on the site for rally car use (28 days each year), the use of the area for six four-wheel drive vehicle skill events each year, off-road driver training activities and up to four ‘promotional’ events each year. In 1994, the Council was of the opinion that use of the site for motor sports created no statutory nuisance (WDBC, personal communication). At that time, the site was also being considered as a mountain-bike course. It should be noted that WDBC (1991) had refused permission for the use of the GDC site for the purpose of storage of topsoil on the grounds that vehicles would disturb the surface of the land. More recently, because of a failure to gain road access to the site for the purpose of car rallies, permission to use the site for such purposes has lapsed. It seems probable that the agricultural land to the south of the GDC site has become significantly contaminated as a consequence of the aerial transfer of mine wastes in the direction of the prevailing wind as a consequence of natural processes, but enhanced by vehicle activity in the central, most-contaminated, area of the mine wastes. There is a significant transfer of mine wastes to the south by wind action, but usually this seems to be restricted to a height of approximately 1.2 m above ground level and most of the

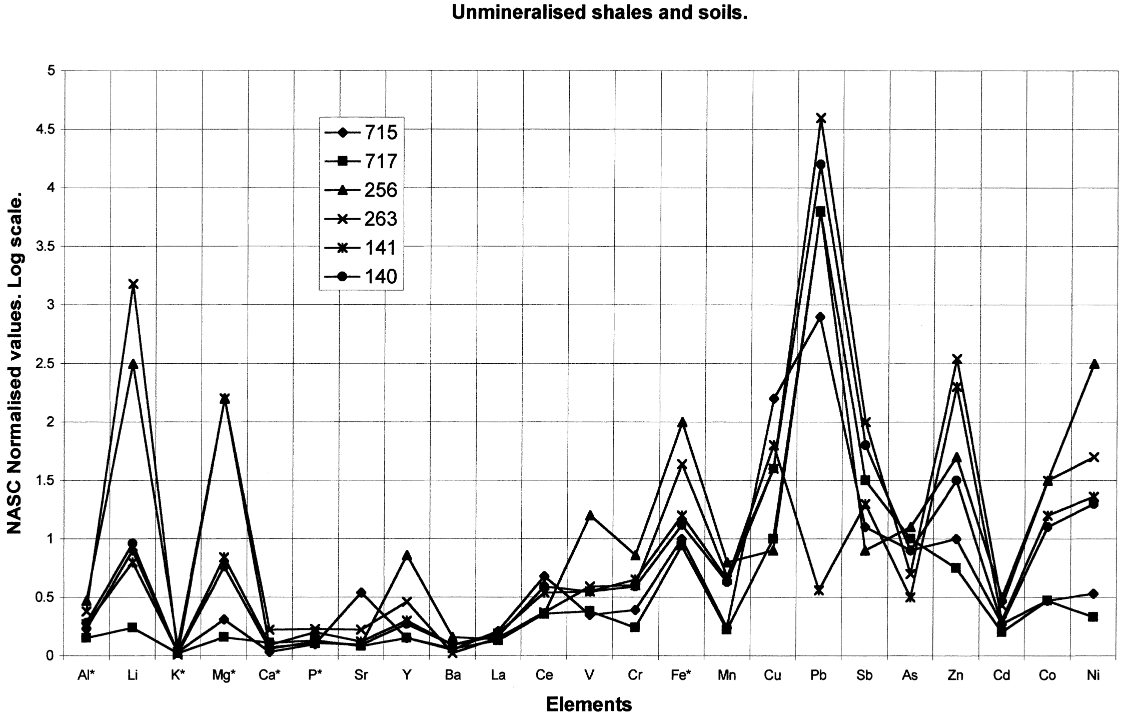
Unmineralised shales and soils.

Fig. 11. NASC normalised values for regionally common shales and slates that are not believed to be mineralised by GDC type ores. A relative enrichment in Pb, Zn and Ni is probably related to a different episode of mineralisation present in the region.

suspended material is trapped by coniferous trees and vegetation at the perimeter of the mine site. The presence of vegetation to limit the transfer of dust is described by Heath et al. (1999) with reference to deposition of Cu and Zn on open field sites adjacent to motorways and major roads.

4. Factors related to aqueous transfer of leachates to rivers from mine wastes

Having commented upon the difficulties and problems that are encountered when attempting to sample heterogeneous media such as mine wastes in a representative manner, there are also problems when sampling the aqueous environment with respect to the transfer of the wastes to uncontaminated areas. There are two important factors that need to be considered in any holistic assessment of risk with respect to mine wastes and contaminated land namely riverine and estuarine transport processes.

4.1. Riverine transport

Information related to seasonal characteristics of river flow is essential when the movement of temporary sediment stores in river–estuary systems (see Bale et al., 1985). Fig. 15 presents data from the Environment Agency — NRA Records — for river flow rate for the river Tamar for the years 1990–1998. This illustrates the very large seasonal differences in river flow. Over very short periods of time (e.g. 1 h) the river can be in flood and remove surfical sediment enriched in mine wastes. With respect to transport of mine wastes and human health risks, transfer of fine-grained material to flooded areas along the river occurs mainly in the winter, but also occasionally in the summer. In the area, local abstraction of water by a small hydroelectric plant can reduce the flow in summer months such that a danger to fish stocks can occur. Spatial and temporal factors such as those related to the presence of decaying organic matter and redox states together with the forma-

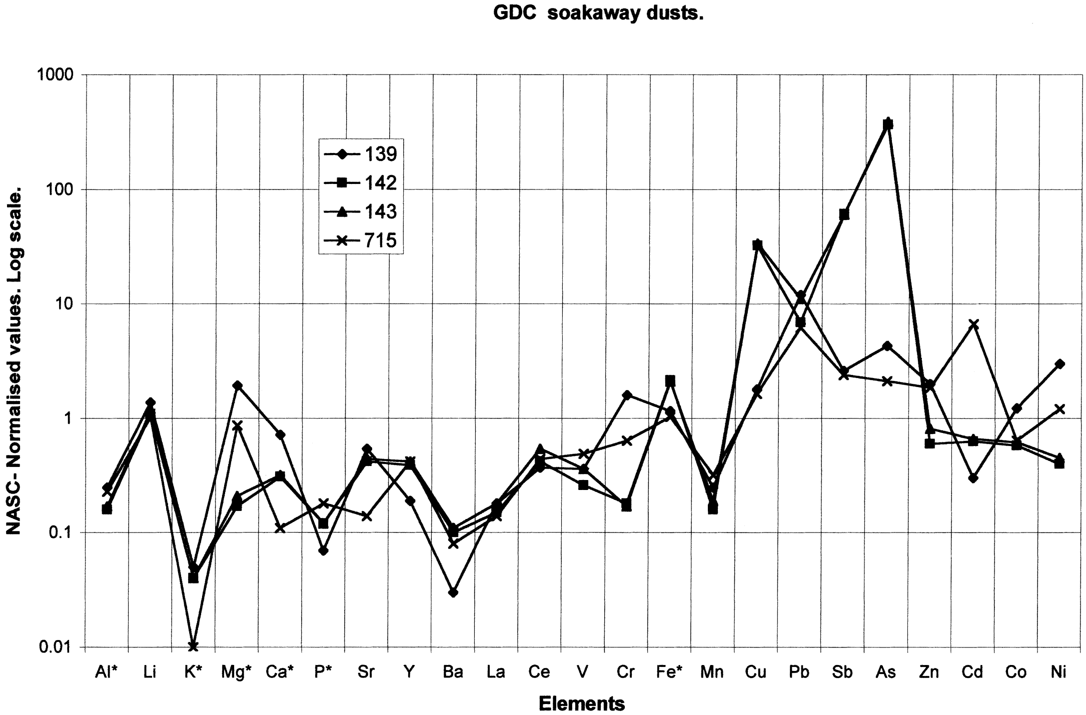

Fig. 12. NASC normalised values for samples taken at a domestic soakaway site; samples 143 and 715 are for soils taken at the site before the tipping of GDC wastes; samples 139 and 142 for the same sites after the tipping of the wastes. The site-specific contamination by GDC mine wastes is now apparent.

tion of metastable diagenetic phases can promote the rate of loss of elements present in the interstitial sediments of the Tamar when disturbed (Watson et al., 1985). Knox et al. (1984) present an excellent account of the importance of the recycling of interstitial water as a consequence of a tidally energetic system. This results in the periodic injection of arsenic and manganese from interstitial waters of the underlying sediments and an active turbidity maximum which is effective in removing manganese and As^{3+} at the freshwater/brackish water interface. The As^{3+} profiles are correlated with those of manganese with both fresh and estuarine maximum; As^{5+} profiles correlate with those of the ammonium ion. Overall, the end effect is to remove the mine waste elements from the system by a combination of water flow and redox cycling for the riverine and estuarine sediments. These processes control the rate of loss of mine wastes from the system with respect to the fraction that becomes mobilised; the bed sediments retain the larger masses of mine wastes which are transported slowly by fluvatile processes between the river banks. Zhao et al. (1999) have described the importance of the spatial variability of sediment grain size for flood plain deposits.

Fig. 16 (see Fig. 1b for sites) illustrates the seasonal significance of a single source mine waste input into the River Tamar, for the year 1993, via the Clitters addit (R12E050), which discharged the highest levels of copper, and Phillips (R12044) mine addits and the Blanchdown (R12E004) stream into the river Tamar adjacent to the GDC site. These values may be compared to those at Horsebridge (R12E002), just before the Tamar enters the mineralised region where the values are similar to those for the headwater region of the Tamar at the Tamar Lakes, N Devon which is not mineralised. Although each input is subject to variability, overall, throughout the year they tend to be similar and illustrate that large reservoir of

Table 6
NASC-normalised values for indoor dusts after the discharge of GDC mine wastes to a soakaway (analysis by ICP on leachates)

Element	Sample 546	Sample 544	Sample 545	Sample 252
Al[a]	0.06	0.02	0.02	1.17
Li	0.24	0.03	0.06	0.34
K[a]	0.032	0.08	0.03	0.52
Mg[a]	0.4	0.06	0.08	1.06
Ca[a]	0.68	0.17	0.04	0.44
P[a]	0.06	0.04	0.02	0.72
Sr	0.36	0.14	0.02	0.8
Y	0.27	0.2	0.08	0.5
Ba	0.06	0.09	0.01	0.77
La	0.16	0.05	0.14	0.23
Ce	0.31	0.04	0.12	0.78
V	0.17	0.02	0.08	0.61
Cr	0.17	0.16	0.05	0.96
Fe[a]	0.37	0.03	0.17	0.92
Mn	0.15	0.01	0.03	0.08
Cu	0.24	2.2	0.09	3.3
Pb	1.8	1.7	0.5	4.3
Sb	3.3	0.5	8.5	2.6
As	1.9	2.5	1	4.3
Zn	0.74	1.34	0.26	4.8
Cd	0.01	0.03	0.03	0.2
Co	0.27	0.09	0.12	0.54
Ni	0.29	0.16	0.09	0.78

[a] Elements measured as %. All other elements in mg/kg.

leachable elements that still remain in the mine wastes. Some drainage streams from the GDC wastes enter the Tamar close to the potable water extraction site; one in particular clearly drains the iron-rich tailings tip at the GDC and is associated with an enhancement in radium-226 and Po–Pb^{210} from the solution of uranium residues deep in the GDC and also by scavenging elements from the water.

