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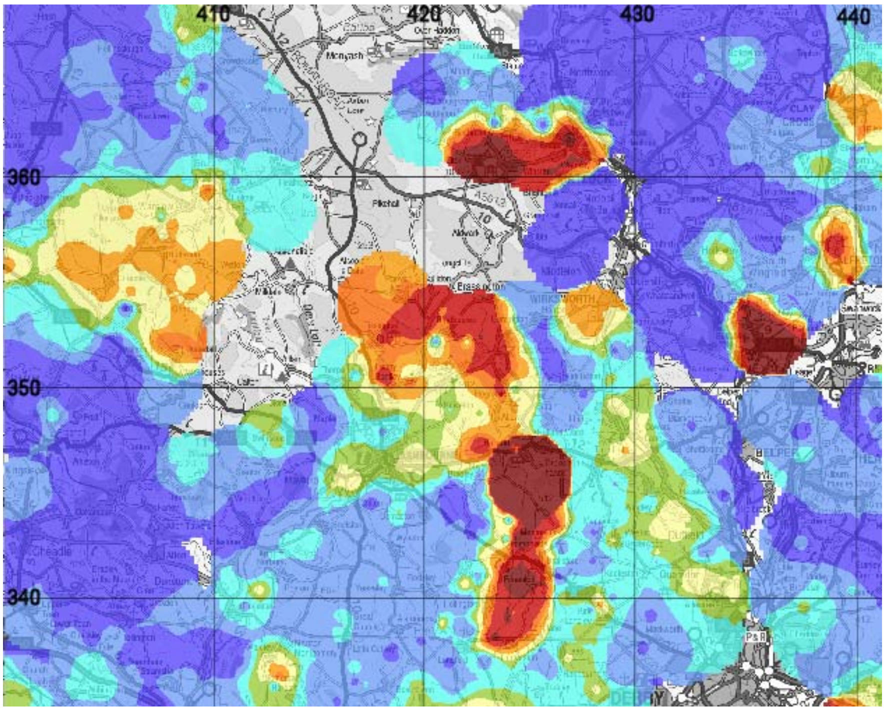
Evidence for repository-relevant element dispersion from the geosphere into the biosphere.

Chemical and Biological Hazards programme

Commissioned Report CR/07/057N

Project Report for United Kingdom Nirex Limited



BRITISH GEOLOGICAL SURVEY

CHEMICAL AND BIOLOGICAL HAZARDS PROGRAMME

COMMISSIONED REPORT CR/07/057N

Evidence for repository-relevant element dispersion from the geosphere into the biosphere.

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Natural analogues, dispersion, repository, geosphere.

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Molybdenum in stream water, south Derbyshire, UK.

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Evidence for repository-relevant element dispersion from the geosphere into the biosphere.

1. Abstract

In an attempt to establish element dispersion patterns in the environment, and to improve our understanding of their pathways and mechanisms of transfer of elements from the geosphere to the biosphere, natural geochemical anomalies identified by regional geochemical surveys have been examined. The aim was to apply the principal of 'natural analogues', i.e. using the behaviour of naturally-occurring elements and isotopes to predict by extrapolation the behaviour of radiogenic elements and isotopes, related to a possible source in a generic nuclear waste repository.

The extensive geochemical data holdings of the British Geological Survey, mostly those derived from the long-running Geochemical Baseline Survey of the Environment (G-BASE) and Mineral Reconnaissance Programme (MRP) projects in the UK were used as the principal resources.

Although this study was of necessity relatively brief (the topic is potentially far-reaching), a wide range of elements was examined at a number of different mineralisation centres, mining sites and other anthropogenically contaminated sites to address the widest possible range of environmental conditions. Although most elements were found to follow conventional predictions of mobility and dispersion, several exceptions were found.

2. Executive Summary

Although this has only been a brief and limited study, it has covered a wide range of elements in a variety of natural and anthropogenically modified anomalous systems. For the most part, element behaviour has followed established norms of theoretical resistate or mobile character, though there are important exceptions. The concept of an 'insoluble' element may no longer be entirely justifiable, thanks to improvements in analytical methods, but elements such as Nb (and, to a lesser extent, Zr) must still be regarded as essentially immobile under normal surface conditions. In contrast, chloride (irrespective of isotope) is highly mobile and essentially conservative, i.e. non-interacting. Variables such as Eh, pH, organic matter and counter-ions are the dominant controls on element solubility, complexation and mobility. A few elements, such as Sr, are much more mobile than their published thermodynamic Eh-pH diagrams might suggest, whereas others, such as Rb and Cs, are less so. Copper can be mobile in alkali solution if levels of Cl^- and organic matter are high, as in coal waste effluents, whereas it is normally immobilised by near-neutral pH levels in natural anomalies. The mobility of molybdenum is likely to be higher in alkaline waters than in acid ones, and radiogenic technetium will probably behave in a similar manner. Regional data for some elements such as Se, Br and I have only recently become available and further improvements in analytical techniques are awaited to confirm the mobility of these elements at low natural concentration levels in solution.