4.2. Estuary transfer to the sea

The next stage in an appraisal of a holistic examination of the mine wastes is their transfer to the Tamar estuary and an eventual transfer to the sea. In relation to climatic/weather change and the expected increase in the level of the sea by between 20 and 90 cm over the next 100 years, redistribution of deposited mine wastes along this ria coast is probable. Off shore, in places there are considerable deposits of ore minerals that may become remobilised or redistributed. Within the estuarine system the current flood plain will be flooded and fine-grained mine wastes will be remobilised. Of particular importance will be the extent of any additional vegetation that could add a significant mass of organic matter to the estuary and hence provide redox systems for the recycling of the ore elements. The distribution of Tamar sampling sites is given in Fig. 1c. There is a need to re-evaluate possible changes in the transfer of mine wastes to the Tamar in relation to the degree and type of weathering of the source materials.

Table 7 presents data for the average concentration (mg/kg dry sediment) for total P, Fe, Mn, Zn, Cu, Pb ($n = 114$) and As for sediments collected along the Tamar at 19 stations between 1976 and 1977. Fig. 17 illustrates data obtained in May 1977 showing the influence of the turbidity maximum, near the fresh/saline water interface, in retaining the characteristic mine waste elements in the river and estuary as fine-grained sediment builds up in the summer months along the upper reaches of the river. Fig. 18 illustrates the potential role of iron in the summer months in the retention of elements compared with the rather constant value for phosphorous which is controlled by marine inputs and seasonal inputs from agricultural practices. Fig. 19, for December 1977, illustrates the removal of the turbidity maximum sediment and its element load as a consequence of high river flow in the winter months and the transfer of sediment towards the mouth of the estuary. Fig. 20 illustrates the fairly constant concentration of iron in the sediments, thus illustrating the removal of the mobile fine sediment fraction and in particular the oxidation products of redox recycling. In Figs. 17 and 19 the concentration of manganese shows the most obvious changes in concentration. Fig. 21 presents data for arsenic in sediments for August 1980 and May 1997 and illustrates a general decrease of concentration downstream with perturbations at the GDC site near the tidal limit, at the estuary/sea interface which may be related to fractionation of sediment and other local inputs

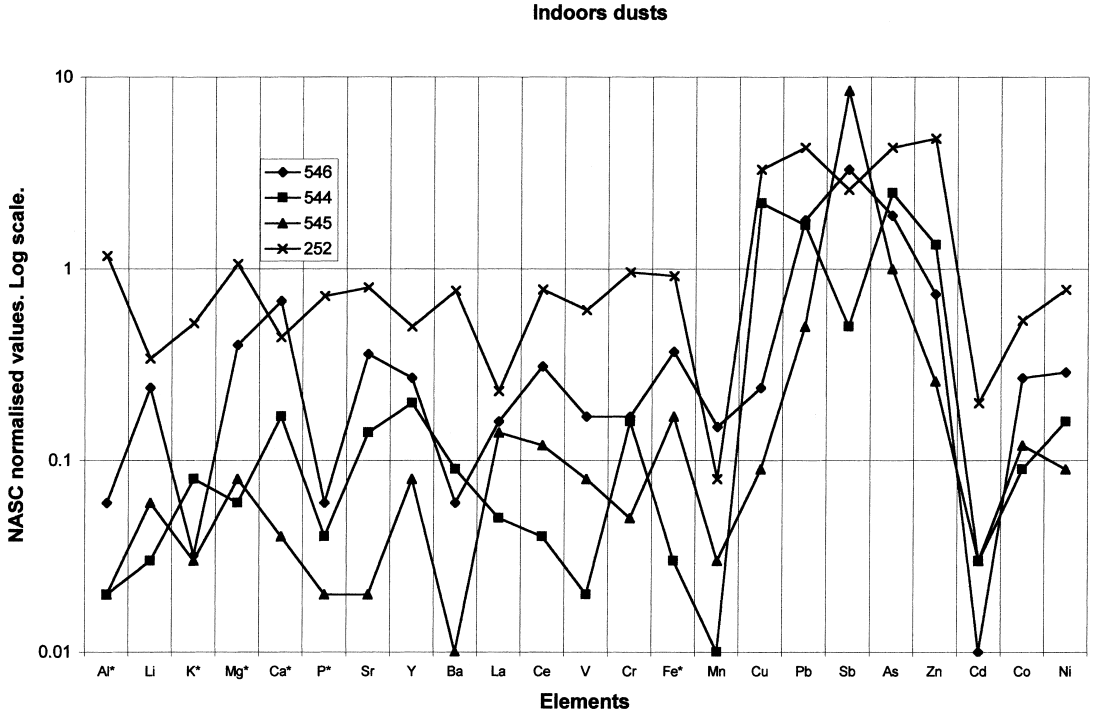

Fig. 13. The introduction of the GDC chalcophilic ore signal into domestic premises by analysis of surface dusts, as a consequence of the discharge of wastes into a soakaway. The samples illustrate an enrichment in the chalcophilic mine elements, Cu, Pb, Sb, As and Zn.

derived from the City of Plymouth, the Royal Naval Dockyard at Devonport before values become rather similar in the marine sediments. The slight enhancement in levels of elements at the extreme part of the estuary may reflect energy driven fractionation and differentiation of sediment on the basis of density of minerals or a marine input. The concentration of arsenic in the adjacent coastal sediments is greatly influenced by sand and heavy mineral content, typical values vary between 5 and 60 mg/kg.

The sunken ria coastline of S Devon is subject to progressive siltation; therefore, as the bedload of sediment increases, future discharges of mines wastes may be more available for deposition across the flood plain of the Tamar. Of particular importance is the deposition of fine silts on land that is used for growing vegetables or grazing by animals, following periods of flood. At the confluence of the Tamar and the Tavy, at Bere Ferrers, the soil over the low lying area which has been subject to historic and current flooding contains between 95 and 180 mg As/kg. Overall, the pattern of elements in the freshwater to estuarine sediments is similar, hence the mine wastes have been transported over a distance of approximately 30 km without major fractionation and differentiation, except for Mn which has been described by Ackroyd et al. (1986), and Ba which may reflect the deposition of colloidal barium sulfate by seawater. For the Tamar, there is a net export of the chalcophilic mine waste elements from the land to the sea.

In estuarine sediments, apart from seasonal redox changes, most elements are either present within the crystal lattices of minerals or absorbed on to surfaces of minerals or detritus (Morris et al., 1982). For many published data, an emphasis upon chemical composition by way of gross chemical analysis provides no information

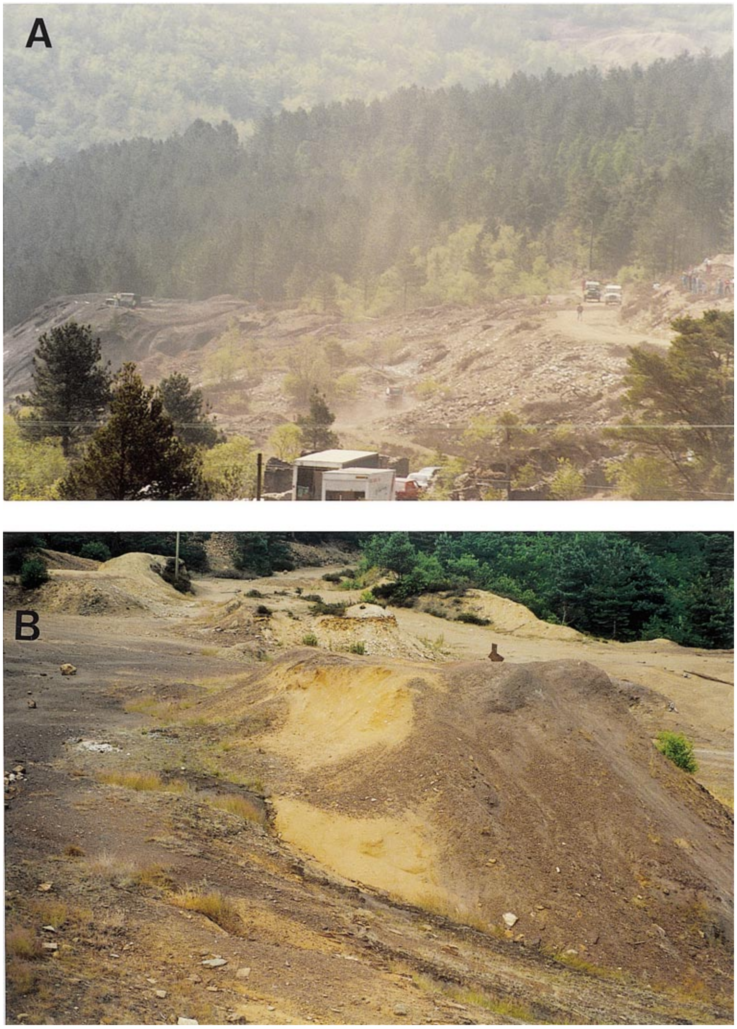

Fig. 14. (A) Illustrating the production of mine waste dusts as a consequence of using the area for four-wheel car racing. The dusts can be clearly seen to a height of at least 100 m. (B) Surface of mine wastes before vehicle disturbances.

concerning the actual sites where the elements are held. For example, in the NE Irish Sea off the coast of Cumbria, England, Hamilton (1999) describes the presence of radioactive alpha emitters, e.g. ^{210}Po, Pu, Am, derived from the discharge of authorised radioactive wastes by the British Nuclear Fuels Ltd. at Sellafield, Cumbria into nearshore waters; they are mainly restricted to the surfaces of the iron minerals magnetite and hematite. Not all of the iron minerals are labelled with radioactivity, indicating the probable uptake of radionuclides near the discharge point, transfer along the bed sediments by tidal scouring and loss of the radioactivity possibly by desorption, scouring and abrasion. Therefore, the presence and performance of one individual mineral phase may control the uptake loss of elements within an area. Unless the distribution of elements in sediments is known, there is limited use of total or sequential analyses of elements when attempting to evaluate their mobility and availability. In the Tamar, iron minerals are present, but their dis-

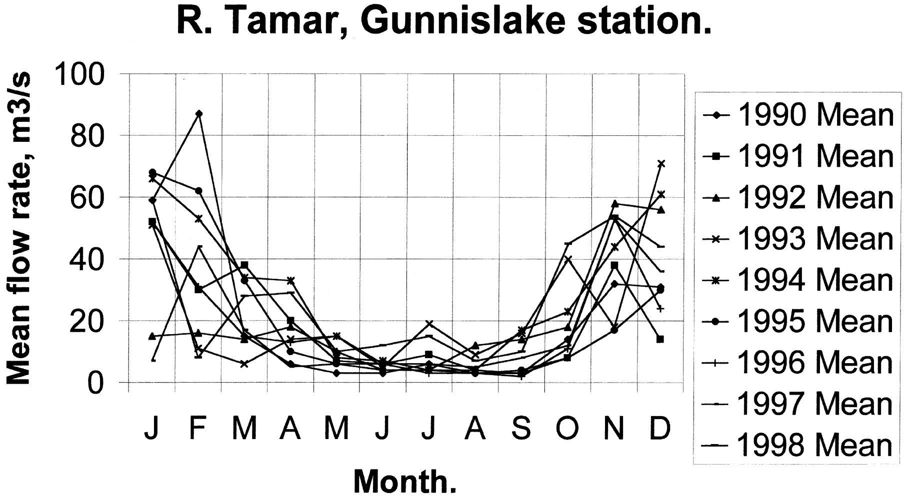

Fig. 15. Monthly flow for the river Tamar at Gunnislake, 1990–1998 illustrating seasonal variability. Data by courtesy of South West Water, Exeter, Devon.

tribution and abundance are not documented. Within the river iron flocs are abundant and have the ability to scavenge elements from the water column and also to encapsulate solid materials. With the ageing processes, such materials are not rapidly brought into solution when environmental states change compared with the very rapid exchanges that take place for adsorbed elements on iron minerals.

For all UK coastal waters, over the past 10–15 years there has been a very large decrease in the concentration of industrial wastes because of the

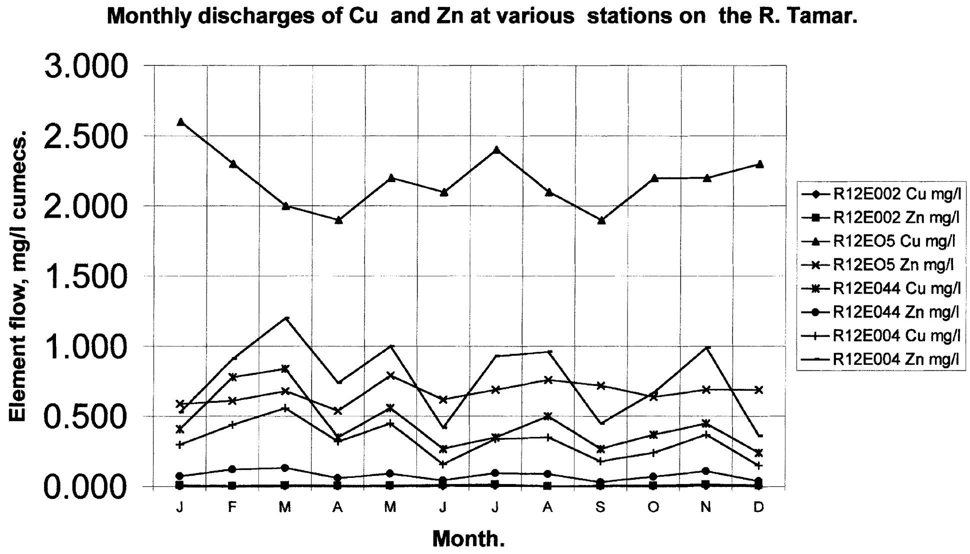

Fig. 16. An example of seasonal monthly discharges of copper and zinc to the river Tamar. Station R12E050 for the Clitters addit, Gunnislake illustrating maximum input of copper. Station R12E002, Horsebridge sampled upstream of the mineralised region. Samples RE12004 Blanchdown inlet. Sample R12E044, Philips addit. (see Fig. 1b for localities).

Table 7
Average values for the total concentration of P, Fe, Mn, Cu, Pb and As for river Tamar sediments sampled between 1976 and 1977, together with NASC values[a]

Date		P_2O_5 (%)	Fe_2O_3 (%)	Mn (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	As (mg/kg)
Sept. 1976	Average	0.38	7.65	1044	522	299	226	115
$n = 19$	S.D.	0.06	1.21	375	84	72	34	36
Feb. 1977	Average	0.39	7.78	1097	565	489	225	108
$n = 19$	S.D.	0.04	1.01	326	148	139	35	22
Sept. 1977	Average	0.37	7.47	1041	528	330	192	107
$n = 19$	S.D.	0.05	1.01	733	85	82	43	45
May. 1977	Average	0.38	7.58	947	533	326	237	121
$n = 19$	S.D.	0.04	0.86	252	67	34	33	36
Nov. 1977	Average	0.37	7.71	1086	532	376	225	111
$n = 19$	S.D.	0.05	1.5	483	105	119	36	34
Dec. 1977	Average	0.37	7.71	1086	532	376	225	111
$n = 19$	S.D.	0.05	1.5	483	105	119	36	34
Total	Average	0.39	7.52	1041	530	367	224	117
$n = 114$	S.D.	0.08	1.03	436	103	115	42	47
NASC value		0.22	3.3	850	95	45	20	28.4

[a] Analysis by XRF, crystal dispersion spectrometer.

large reduction in heavy industry. A major consequence of this is the reduction of iron to coastal waters, especially off industrial sites. While many other improvements have been made to the quality of coastal waters, it is possible that the loss of iron in future years will alter the transport pathways and rates of transfer of elements from sediments to the aqueous environment. For example,

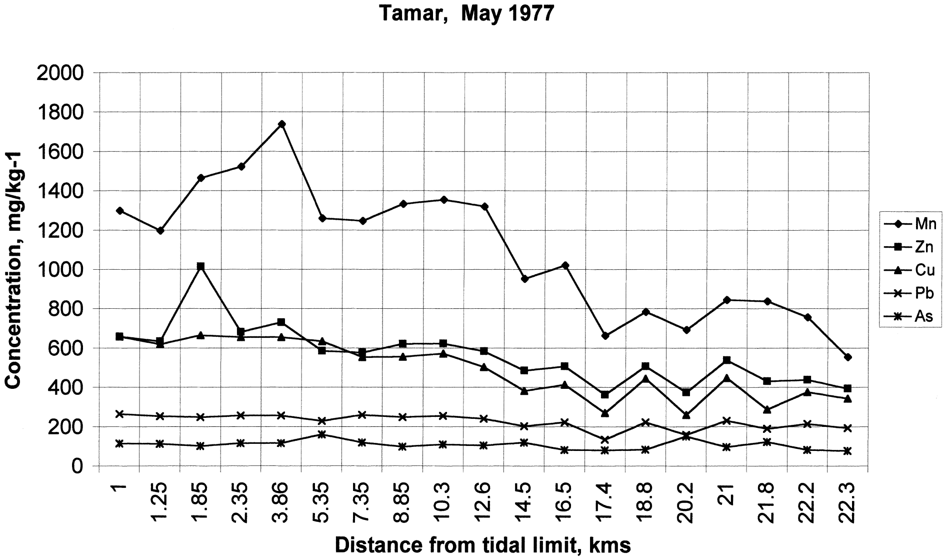

Fig. 17. River Tamar. An example of the presence of the turbidity maximum in summer months for Mn, Zn, Cu, Pb and As.

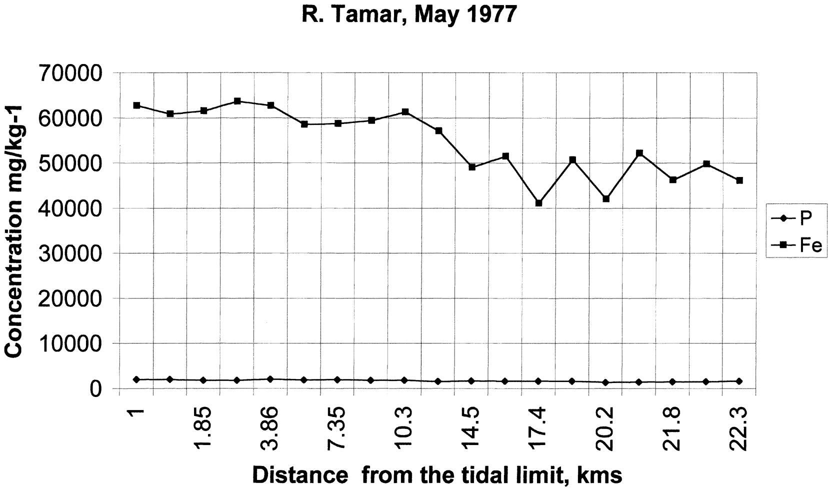

Fig. 18. River Tamar. An example of Fe associated with the turbidity maximum compared with a fairly constant concentration of P for summer months.

in the absence or a reduction in the scavenging power of iron (and manganese), the rate of dilution of contaminants and pollutants is likely to increase. At the same time, if one particular phase is present in a system to which elements and their compounds are concentrated then there will be an enrichment in elements. In relation to sustained climatic change in the region, summers are becoming drier and winters warmer and wetter; storms are more frequent and changes in the direction of the prevailing winds. All these factors result in disturbances to and changes in sites of deposition and resuspension of sediments in the region.

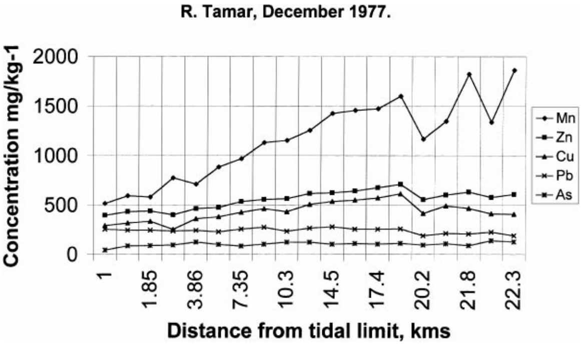

Fig. 19. River Tamar. An example of the loss of the turbidity maximum in winter months for Mn, Zn, Cu, Pb and As.