It is important to note that there are limitations to this report. The main limitation is the use of available data with a sampling regime which was not designed with the study of element dispersion as its main aim. If new studies were undertaken to investigate element dispersion specifically, these would require a specialised sampling system which would aim to follow the dispersion of an element from a well-defined bedrock source into soils, groundwater, and surface drainage, following streams at a suitably high sampling rate and analysing sediments and waters to establish the rate of concentration tail-off, and changes in substrate host and element speciation over an area sufficiently large for background conditions to be re-established at its boundaries. This may be an idealised situation, and may not be easily attainable, but should be a 'gold standard' to be aimed for.

The transfer of elements from the geosphere to the biosphere is clearly dependent primrily on their mobility, and this has been examined and assessed carefully in this study. The actual mechanisms of bioavailability and element uptake into biota are highly complex. Many academic studies have compared element concentrations in plants and soil organisms and in their host soils, and some empirical data exists on this topic in BGS, but on a very local, not a regional, scale. However, a thorough examination of these processes would require a much more focused and multidisciplinary project than was possible within this desk-study.

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3. Introduction

United Kingdom Nirex Limited (Nirex) has developed a phased geological repository concept (PGRC – Nirex, 2003) in which intermediate level (ILW) and certain long-lived low-level wastes (LLW) would be placed in vaults deep underground (~600m) excavated in a low permeability rock (Nirex, 2003). Physical containment of radioactive wastes would generally be achieved by cementing the wastes into (mostly) stainless steel containers. These would be placed in vaults that would be backfilled with a cement-based material (Nirex Reference Vault Backfill (NRVB) – Nirex, 1997), after all the waste has been emplaced and at a time determined by future generations. Over time, groundwater flowing into the repository would react with the NRVB to create a highly alkaline environment and corrosion of steels and other items in the wastes would result in a low Eh. These conditions are beneficial in reducing the solubility of many key radioactive materials (Chambers et al., 2003). In addition to these physical and chemical barriers, the rock mass would act to isolate the waste and form a third barrier to radionuclide migration.

Ultimately radionuclides and other potentially toxic or hazardous substances may dissolve in groundwater and enter the rock mass (or geosphere) adjacent to the repository and migrate in the direction of groundwater movement. A number of processes including sorption, diffusion, co-precipitation and dilution may reduce the concentration of the more reactive dissolved species. Ultimately, some dissolved species may enter the subsoils / soils, and water bodies that make up the biosphere. They may ultimately pose a risk to man through external exposure and by the consumption of contaminated animal and plant materials, drinking water and soil or inhalation of suspended particulates and gaseous species.

Modelling the fate of contaminants in the ‘biosphere’ is complex because of the large number of processes involved and the dynamic nature of the surface environment. Nirex risk assessment calculations typically extend to one million years in to the future and so have to consider the effects of changes in climate, geomorphology, soil types, biodiversity, as well as human responses to, and constraints imposed on, these factors in terms of agriculture and hunting etc. In practice, this is achieved by defining a number of scenarios and calculating for each the expected transfer of contaminants from the geosphere, through the biosphere to an exposed group of humans.

The processes involved in the transfer of dissolved species from the geosphere into the biosphere and subsequent dispersal are not unique to repository-derived radionuclides, but apply also to stable elements and radionuclides naturally present in the environment. The resulting geochemical dispersal patterns or ‘geochemical anomalies’ in soils and water bodies are used as an exploration tool to locate buried ore bodies in the underlying geosphere. In the current context, it was thought to be useful to capture the experience gained in geochemical exploration to better inform the likely dispersal patterns of radioelements as they migrate to and through various types of soil profiles under differing climate regimes. A particular aspect of interest is the competition between upward migration to the rooting zone of plants and sub-horizontal transport to the banks and bed of stream channels, and subsequent discharges to freshwaters. Detailed investigation of this topic is outside the scope of this study, but could form the basis of future work.