4.3. Evidence for historical deposition of mine wastes

A record for the historical deposition of elements which have been discharged to the mouth of the Tamar estuary is illustrated in Fig. 22 The original data of Clifton and Hamilton (1979) have been extended from 1975 to 1998 by coring at the same site, together with additional data for arsenic. The production of copper ore from GDC is also indicated. In the 1900s, a slight increase in levels of arsenic may reflect the post copper mining era when arsenic was recovered at the GDC and other mines. It appears to have taken approximately 25 years before the concentration of elements directly related to mining rapidly increased in the Tamar (and Tavy) sediments. Since that time, levels have been maintained, although recently, after 120 years since mining first commenced there is an indication that the levels are decreasing. The silicon (quartz, sand) record probably reflects the disturbance of the mining sites as a consequence of mining activities, especially the need to mine larger volumes of rock to extract the diminishing reserves of copper ore and the associated extension of waste rock piles at the mines. Overall, the mining activity has resulted in a significant increase in the deposition of various elements in the estuarine sediments.

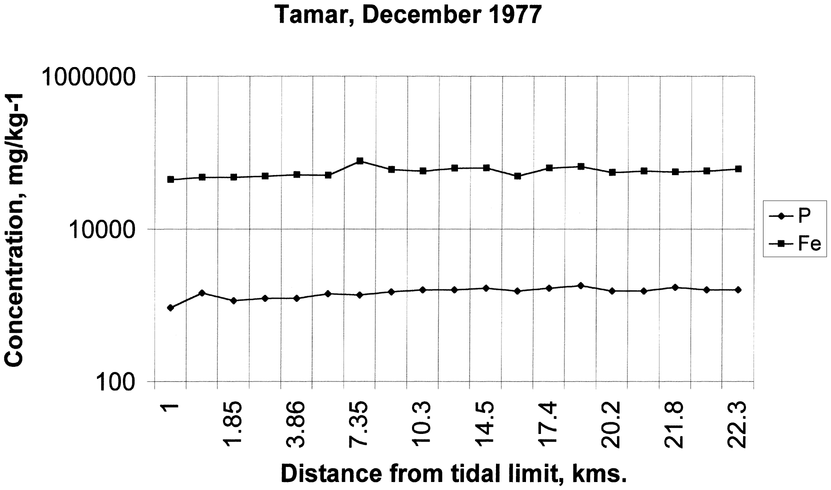

Fig. 20. River Tamar An example of Fe depleted in winter months and a fairly constant concentration of P.

Since the 1950s, there has been a significant silting up of the ria type estuary which has probably impeded the flushing out of the mine wastes from the system. If the silting continues it seems probable that with the attendant flooding, the low-lying areas along the Tamar and Tavy will become more contaminated by the mine wastes. Hudson-Edwards et al. (1996) described the historic metal mining inputs to sediment of the river Tees, England. Here, valley floor morphology, channel pattern and depositional style have strongly controlled the transfer and storage of sediment-associated elements. Historical interactions between the mine and domestic and industrial wastes at the mouth of the Tamar are not known. The core site is in close proximity to

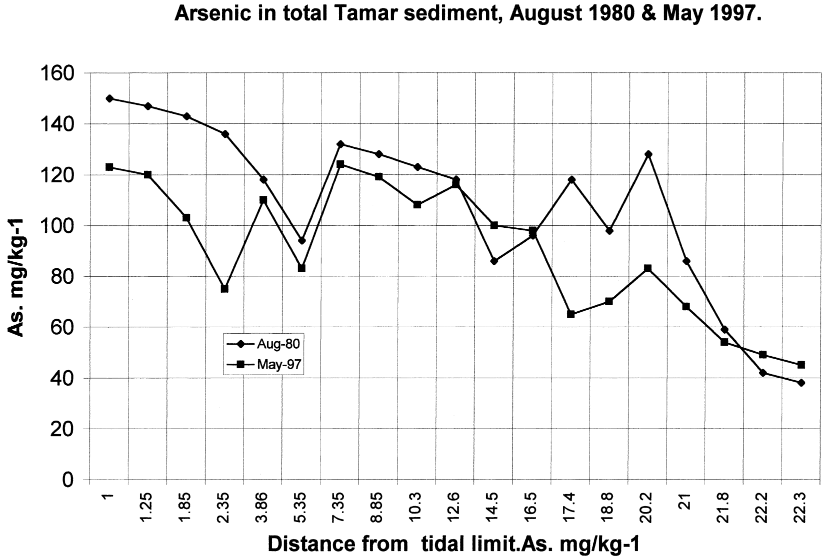

Fig. 21. Similarities between the concentration of arsenic in Tamar sediments for August 1980 and May 1997 illustrating a gradual decrease in concentrations downstream. Localised increases in concentration reflect the proximity of local inputs.

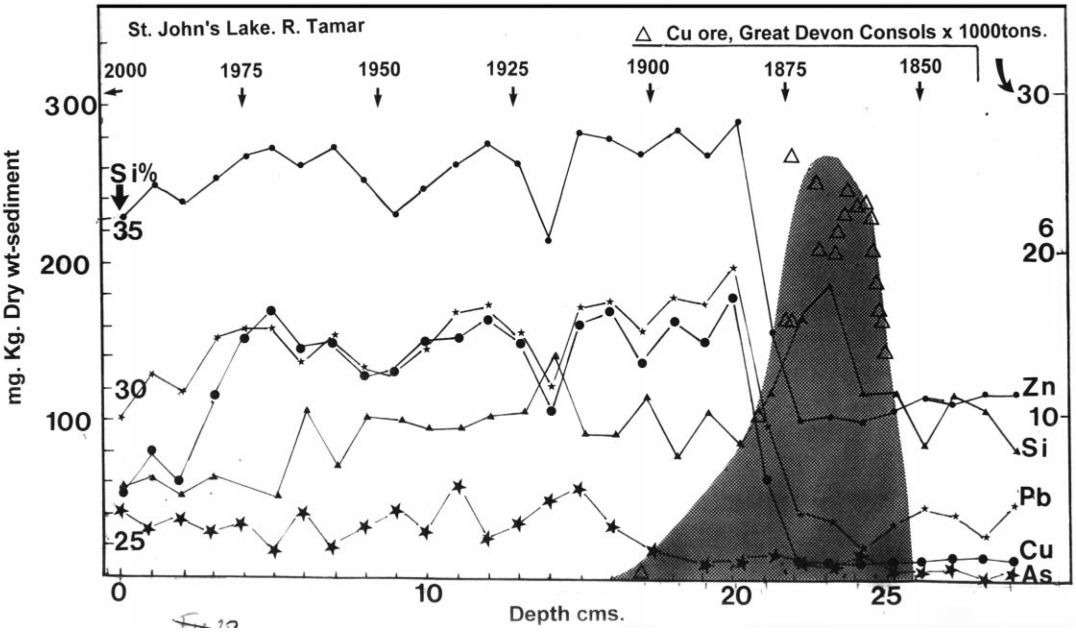

Fig. 22. Profiles for elements in a dated sediment core for the River Tamar at St. Johns Lake (see Fig. 1c) together with an indication of total tonnage of copper extracted (dark area) from the Great Devon Consols mine. The core covers the time interval of approximately 1850–2000.

several sewage discharge sites for which releases of effluent have only recently been reduced by construction of new sewage works in the Plymouth region. Overall, since the late 1800s, there has been a decline in the deposition of mine related wastes in sediment at the marine end of the estuary.

Clifton and Hamilton (1979) obtained a value of 1.14 cm/year for the sedimentation rate at St. Johns Lake. At a nearby site, but slightly downstream at a more exposed site, Readman et al. (1987) obtained a sedimentation rate of 0.8 cm/year. The profile for polyaromatic hydrocarbons (PAHs) at that site indicated pre-1930 levels of < 30 ng (g dry sediment) with an exponential increase towards the top of the core which was retrieved in 1980, where individual PAH concentrations range from 100 to 1000 ng (g dry sediment). The source of the PAHs is attributed to the burning of fossil fuels that co-vary with increases in zinc, lead and copper. The PAHs are considered to be derived from an increase in petrol- and diesel-driven vehicles, especially after 1961 when a major road bridge was opened across the mouth of the Tamar estuary.

Other sources of PAHs, such as from the burning of coal in Plymouth and the adjacent Royal Dockyards, are not considered to be significant as they have remained fairly constant except in recent years. Readman et al. (1987) did not detect any signal attributable to the burning of large amounts of coal or its transport along the Tamar in the 1900s for fuel to be used by mines for domestic and industrial purposes in Plymouth, especially at the Royal Naval Dockyards opposite to the core site. Considering the large use of coal in the area (imported mainly from S. Wales) and the numerous coal bunkering wharves in the area, it is strange that its signal in the sediments is not obvious (see Hamilton et al., 1979 for the coal in the Bristol Channel).

The concept of Chemical Time Bombs (Stigliani, 1991; Konsten et al., 1993) needs to be considered. With longer periods of drought in the summer and then heavy rain, mine wastes are being opened up to weathering processes; in the summer they generate considerable amounts of dust. Deterioration of the environment also occurs because of the excessive tourist traffic in the summer months which has already caused closure of some footpaths. If properly developed the mine sites are a major potential tourist asset. Their use for general and domestic building, albeit the land is often cheap to purchase, is likely to be uneconomic and not acceptable in relation to the potential risks that are involved.

5. Mine wastes in relation to human health

In this paper, I have focused attention upon arsenic simply because it is an element whose toxicity is accepted, globally very large numbers of people have been poisoned or have died following intake, but it still remains the most common source of acute element poisoning. In 1900, several thousand people were poisoned in the Manchester district of England following intake of beer. Sulfuric acid had been used to generate sugars in the brewing processes and had been contaminated with arsenic (1.5–3.0 mg As/l) derived from the use of Spanish pyrites as the source materials (Renolds, 1901). The predominant cause of death was cardiac failure. Another diverse source of arsenic (15–24 mg As/kg) was traced backed to sodium phosphate, a waste product in the refinement of aluminium from bauxite ore used as a stabiliser in dry milk concentrate. The incident occurred in Japan in 1955; 12 000 infants were poisoned and there were 130 fatalities. These mass poisonings, of which there have been many, provide a good clinical picture of the diversity of acute and subacute symptoms arising from exposure to high does of arsenic. Here, I do not propose to discuss the toxicity of arsenic in depth; recent clinical and environmental reviews of the subject have been provided by Fowler (1983), Lederer and Fensterheim (1983), Bates et al. (1992), Nriagu (1994), Abernathy et al. (1997).

Measurements of arsenic in samples often refers to total arsenic, for many samples arsenic is present in both organic and inorganic forms. Bright et al. (1996) have described the presence of unidentified species of arsenic in lake water and sediment pore waters. They observe the presence of methylated arsenicals and other unidentified compounds that comprise a substantial proportion of the total arsenic budget. It is the inorganic forms that are mainly toxic, especially arsine gas (Squibb and Fowler, 1983). The bioconversion processes of inorganic to organic forms is often alluded to as a detoxifying process which has its roots in organic evolution. In vascular plants, arsenic often exists in an inorganic form together with arsenosugars and some arsenite. Koch et al. (1999) note that for one study on hot springs, the speciation of the majority of the arsenic is unknown. Speciation of elements needs to be identified in order that total levels of elements can be related to toxicity for different species of the elements. Species of microorganisms utilise arsenic as a source of energy and play a role in the cycling of arsenic in the environment (Ahmann et al., 1994). In SW England most houses contain moulds and hence may be involved in the speciation of arsenic indoors; the production of arsine gas by such processes within rooms has not been demonstrated, albeit indoor levels of arsenic in dust can be high.

Clinical manifestations of arsenic poisoning are large in number, but a correct diagnosis by general practitioners is not to be expected unless prior exposure to arsenic is identified. An individual's susceptibility to acute and chronic arsenic poisoning depends upon many factors. The fatal dose from inorganic arsenic oxide is between 1 and 2.5 mg As/kg per body weight (Pershagen, 1983), but depends upon many other factors, such as diet, genetic matters and overall state of health. The detection of arsenical poisoning is best determined in 24-h urine specimens, while analysis of hair and nail clippings are also useful indicators of uptake. The International Agency for Research on Cancer (IARC, 1980) has concluded that there is sufficient evidence that arsenic is a carcinogen with respect to lungs (on the evidence from inhalation of arsenical dusts by smelter workers) and skin cancer (mainly from contaminated well water). Unfortunately for humans, there are no suitable animal analogues in order to study the carcinogenicity of arsenic. Acute and chronic effects of inorganic arsenic may involve several organs, e.g. cardiovascular system, skin abnormalities. It seems reasonable to expect that areas where arsenic is abundant should focus attention upon any involvement with human health. In the region there have been a number of small reconnaissance studies, but so far, there has not been a comprehensive evaluation of any potential hazard to health of individuals.

Johnson and Farmer (1987), in a limited study, noted that urinary levels of arsenic in Cornwall were only slightly elevated, but they observed a significant increase in inorganic arsenic and monomethylarsonic acid in urine, but only for two pre-school children. Kavanagh et al. (1998) observed elevated amounts of inorganic and organic arsenic in the 'exposed' population's urine with those of a control group. In 14 out of 17 samples from Gunnislake and 7 samples from the GDC, inorganic arsenic was detected in urine. The authors conclude that the studied population in Gunnislake and the GDC area is chronically exposed to inorganic arsenic. Furthermore, that inhalation is the prime route of entry of arsenic into the body as no other possible exposure route has been identified. Kavanagh et al. (1998) have determined concentrations of arsenic in GDC soils of up to 5.2% with a high potential for the generation of respirable or ingestible dusts. In this study 3–6% total arsenic was present in room dusts for a house near to the GDC mine. Background levels of arsenic in soils of the SW vary between approximately 15.0 and 70 mg/kg. Abrahams and Thornton (1987, 1994), Thornton (1995, 1996, Farago et al., 1998) note that 97% of the total of arsenic in dry matter intake by livestock in the mineralised areas is from ingestion of herbage. Soils from the contaminated sites in Germany contained between 102 and 232 mg As/kg in the top 50 cm of soil (Schulze et al., 1997).

In the UK, HSE adopts a value of 0.1 mg As/m^3 of air averaged over an 8-h period (HSE, 1989). For UK urban air, Hamilton (1974) obtained a value of 6.6 ng/kg air for samples collected in 1969; Peirson et al. (1973) obtained a value of 6.5 ng/kg air. Salmon et al. (1978) observed a decrease for levels of arsenic/l in air from approximately 15 ng/m^3 in 1957 to approximately 4 ng/m^3 in 1974; levels in winter were always greater than those for the summer. On a global scale, natural sources of arsenic in the air can be significant, for example Hinkley et al. (1999) calculate that emissions of arsenic from quiescently degassing volcanoes amounts to approximately 135 tons/year which may be compared to approximately 10 000 tons in total for Pb, Ag, Cd, In, Tl, Zn, As, Se, Sn, Sb, Te, Bi, Re and Au. Globally, the As/Sb ratio is approximately 27. Shotyk et al. (1996) describe an enrichment of arsenic (As/Sb ratio of approx. 3.0) and other elements in a peat core extending back to Roman times, indicating that the anthropogenic fluxes of elements have exceeded the natural fluxes for more than 2000 years.

For environmental exposure, it is generally acknowledged that the most hazardous route of entry for arsenic into the human body is via intake of drinking water. Reference levels for arsenic in blood and urine for Europe have been described by Kristiansen et al. (1997). In SW England data are sparse, but there is no evidence that this route is important. For urine, for the UK population, White and Sabbioni (1998) obtained a mean value of 3.65 μg/l (< 0.5–48.2) for the general population ($n = 180$); 4.24 (< 0.5–48.2) μg/l for individuals who had ingested seafood in recent times and a mean of 2.90 μg As/kg (range 0.5–14.6 for those who had not). For Spain, Ruiz-Navarro et al. (1998) obtained similar values of 3.40 μg/l (females, $n = 30$)and 4.12 μg/l (males, $n = 19$). Trepka et al. (1996) describe the arsenic burden among children in urine. They obtained a value of 5.1 μg/l for an area heavily contaminated by copper mining and smelters; 4.3 μg/l for a coal mining area and associated chemical plants and 4.0 μg/l for an uncontaminated control site ($n = 950$). This data indicates that there is not a major transfer of arsenic into the body of toxicological concern for heavily polluted areas; enhanced levels of arsenic in relation to consumption of fish was noted.

The distribution of arsenic (total) in whole blood ($n = 119$ for individual samples and $n =$ 2480 for a mean sample) obtained by Hamilton et al. (1994) is given in Table 8. No major differ-

Table 8
The concentration of arsenic in whole blood, SW England compared with average values for the UK (Hamilton et al., 1994)[a]

Sample	Concentration (μg/l)	n
Average values UK. Blood	2.6 ± 1.6	119
SW England		
Mining areas	2.7 ± 1.7	8
Non-mining areas	2.6 ± 1.6	8
Rural non-mining areas	1.5 ± 0.3	9
Average SW England	2.2 ± 1.9	25
UK blood master mix	2.5 ± 1.8	2480

[a] Analysis by spark source mass spectrometry.

ences were observed for the general population and that of SW England, although the study was not concerned with particularly exposed groups of the population. Two tin-miners from Cornwall had twice the levels of total arsenic in their blood, but they also consumed seafood, which in the area is particularly enriched with organic arsenic from mine wastes that are discharged in mine waters directly into the sea.

While it is possible to investigate almost all aspects of elements in the mine wastes and their effect upon biota and flora of the region, the same level of investigation is not possible for human beings for a number of reasons. In the late 1970s in SW England, considerable progress was being made with respect to mortality and morbidity of the population and livestock in the close proximity to mine wastes. This was supported by the general practitioners and the veterinary profession in the region. This no longer applies for a number of reasons, principally lack of time, costs, the implications of the research with respect to legal claims and the difficulties and costs of obtaining the required information from medical statistics. It is accepted that the main resources need to be directed towards the health of the population as a whole. Nevertheless, today it is clear that concern is also expressed for small populations and individuals who are exposed to hazardous situations. Even today there is a lack of any substantial and representative body of data to describe the concentration and distribution of arsenic in SW England in water, soils, flora, livestock and humans.

It is clear that an economic and rapid assessment of the concentration of all elements in mine wastes is no longer a problem. There are even well-equipped mobile laboratories that can produce data on site, hence the very important aspect of sampling can be achieved in an economic manner. Similarly, multi-compound organic instrumentation also permits an identification of most organic compounds in quite complex mixtures and an identification of characteristic molecular markers for specific compounds. Using these two approaches, it is possible to identify the distribution and concentration of all substances that are likely to be of concern to human health and to that of the environment. On the basis of the data, sites can be ranked with respect to degree and the expected hazard for a particular use. In a similar and economic manner, very simple, rapid and economic tests based upon immunochemical methods (see Van Emon et al., 1996) such as uptake of neutral red by lysosomes (Lowe and Pipe, 1994; Svendsen et al., 1996) as an index of state of cell health or simple physiological tests can provide information with respect to the state of health for organisms living on mine wastes or associated aqueous environments. Furthermore, biomarkers in environmental exposure assessment have an important role to play (IEH, 1996). This battery of simple and economic tests can be used today in order to rank relative toxicity of contaminated land. Alternatively, toxicity tests can be made on leachates from mine wastes using various organisms as detectors. For the 3rd Millennium, it is not unreasonable to expect the availability of similar simple, rapid and economic tests on humans in order to determine whether or not a detriment to health exists for those living near mine wastes, thereby linking source with an ultimate impact upon the health of humans and the environment. Blood, urine and faecal analyses remain the best samples in order to determine body burdens of elements, together with the post mortem samples of tissues and organs. However, other more available materials such as hair, nails and urine are usually available and such preliminary tests of cell health using buccal and nasal smears seem promising. Hartwell et al. (1983) describe relationships between arsenic in hair and distance from a zinc–copper smelter; the 1–5-year-olds had the highest tissue metal levels across all age groups. A further sample worth considering in order to detect early biochemical changes are skin moles which can be readily removed by localised freeze treatment.

In England and Wales, unless the Ministry of Health, or a member of the medical profession identifies a form of morbidity which is associated with proximity to mine wastes, then no concerns are raised beyond a precautionary need to leave mine wastes undisturbed. In SW England at least, this seems to be ignored; over recent years, public health workers have not demonstrated any ill health that is associated with arsenic (SW Devon Health Authority, 1996 — personal communication). From my own experiences it seems possible that within SW England, with a few exceptions, the required expertise does not exist in order to recognise toxic effects that may arise because of proximity to mine wastes. However, this is not surprising as the early symptoms are likely to be general and not specific with respect to classical symptoms of arsenic poisoning.