Specific areas of interest within the limitations of this study include the geometry and size of the surface geochemical anomaly in relation to the location, size, geometry, flux or concentration leaving the source of the anomaly; and the extent to which the above is influenced by geology, hydrogeology, geomorphology and soil type.

3.1 An outline of the aims of this project

This project examined data for existing geochemical anomalies observed in regional and smaller-scale geochemical surveys carried out by the British Geological Survey (BGS) and others in order to elucidate and evaluate the mobility and dispersion behaviour of a range of elements related to those that may be present in such a geological depository. This report therefore presents information to illustrate the potential behaviour of radionuclides in the geosphere, and their possible subsequent transfer to the biosphere, by comparison with the behaviour of naturally-occuring analogue elements. To be fully comprehensive, a wide range of stable and long-lived radioisotopes of both common and rare elements would be involved, and studies would include multiple sample media, including plants and possibly animal matter. Of necessity, this current project includes only a limited review of a potentially much wider field of study. The principal use of this report should be the identification of geochemical anomalies suitable for further, more detailed, investigation.

3.2 Environmental chemistry and geochemistry – a brief overview.

Although the chemistry of the elements likely to occur in long-lived low-level and intermediate-level nuclear waste is well known and their theoretical thermodynamic behaviour is well characterised (even for the micro-trace transuranic elements), 'real-world' environmental chemistry and geochemistry is often far more complex than conventional laboratory chemistry would suggest. For example, we are dealing with complex mixtures of interacting chemical species and conditions, plus extra complications due to sorption onto substrates such as clay minerals and organic residues, and co-precipitation by hydrous oxides of iron and manganese. Colloidal suspensions of these substrates, especially those involving humic and fulvic acids, may also be more important carriers of elements than are true solutions. Equilibrium thermodynamic calculations and Eh-pH phase diagrams based on simple chemical species mixtures, such as those presented in Brookins (1988) and Choppin *et al* (2002) consequently rarely give more than a first-order estimate of real-world geochemical behaviour. The situation is similar for solution equilibria and reaction kinetics, where theoretical considerations and geochemical models are often confounded by the complexity of natural systems. The examination of element geochemistry in the 'real world', by using real environmental geochemistry data, is therefore a major strength of this study.

3.3 Choice of elements to study

The elements and isotopes of greatest interest are those present in substantial amounts in a repository containing intermediate and long-lived low-level nuclear wastes. These may contain a wide range of elements, depending on the source and previous treatment applied to the waste, and will include the longer-lived fission products, natural and artificial actinides and their decay-series 'daughter' elements (e.g. Ra), heavy metals such as Cu, Cr and V stripped from stainless-steel process vessels and metals such as Zr and Mg used in reactor fuel rods. Many, indeed, are relatively common elements in the wider natural environment. The fission products from uranium-based reactors typically have a bimodal mass distribution with mass-centres at Tc and La. These elements therefore fall into two ranges, mainly Sr to Cd and Te to Sm (Fig. 1) and radioisotopes of all of these elements may be present.