In relation to environmental pathways for arsenic and its compounds, the main route of entry of concern is intake via water. In 1820, Ayrton Paris was the first to observe a relation between arsenic and skin cancer in Cornwall. The concentration of arsenic in surface waters in Cornwall has shown soluble arsenic in specific catchments to range from 10 to 50 μg/l (Aston et al., 1975). Arsenic in drinking water rarely exceeds 10 μg/l. In the commercial treatment of water, arsenic is efficiently removed and most concern is focussed upon the untreated well-water. Throughout the world there have been a very large number of reports (see Nriagu, 1994; Abernathy et al., 1997) that illustrate severe arsenical poisoning from drinking contaminated well-water which has involved large numbers of people. There have been numerous reports of poisoning, but possibly the largest occurs in West Bengal, India, covering an area of 34 000 km^2 with a population of 30 000 000 (Das et al., 1994; Chatterjee et al., 1995; Chatterjee and Mukherjee, 1998). At least 800 000 people are drinking contaminated water and more than 175 000 show arsenical skin lesions. The maximum permissible limit for arsenic in drinking water, recommended by the WHO, is 0.05 mg/l and 2 μg/kg body weight for daily intake by ingestion. The average dissolved concentration of arsenic in the wells in West Bengal is 0.2 mg/l and the highest concentration, approximately 4 mg/l. Relations between verified cases of arsenical poisoning and intake of contaminated water vary with geography; human poisoning occurs for concentrations of > 0.2 mg/l. A factor of only 4 between the acceptable maximum and the onset of disease is very small when all the variables concerning intake are considered. Astolfi et al. (1981), from observations made in Argentina, conclude that regular drinking of water containing > 0.1 mg As/l leads to recognisable signs of intoxication and ultimately, in some cases, to skin cancer. An ecologic study of skin cancer and environmental exposure in the USA to arsenic (Wong et al., 1992) found little difference between the incidence of skin cancers for polluted and unpolluted sites. Clearly the relations between levels of arsenic, together with other elements, in potable water and the onset of disease or impaired health needs to be considered further.

Although beyond the immediate scope of this paper, additional studies have illustrated that, because of the presence of large amounts of iron and manganese in circulating ground waters of the region (W Devon), when they are precipitated upon contact with air, several potentially toxic elements are efficiently scavenged from the water and are contained within or adsorbed onto the surfaces of hydrated manganese and iron oxides. A sample of these black deposits taken from well-water at a domestic site that contained $<$ 0.01 mg As/l was associated with large amounts of Ca, Fe and Mn together with unusually high concentrations of other trace elements, for example, Ni 130, Cu 58, 772, Zn 7875, As 169, Hg 47, Pb 3140, Sn 227, Cd > 50 and Sb 57 mg/kg, respectively. Within SW England there are between 20 000 and 30 000 wells; the quality of well-water is usually high and there are no known

Table 9
The concentration (μg/l) of dissolved elements in river water, river particulates and soils (see Martin and Meybeck, 1979) and in well-water from unmineralised shale, S Devon together with NASC values (analysis by ICP-MS)

Element	River dissolved	River particulates	Soils	Well-water	*N*
Rb	1.5000	100.00	0.80	0.01900	0.01000
Li	12.0000	25.00	42.00	0.50000	0.04000
Cs	0.0035	6.00	4.00	0.01100	2.90000
Ca	13 300.0000	21 500.00	45 000.00	23.30000	0.18000
Mg	3100.0000	11 800.00	5000.00	1.90000	0.00060
Ba	60.0000	600.00	500.00	0.02400	0.00300
Sr	60.0000	150.00	250.00	0.12000	0.00200
Al	50.0000	94 000.00	71 000.00	0.00700	0.00014
La	0.0500	45.00	40.00	0.00002	0.00040
Ce	0.0800	95.00	50.00	0.00002	0.00025
Pr	0.0070	8.00	35.00	0.00001	0.01400
Nd	0.0400	35.00	35.00	0.00007	0.00180
Sm	0.0080	7.00	7.10	0.00023	0.02900
Eu	0.0001	1.20	1.50	0.00002	0.20000
Gd	0.0080	5.00	6.50	0.00006	0.00750
Tb	0.0010	1.00	0.70	0.00001	0.10000
Ho	0.0010	1.00	0.40	0.00003	0.30000
Er	0.0004	3.00	2.00	0.00005	1.25000
Tm	0.0001	0.40	0.60	0.00002	2.00000
Lu	0.0010	0.50	0.40	0.00002	0.20000
Sc	0.0040	18.00	7.00	0.00400	1.00000
Ga	0.0900	25.00	20.00	0.00170	0.01800
Ti	10.0000	5600.00	3800.00	0.00600	0.00060
Th	0.1000	14.00	9.30	0.00002	0.10000
Hf	0.0100	6.00	6.00	0.00006	0.00600
Zn	30.0000	250.00	90.00	0.21000	0.00700
Ni	0.5000	90.00	50.00	0.01300	0.02600
Cu	1.5000	100.00	4.00	0.08800	0.05900
Pb	0.1000	100.00	35.00	0.00068	0.00680
Co	0.2000	20.00	8.00	0.01100	0.05500
As	1.7000	5.00	6.00	0.00160	0.00094
Mo	0.5000	3.00	1.20	0.00092	0.00540
Sb	1.0000	2.50	1.00	0.00013	0.00013
Cd	0.0200	1.00	0.35	0.00011	0.00550
Ag	0.3000	0.07	0.05	0.00018	0.00600
V	1.0000	170.00	90.00	0.00300	0.03000
Cr	1.0000	100.00	70.00	0.00400	0.00400
U	0.2400	3.00	2.00	0.00017	0.00710

incidences of chronic poisoning caused by intake of contaminated well-water and the water is safe to drink. Nevertheless, published data on this topic is scarce. An example of the composition of well-water, normalised against NASC (Table 9), sampled at a depth of approximately 250 m in shales just to the south of the mineralised region is given in Fig. 23. Data in Table 9 are provided for dissolved elements in river water, those in particulate phases and soil compared to the well-water sample. There is no obvious sign of the characteristic ore element abundances.

For groups of individuals that are potentially at risk, for example those undergoing home renal dialysis, ion-exchange units are used to remove elements from the water supply. While the scavenging action of hydrated oxide formation is beneficial in removing elements from a supply, it is

Table 10
The concentration (minor and trace elements, mg/kg), for some elements in particulate matter removed from domestic beds, sampled in mineralised and non-mineralised regions (analysis by ICP on leachates, and for arsenic, AA after hydride generation)

Sediment type	Sample	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	Ce	La	Li	Sr	Y
Shale	v800	0.47	0.59	0.41	1.02	0.30	0.24	0.02	0.14	20	24.4	4.1	28.5	0.1
Shale	v804	0.29	0.15	0.18	0.73	0.36	0.24	< 0.01	0.07	2	3.6	< 1	27.3	0.1
Shale	v801	0.42	0.53	0.35	1.20	0.32	0.11	< 0.01	0.14	7	10.6	3.5	24.7	0.1
Shale	v802	0.20	0.37	0.22	1.06	0.42	0.45	< 0.01	0.05	4	6.4	2.5	21.6	0.1
Limestone	v803	0.63	0.17	0.20	2.25	0.42	0.39	< 0.01	0.27	7	12.2	2.4	39.1	0.1
		Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	V	Zn	Cd	Ba	As
Shale	v800	18	59	331	108	39	18	67	< 1	4	209.3	< 1	101.6	8.0
Shale	v804	2	31	87	33	16	11	24	< 1	2	147.5	< 1	14.6	< 1
Shale	v801	4	120	131	78	28	21	120	< 1	4	897.9	2.0	144.9	< 1
Shale	v802	3	23	141	32	23	11	435	< 1	1	235.5	< 1	43.3	< 1
Limestone	v803	2	29	39	20	46	7	42	< 1	2	449.3	< 1	22.0	< 1

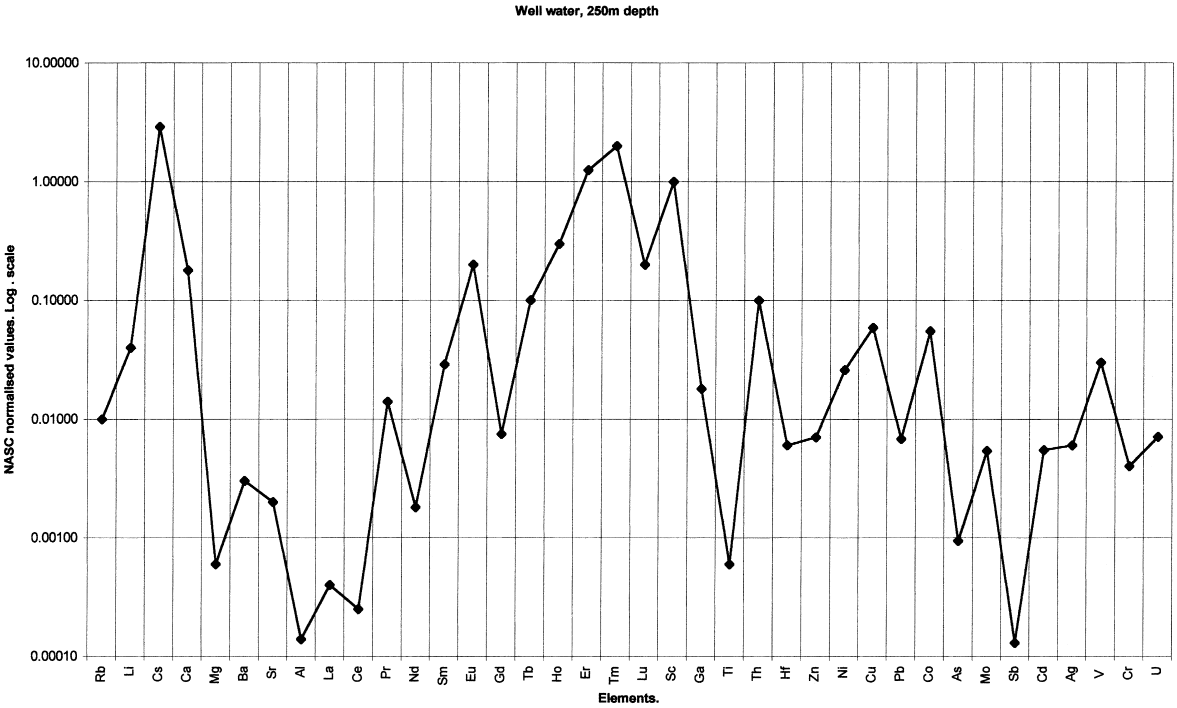

Fig. 23. NASC normalised values for well-water sampled at a depth of approximately 250 m in a shale just outside the mineralised area.

conceivable that following local periods when reducing conditions may develop, minerals will be brought into solution and so enter the supply. Two situations are under consideration: one when organic agricultural wastes penetrate to the collecting waters; and the other as a consequence of sustained changes in weather patterns, when during droughts there is greater penetration of oxygen with depth in association with episodes of high rainfall when the surface waters are rich in organic matter. Situations are likely to be site-dependent and may not be covered in general monitoring surveys in the region. Indicators of possible concern can be seen when the inner walls of kettles become black because of the presence of organic matter, especially for supplies that are at the end of a distribution system.

Globally, skin cancer and skin abnormalities are associated with exposure to arsenic following intake of contaminated drinking water; the current view prevalent in SW England is that such states relate to exposure to sunlight and not exposure to arsenic. Clough (1980) indicates a need for a more detailed epidemiological survey of melanoma and other skin cancers in Devon and Cornwall. Within SW England it seems probable that some individuals suffer from ill health because of proximity to mine wastes; data are required in order to improve knowledge and to provide firm scientific information for the risk assessment process.

It is obvious that, following exposure to many diverse elements present in the mine wastes, some are at potentially high concentrations and it can be difficult to identify which element is responsible for which type of detriment to human health, if any, with respect to many confounding factors. In risk assessment, it is pointless focussing attention upon one element to the exclusion of all others. It also has to be acknowledged that when more than one element is associated with a detriment to human health, precise clinical diagnosis is difficult, hence a need for general collective indices of harm. For occupational exposure, the

HSE (HMSO London, 1991) has provided general indicators of health for use by medical practitioners who are exposed to toxic substances, for example, impaired co-ordination, skin irritation, defatting and dermatitis, conjunctivitis, tremors, loss of appetite, nausea, diarrhoea, etc. Since 1960, I have spoken to seven miners who worked the mines of the region during the past 100 years and who all lived to be > 75 years of age; information has also been gained directly from them that had been passed on to them by their fathers and grandfathers who also worked the mines. The main cause of death was caused by underground rock falls, pneumoconiosis and pneumonia, ill health related to poor diet, having to walk considerable distances in rain and working in mines noted for high water content. The most common type of morbidity that was associated with working arsenic ores was the occurrence of various types of skin disorders manifest by colour changes and skin cancers which occurred all over the body. Similar disorders were associated with the underground pit ponies, together with foot rot, possibly reflecting long exposure to water containing dissolved elements.

For W Devon and the adjacent region, only scattered incidents are recorded where exposure to arsenic-rich mine wastes have been related to morbidity. On statistical grounds, individual cases and small numbers of individuals can be ignored and considered as chance phenomena. Because of the extremely high concentrations of arsenic and other elements in SW England, coupled with the lack of almost any evidence that their presence is a cause for concern to human health, it is essential that when incidences are reported that involve proximity to mine wastes they are considered in detail. Indeed, in keeping with approaches adopted in radiological protection, such individuals or groups should be designated as Critical Groups (Pentreath, 1980) and be subject to clinical observation. It is only by collecting data on those who are exposed that realistic levels of exposure can be identified.

So often, in instances where single or only a few individuals are concerned, little attention is paid on the grounds that the numbers concerned are statistically insignificant. In relation to mining wastes and individuals, more detailed studies may improve our understanding of pathways that result in an impairment to health. Because of the lack of any central information system in SW England through which information about possible harm to human health can be obtained, it is worthwhile noting the following:

(i) There is at least one recorded incident where a motorcyclist contracted arsenic poisoning after riding over the GDC site in rain. This is of interest with respect to the solution of arsenical sulfates in rain water and subsequent ingestion. In one house close to the GDC mine, indoor dust collected at a height of 2 m in rooms contained 3145 mg As/kg and 79 mg Sb/kg; external soil-dusts contained, for example, 60 330 mg As/kg, and 1144 mg Sb/kg, ($n = 4$, assay by neutron activation analysis). The As/Sb ratio of these dusts was between 40 and 65. A male occupant of the house contracted skin cancer after living in the house for 8 years. Despite his place of residence, the cancer was attributed to exposure to sunlight and not to the proximity to mine wastes a few metres away. In another example, a small number of individuals living on a heavily contaminated mine waste site, with arsenic levels in excess of 1000 mg/kg have a variety of skin disorders together with probable skin cancer, but exposure to arsenic has not been proven.

(ii) Analysis of hair ($n = 4$, male and female analysis by neutron activation) from the site where the GDC waste was used in a soakway, gave values of: 0.104 and 0.095 mg As/kg, and 0.022 and 0.048 mg Sb/kg, respectively, with an As/Sb ratio of approximately 5, that is quite different to the GDC wastes. Repeat analyses 2 years later gave very similar values. The As/Sb ratio may be useful in identifying source materials for the elements. There appears to be no evidence that the GDC materials had entered the body.

(iii) In relation to the Pitts Cleave site, several ground workers complained of illness after working for several months among the contaminated wastes. Symptoms common to all those affected were physical fatigue, excessive lassitude and mental tiredness, skin rashes and general irritability. One individual, who had worked on the site from December 1995 to May 1996, provided a sample of urine on 26 April 1996 which was analysed by the Public Analyst. The individual was asked to refrain from intake of any marine foods for 1 week before the sample of urine was obtained. It contained 42 μg As/l total of which only 3 μg/l was inorganic (reducible) implying a source from ingestion of seafood, albeit the individual did not consume seafood. The clinical evaluation identified that this was a normal level. In September 1996, a sample of head hair from the same individual contained 11.0 mg As/kg compared with a value of 0.46 mg/kg for head hair from the soakaway site who did consume seafoods. The individual suffered from a skin disorder, but following clinical examination by a dermatologist arsenic was not implicated. There seems to be a need to improve the clinical aspects of exposure to mine wastes, indeed a means whereby general practitioners can be made aware of possible exposure. More importantly, as is so common in these cases, the time taken for clinical evaluation is far too long and the expertise who become involved often have no experience of arsenic poisoning.

(iv) Because of the association between the human skin and skin cancers it is reasonable to consider skin as a material for monitoring exposure to arsenic, or more probably its use as an indicator of biochemical compounds that are precursors to disease. A preliminary study was initiated in order to sample bed in domestic premises. The reasoning being that if arsenic is related to the skin then it may build up in the skin and be shed together with squamous epithelial cells within the bed, then reworked and concentrated by bed bugs or in their faeces; hence, if in a closed system the concentrations of arsenic and other biomarkers would be enhanced. There is of course a need to consider the composition of bed materials, types of washing agent used to clean them and ingress of general household dust. A Vorwerk VK122 ET340 vacuum cleaner was found to be far more efficient in removing carpet dust than other commercial types of cleaner (see Hegarty et al., 1995). By removing the motorised head and installing an absolute filter cloth this was used as a probe to collect the dust. Quite surprisingly a few minutes of 'in bed' vacuuming produced 50–100 ml of dense white material; microscope examination showed that it consisted of skin cells, live and dead bed bugs, faecal debris and fibre.

Some preliminary data are given in Table 10 obtained by ICP after treatment with an oxidising acid leach media; As and Sb were determined by atomic absorption spectrometry after generation of the hydrides. Samples of bed dust, v800 and v804, were obtained from two houses in the GDC soakaway area; v801 from a village distant from the mining area; v802 from the outskirts of Plymouth and v803 from Oxford some 250 km away. The aluminium oxide levels reflect general inorganic rock dust. Allowing for the unusual source matrix of the samples and difference in the abundance of elements at each home, levels of Fe, Cr, Cu, Mn, Mo, Pb and Zn may be of use in an evaluation of elements from within beds. For sample v800 the As data probably reflect ingress of arsenic into the bed via general household dust. Indeed, this sample was taken from the private house adjacent to the soakaway site from an upper floor room where the window was open during the discharge of the GDC wastes. After cleaning of bed materials and the room a later sample of bed debris did not contain any arsenic. Das et al. (1994) obtained concentrations of arsenic in skin scale of between 0.45 and 12.78 mg/kg, but for some of the samples, secondary contamination had probably occurred. Molin and Wester (1976), using neutron activation analysis, present one of the few papers on loss of elements from normal skin by desquamation; of the 21 elements analysed Ca, P and K (2–8000 mg/kg), Br 36 mg/kg, Fe 29 mg/kg and Zn 40 mg/kg, arsenic was present at a concentration of 0.18 ± 0.16 mg/kg dry wt. amounting to a calculated daily loss by desquamation of 0.1–0.2 μg/24 h and a urinary excretion loss of 180 μg/kg per 24 h.

A further two samples of human skin scar tissue from two female donors were obtained from a leg site after surgery. Prior to sampling the cornified scar tissue had been encased in a plaster cast for 6 weeks. The surface layer of the wad of skin was removed with a quartz knife, then analysed by ICP using the acid leach method. Apart from approximately 30 mg/kg for Zn, < 1–3 mg/kg were obtained for the trace elements, and < 0.02% for the major elements as oxides. The major elements originated from the plaster cast and the Zn from an ointment. Until more is known linking exposure to various elements and excretion via skin, the use of bed debris to relate exposure from diverse and composite sources of contamination cannot proceed, but is worthy of consideration.

A problem that is associated with all biological measurements for arsenic in body fluids and tissues is the contribution which is derived from the ingestion of seafood enriched in organic arsenic compounds. For the UK population, MAFF (1998) estimates for daily intake of arsenic mg/day are a lower bound of 60 mg/day and an upper bound of 70 which is associated with fish eaters. Hamilton (1979), for the MAFF UK total diet samples, obtained a value of < 50 mg/day for samples taken from the 1966–1967 survey. MAFF (1982) obtained a value of 90 μg/day for the 1974–1978 survey. Sapunar-Postruznik et al. (1996) obtained a value of 11.7 μg/day for Croatia; Mohri et al. (1990), 182 μg/day for Japan; Gartrell et al. (1985), 61.5 μg/day for the USA; Hubert et al. (1989), 148 μg/day for The Netherlands; and Buchet et al. (1983), 12.0 μg/day for Belgium. Such a range in values is quite surprising.