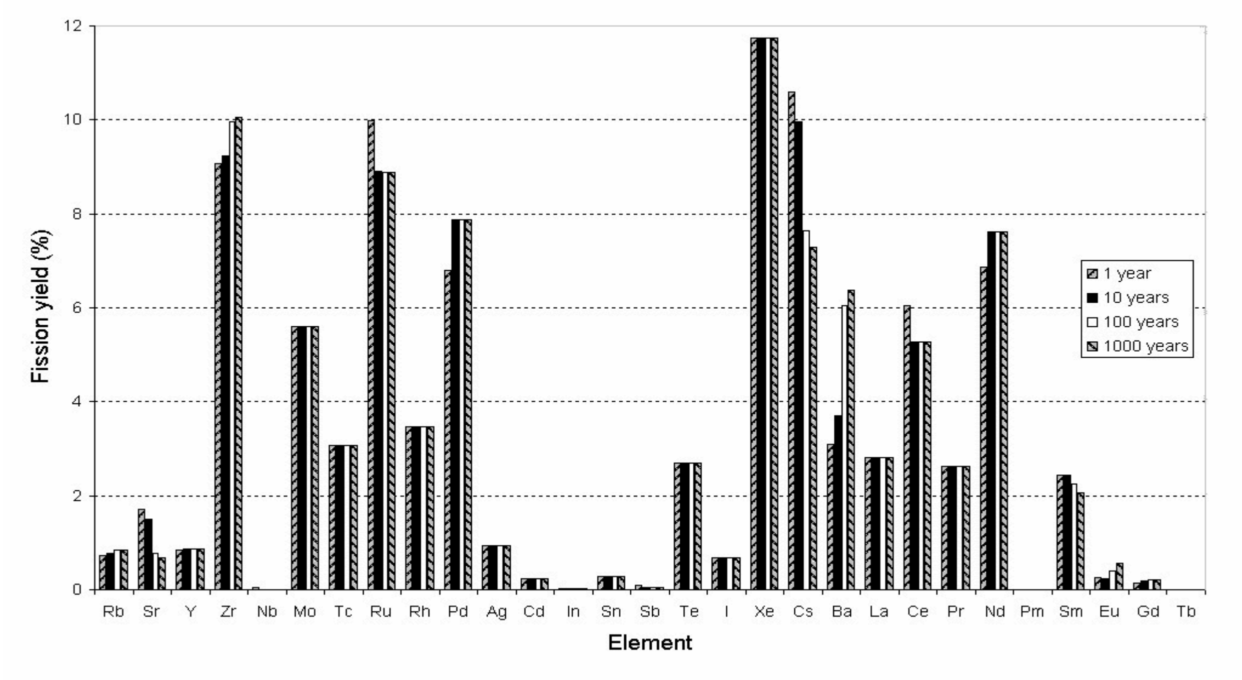


Figure 1. Typical fission product yields (as percent by mass) with different 'cooling times' after the fuel has been used.

The elements considered most useful for this study therefore include:

a). Naturally-occurring radioactive elements – Th, U

b). Natural analogues for such radiogenic nuclides as the actinides.. These include Y and lanthanides such as La, Ce and Nd as analogues of the actinides, including the transuranic elements. However, it must be remembered that many actinides have a more diverse and complex redox chemistry than the lanthanides, so there are limits to the extent to which lanthanide behaviour can be extrapolated. Radon is of considerable interest, but much data on ^{222}Rn migration is available from other sources so there is little need to use noble gases such as Kr and Xe as Rn analogues, and although the dispersion of radionuclides of Kr and Xe may be of interest in gas dispersion studies, no regional geochemical data are available.

c). Naturally occurring stable elements as analogues of radionuclides e.g. ^{36}Cl, ^{79}Se, ^{126}Sn, ^{129}I and ^{135}Cs, plus any other activation and fission products which may be present such as Tc. These include Rb, Sr, Ag, Cd, Sb, Re and Te, although Te data are scarce and generally poor. The platinum-group elements Ru, Rh and Pd are also of interest but they are hardly ever determined in non-specialist geochemical surveys on account of their very low natural abundances. Some data from studies of Pt deposits may be available, but this is very limited and is consequently not included in this report. Rhenium, suggested as a possible analogue for Tc, is of such a low natural abundance that it is hardly ever determined in geochemical surveys. There may now even be more contaminant Tc in the environment than natural Re. Technetium geochemistry differs strongly from its other group co-member manganese in that the most stable Tc species is the soluble pertechnate anionic TcO_4^- which, unlike permanganate, MnO_4^-, is not strongly oxidising. Rhenium is more chemically similar in behaviour to molybdenum than to manganese. Consequently molybdate, MoO_4^{2-}, is a more reliable analogue species for Tc in spite of its different ionic charge, so Mo is a particular element of interest, as it is also an important fission product.

d). Analogues of the longer-lived daughter products of the various natural and radiogenic element decay series (See Fig. 2). For example, barium is a close analogue of radium, Ra, providing the pH remains above 2.6 (Brookins, 1988) and is much more abundant (and may therefore modify the behaviour of Ra). Lead and Bi may also be produced and natural occurrences of these are examined, but in a repository, much larger amounts of Pb will be present as shielding materials than would be produced from radioactive decay series. The environmental behaviour of natural Pb is well characterised, so this is not really a major point of interest. However, ^{210}Pb is a decay product of ^{226}Ra and although short-lived (half-life 22.3 years) it is more controlled by Ra and Rn movements.

e). Other elements such as Cr, V, Ti etc. present as special steels and other alloys, with copper and lead from canisters and shielding. Also resistate elements such as Zr, used in cladding and traditionally seen as geochemically immobile. New data for the behaviour of these elements in surface waters is now available, due to significant recent improvements in analytical methods such as Inductively-coupled plasma mass spectrometry, ICP-MS.

The complete list of elements examined in this report is: (in alphabetical order). Ag, Ba, Bi, Cd, Ce, Cl, Cr, Cs, Cu, I, La, Mo, Nb, Pb, Rb, Sb, Se, Sn, Sr, Tc, Te, Th, Ti, U, V, Y, and Zr.

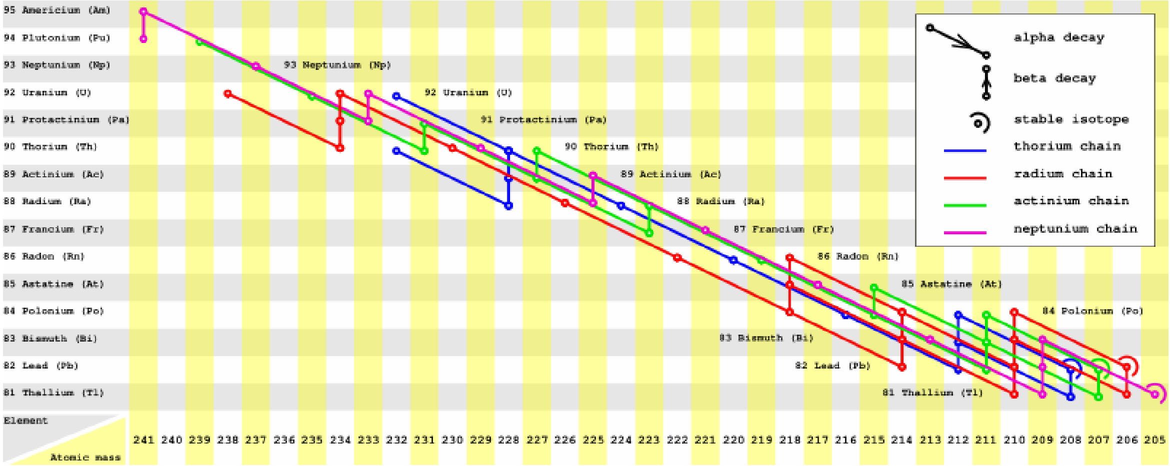


Figure 2. The four main radioactive decay chains.

For convenience, and in order to compare behaviour in groups, the elements described are shown on a Periodic Table as Figure 3.

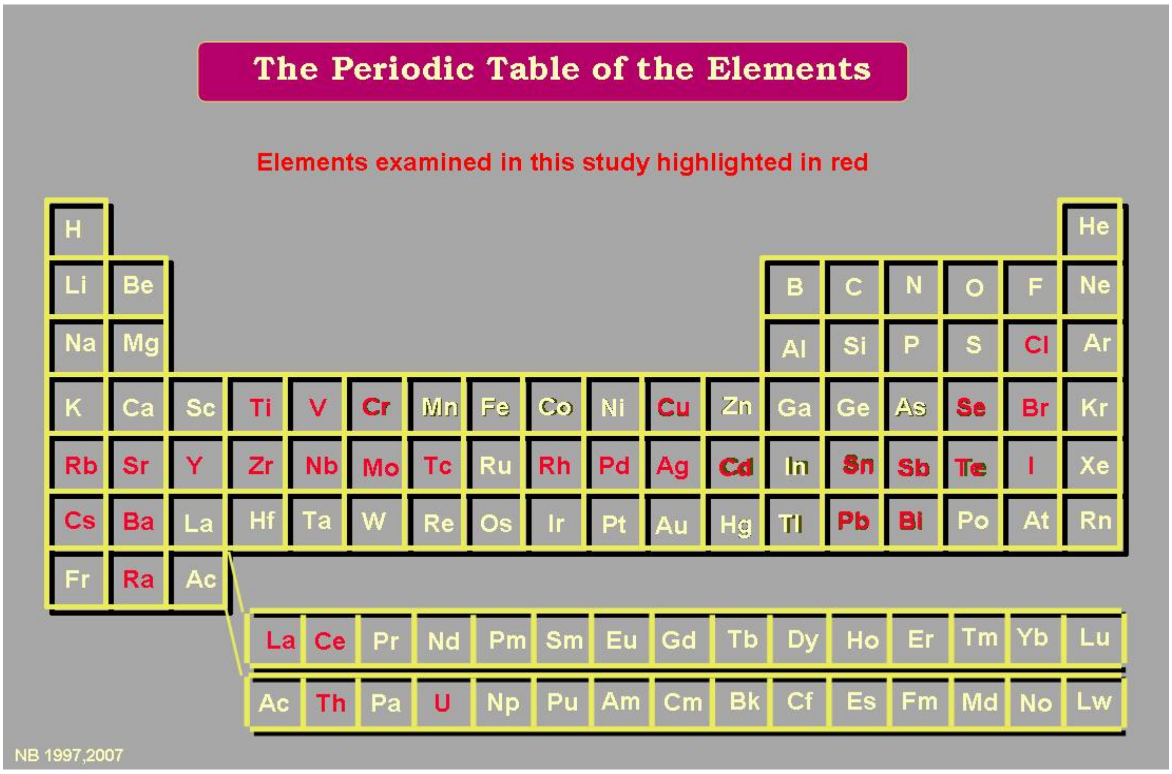


Figure 3. Periodic Table showing elelments examined in this study.