(v) Arsenic and radon. The tin and copper mines of SW England contain significant levels of arsenic and for many mines, the uranium ores pitchblende and urannite occur as workable ore bodies or are disseminated throughout the ore lodes. Hodgson and Jones (1990) have described the mortality of a cohort of tin miners between 1941 and 1986 from SW England. They concluded that there was a clear relation between exposure to radon and death from lung cancer. Thirteen surface workers with known exposure to arsenic had high rates of lung and stomach cancer. The relative risk of lung cancer due to exposure to radon was not constant, but declined from approximately 10 years from the cessation of exposure. Xiang-Zhen et al. (1993) reports on tin miners exposed to radon in S. China, an adjustment for arsenic exposure reduced the effect of radon exposure to 0.2% per working level month from 0.6% for the excess relative risk. The association between lung cancer, radon and arsenic is also noted by NIH (1994) in a major study concerning radon exposure and lung cancer risks based upon evidence from underground miners. This study also indicated that 11–13% of lung cancers among single-family dwellings in the US may be attributable to an indoor exposure to radon and 9% of all lung cancer deaths. In these studies, it is assumed that arsenic is a lung carcinogen. However, these papers do not contain any substantial data for exposure to arsenic below and above ground and the correlation is based upon a statistical evaluation. In parts of SW England, small numbers of the non-occupationally exposed populations are exposed to relatively high concentrations of radon and arsenic, but quantitative data for exposure levels and effects are not available. Overall, from the historical evidence from mining communities, exposure to arsenic is linked with skin cancers which may be related to intake of arsenic via intake of water containing dissolved arsenic. Today, a further important source of intake of arsenic in SW England is via inhalation of mine dusts and for children the transfer of dust from fingers to mouth.

6. Remediation of contaminated land

With the current concern for exposure to elements from environmental sources there is a need to identify what constitutes contaminated land (Petts and Eduljee, 1994). Because of the very high costs of reclaiming contaminated sites there is a need for better guidance, in particular when assessing the significance of hazards (Beckett and Simms, 1986) Simms and Beckett (1987). At a local level there can be considerable pressure to commercially exploit contaminated land for domestic and industrial buildings. The Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRL — see HMSO London, 1994) introduced the concept of trigger concentrations for a limited number of hazardous substances and site use, for example, the threshold trigger concentration, below which the site may be considered to be uncontaminated for that end use, and a trigger concentration above which

Table 11
UK adopted trigger concentrations for some elements in UK soils; threshold and action levels for grazing livestock and crop growth (HMSO London, 1994; RIVM, 1990)

Element	Trigger concentrations — UK soils		Pastures, grazing land		Action crop growth
	Domestic garden, allotments	Parks, playing fields, open space	Threshold	Action grazing livestock	
Arsenic	10	40	50	500	1000
Boron	3	3			
Cadmium	3	15	3	30	50
Chromium	600	1000			
Copper	130	130	250	500	
Mercury	1	20			
Nickel	70	70			
Lead	500	2000	300	1000	
Zinc	300	300	1000	3000	100

some form of remedial action is essential. The ICRL values (mg/kg) are given in Table 11 for a few elements. The action trigger concentrations with respect to human exposure for arsenic and other elements have not been identified. In Belgium, remediation of soils is required on a short-term basis when a value of 300 mg As/kg of dry soil is exceeded. If the site is landfilled and solidified, the arsenic concentration of the leachate must be lower than 1 mg/l.

In England and Wales, there are a number of organisations responsible for contaminated land. Impact upon the occupationally exposed rests with the Health and Safety Executive (HSE); upon human health, the Department of Health; with respect to clinical studies and impacts on human health in relation to action to cleaning up contaminated sites with the Local Authorities. Overall, the adopted policies require remedial action when the contamination poses unacceptable actual or potential risks to health or the environment, taking into account any costs involved and within the framework of 'suitable for use' approach. This philosophy can be traced back to the Public Health Act of 1936. In the 1990 Environmental Protection Act, the critical statement with

Table 12
England and Wales, Health and Safety Executive guidelines for the classification of contaminated soils[a] (HMSO, 1991)

Element	Uncontaminated soils	Slight contamination	Contaminated	Heavy contamination	Unusually heavy contamination
Sb	0–30	30–50	50–100	100–500	500
As	0–30	30–50	50–100	100–500	500
Cd	0–1	30–50	50–100		50
Cr	0–100	100–200	200–500	500–2500	2500
Cu (available)	0–100	100–200	200–500	500–2500	2500
Pb	0–200	200–500	500–1000	1000–5000	5000
Hg	0–1				50
Ni (available)	0–20	20–50	50–200	200–1000	1000
Zinc (available)	0–250	250–500	500–1000	1000–5000	5000
Ba	0–500	500–1000	1000–2000	2000–1.0%	1.00%
Mn	0–500	500–1000	1000–2000	2000–1.0%	1.00%
V	0–100	100–200	200–500	500–2500	2500
Mg	0–500	500–1000	1000–2000	2000–1.0%	1.00%

[a] Units, mg/kg.

respect to harm is the definition of 'statutory nuisances' — the item of particular interest to this paper is section 79 (a) ' any premises in such a state as to be prejudicial to health or a nuisance'; 'premises' is defined so as to include land; 'prejudicial to health' means injurious, or likely to cause injury, to health. 'It is not necessary to show that the activity is prejudicial to health in order for it not to constitute a statutory nuisance'. It is the duty of every local authority to cause its area to be inspected from time to time to detect any statutory nuisances. Where a local authority is satisfied that a statutory nuisance exists, or is likely to recur, in the area of the authority, the local authority shall serve an abatement notice. The reader should consult documents (DOE, 1994, 1996a,b) concerning new proposals for draft regulations and regulatory assessments with respect to contaminated land that are expected to be implemented in the year 2000. This document, with reference to significant harm being caused, requires the local authority to be satisfied, on the balance of probabilities and in the light of all the relevant information and an appropriate scientific assessment, that harm is being caused by reasons of substances in, on or under the land. At present, guideline values that relate to levels or concentrations of particular pollutants in soil that pose a significant harm to human health are being developed. With respect to the occupationally exposed workers, guidelines for the development of contaminated land have been identified by HSE (HMSO London, 1991) as shown in Table 12. Guidance on statutory requirements concerning how they should operate in theory and practice is likely to be a source of uncertainty and dispute.

Ferguson and Denner (1993) discuss the development of guidelines or trigger values for the assessment of risks from contaminants in soil. Such values need to be based upon realistic estimates of risk for acute and chronic exposure. For many situations, there are considerable uncertainties and sufficient scientific information is not available, especially for multi-element exposure. In the UK, at present, a soil loading of 10 mg As/kg (Table 9) is identified as one below which a site may be considered as uncontaminated. For occupational exposure the HSE (HMSO London, 1991) adopts a value of 500 mg As/kg as unusually heavily contaminated which requires special precautions and is considered to be highly contaminated and often there is a need to remove the contaminated soil at considerable expense. A value of 100–500 mg As/kg is considered to represent heavy contamination. Typical values for uncontaminated soils are between 0 and 30 mg/kg which seems reasonable.

In the light of all the prevailing uncertainties and the lack of identified levels when special precautions are required when considering human health and contaminated land, here I consider the HSE values as they are backed up by a consideration of a detriment to human health, albeit at the workplace. Chappell et al. (1997) also note a need to improve the risk assessment for inorganic arsenic.

In 1994, redevelopment of a railway station, built in the mid-1980s at Gunnislake, E. Cornwall on mine wastes, resulted in their controlled transfer in covered lorries to the United Mines waste facility in Cornwall for burial. (Caradon District Council — personal communication). The site contained As (403–534 mg/kg), Cu (139–283 mg/kg), Zn (29–129 mg/kg), cadmium (1.5–10.5 mg/kg), Mn (217–442 mg/kg) and Fe (21 000–27 900 mg/kg). A return of mine wastes back to old mine sites is an attractive option provided that the elements do not enter the aqueous environment through leaching.

At another site in Tavistock, mildly contaminated land to be used for domestic buildings is reported to have been removed and transported to a repository in Bedfordshire some 400 km away to an area that is associated with extremely low concentrations of As, Cu, Pb, etc. The cost and advisability of such a drastic procedure is uneconomic and unnecessary. Dutre et al. (1988) describe the remediation of a site contaminated with arsenic.

Casual inspection of the region indicates the presence of mine wastes in close proximity to domestic dwellings or where they are even built on the wastes that contain at least 1000 mg/kg of arsenic and other elements. Against this scenario there is the example of the creation of considerable amounts of hazardous dusts at the GDC through commercial and recreational activities and the uncontrolled dispersion of the wastes in the region. It is clear that rationalisation in dealing with these mine wastes is long overdue. The European Environment Agency (EC Europe's Environment, 1998) estimates that in the UK there are approximately 100 000 contaminated sites of which approximately 10 000 may have been identified. The estimated cost of clean up is between 13 000–39 000 million ECU.

Before changes are made to legislation it is essential to determine the extent, if any, of any harm that may have been caused so far. Any proposed trigger or action levels should be realistic. For example, if a health related value of 500 mg As/kg soil is used today, a safe level has to be considerably less. In considering the natural abundance of arsenic and its low transfer to the food chain, a value of 50 mg As/kg soil is reasonable as an upper limit, provided that the use of the site is considered. For a country such as Belgium which is heavily industrialised, Tack et al. (1997) obtained a mean value of 10.5 mg As/kg in soils from Flanders with a range of between 0.82 and 95 mg As/kg. In considering all aspects of contaminated land, the mine wastes that are discussed in this paper require particular attention in order that unnecessary expense is not involved. The current and past practices that have been in existence for a considerable time leave much to be desired. Levels of exposure seem far too high to be acceptable for any purpose, yet there is no substantial body of evidence to indicate that they have resulted in a detriment to human health. This may be an illusion, simply because it has not been sought using the most appropriate tests. If a detriment to health has occurred within the region, then its signal is buried in the general health statistics of the region and is not recognised. If the permissible level of exposure is increased for any element or compound to an unrealistic value then in the future, a failure to identify a detriment to health will be of little value.

7. Conclusions

In relation to the present regulations there is a need to improve risk assessment for arsenic. Particular attention needs to be paid to low level chronic intake of arsenic especially from intake of water and especially for children following ingestion of solid matter from the hands. SW England contains the appropriate environments for such studies. Arsenical pathways through inhalation of fine-grained dusts, together with associated dissolved forms of arsenic compounds, needs to be evaluated in a comprehensive manner.

There is a need to reassess permissible levels of arsenic in soils on the basis of geochemical knowledge and the health of flora, fauna and human beings. An attempt should be made to undertake epidemiological surveys of SW England for arsenic and other elements common to the region. First, there is the need to assess what elements are present, where they are, what are the concentrations and how can the overall integrated effects be determined in an economic manner. Once this is known then suitable populations can be identified for epidemiological surveys.

At present and as described above, the chain of control from government to local authorities needs to be re-examined with respect to available expertise and conflicting interests in the use of contaminated land. Better understanding between scientists, local authorities and the medical profession are urgently needed. So far, most studies have been of very limited extent, lack a holistic approach and are poorly backed up with medical expertise.

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