3.4 Brief theoretical geochemistry of the elements under consideration.

This section gives a brief description of the known theoretical geochemical framework. For each element of interest the effects of pH and redox variation, source and carrier mineralogy, affinity for organic matter, sorption characteristics with respect to clays and other inorganic mineral substrates, and other aspects of known geochemical behaviour are given. As this is mainly intended as a resource for reference purposes, the detailed descriptions of individual element theoretic geochemistry have been placed in Appendix 1 in order to simplify the arrangement of the report, and only a summary diagram of element mobility is given here as Figure 4. This has simplified redox and pH axes, and codes likely element mobility on a four-level colour system. Great care should be taken with such tables, as they are combinations of the theoretical and observed status of element behaviour, in both simple and more complex natural systems, and inevitably have limitations when considering particular environments and conditions. The presence or absence of factors such as dissolved organic matter and counter-ions such as sulphide, sulphate, carbonate or chloride could have a significant impact on element mobility. In some cases, neither the thermodynamic data nor observational data are sufficiently robust to make a reliable prediction of behaviour, especially under the more extreme conditions.

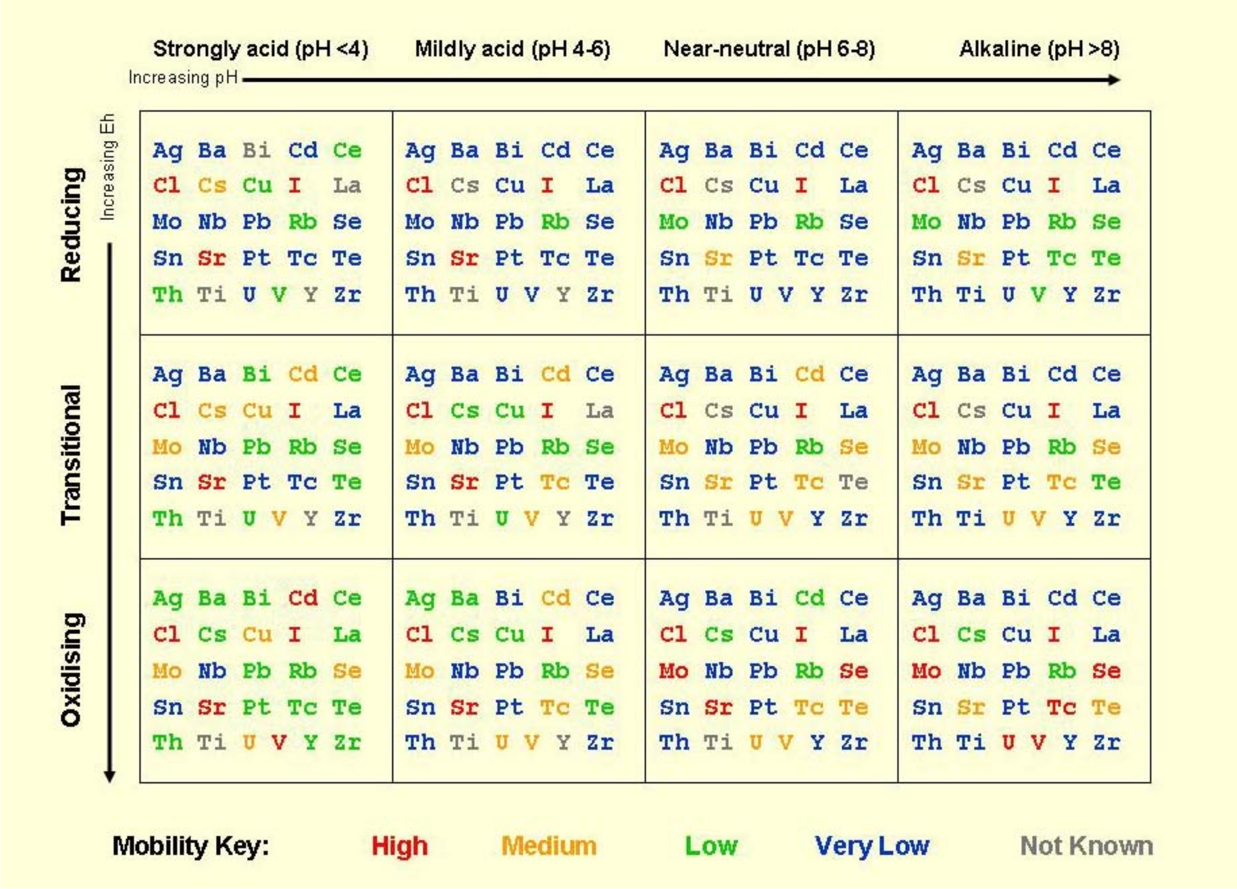


Figure 4. Summary of the probable mobility under natural conditions of the elements considered in this study.

Crustal and lithological abundance data for the elements considered in this study are given in Table 1.

Table 1. Upper Continental Crustal and typical lithological abundances. Values in mg kg^{-1} except for Ti.

	Ag	Ba	Bi	Cd	Ce	Cl	Cr	Cs	Cu	I	La	Mo	Nb	Pb	Rb	Sb	Se	Sn	Sr	Te	Th	Ti (%)	U	V	Y	Zr
Upper Crustal mean	0.07	425	0.15	0.2	64	145	100	3.7	55	0.15	30	1.5	25	20	90	0.2	0.05	2	375	0.005	10.7	0.95	2.7	135	33	165
Mean granite	0.04	700	0.20	0.2	80	200	20	4	12	0.17	55	1.5	20	20	150	0.2	0.05	3	300	0.005	17	0.35	5.0	50	40	180
Mean basalt	0.10	300	0.10	0.2	35	130	200	0.8	100	0.11	10	1.0	20	4	30	0.2	0.05	2	450	0.006	2.2	1.50	0.5	250	30	140
Mean mudstone	0.10	600	0.06	0.8	50	200	100	5	50	1.5	40	2.0	20	22	140	1.5	0.6	6	400	0.009	12	0.75	3.5	130	35	180
Mean sandstone	<0.1	300	0.05	0.04	30	10	35	1	2	0.01	20	0.3	10	10	40	0.05	0.01	0.6	100	0.002	5	0.15	1.3	70	15	250
Mean limestone	<0.1	100	n/a	0.04	10	150	10	0.5	4	1	6	0.4	0.3	5	5	0.15	0.08	<1	500	0.002	2	0.07	2.0	15	15	20

Sources: Henderson, 1982, 1984; Taylor and McLennan, 1985; Reimann and de Caritat, 1998.

4. Availability of data in BGS and elsewhere, including previous geochemical survey projects.

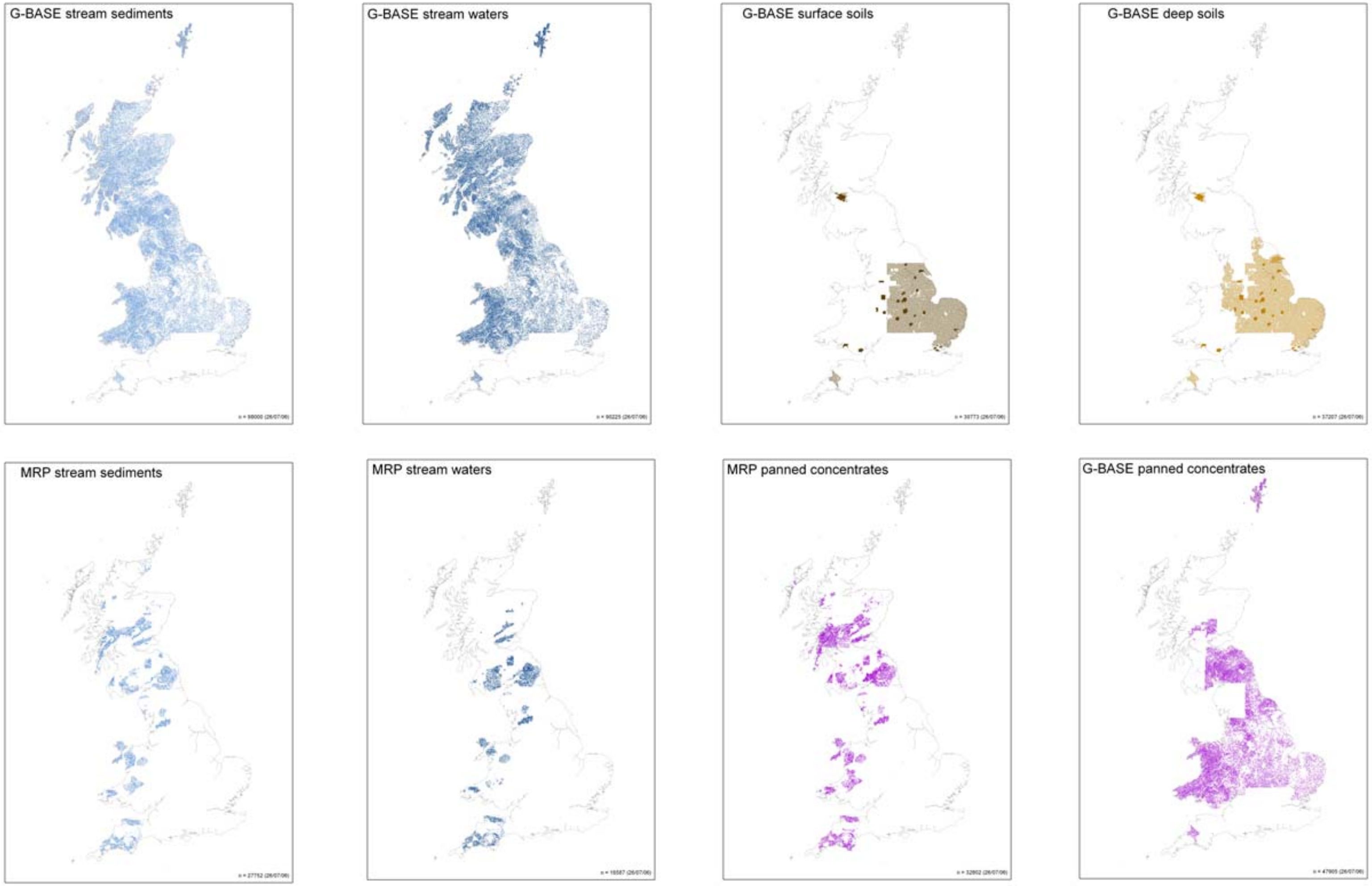
Within BGS, suitable regional geochemical data have been historically produced by two major projects: G-BASE (Geochemical Baseline Survey of the Environment) and the MRP (Mineral Reconnaissance Programme). Of particular applicabililty to this project, however, are those datasets, such as the more recent G-BASE surveys, and those of the Tellus Project in Northern Ireland, where co-spatial stream sediment, soil and stream water samples are available. These have high-quality ICP-MS hydrochemical data, which makes the examination of solution-dispersion trends of the lower-abundance elements (in particular) much more feasible. MRP geochemistry datasets are often targeted at a more limited suite of metals such as Cu, Pb and Zn; and lack the sensitive ICP-MS water data of the recent G-BASE surveys, making them less useful for dispersion studies. The Tellus Project also has high-quality airborne geophysics data. Unfortunately, there are IPR issues with the Tellus data, as it is owned by DETI (Northern Ireland) not BGS, and cannot be used here at present, although it may be accessible in the future. The main disadvantage of G-BASE data for this type of study is that, with a regional survey at a drainage sampling density of one sample per 1.5 km^2 on average, sampling is usually restricted to one or two samples per first-order stream in any sub-catchment, so along-stream profiling and tracing anomalies into higher-order stream systems is not often possible.

The extent of the coverage of BGS regional geochemical projects and surveys can be seen from the following maps **(Figure 5**) of G-BASE and MRP soils, stream sediment and stream water data.

Note, however, that although there is extensive sample coverage for waters and sediments, the range of elements determined has changed significantly over the years. This is especially true of water samples, both MRP and G-BASE, which initially were only determined for four parameters (pH, bicarbonate alkalinity, electrical conductivity and U) in northern Scotland, are currently analysed for up to forty elements and parameters. The more recent G-BASE data (Wales and Humber-Trent regions onwards) are thus more useful for element mobility and dispersion studies.

For reasons of their more limited extent or range of elements, less is made in this report of the G-BASE soils dataset and the MRP data. There is much potential here for further work, but this needs a more careful detailed review than is possible in this short report.

Figure 5. G-BASE and MRP sampling coverages.



5. Geochemical anomalies as exploration tools

The examination of surface geochemical anomalies for the purposes of prospecting for buried mineral deposits has long been an important feature of geochemistry and is fully described in classic publications such as Levinson (1974, 1980). In this type of exploration geochemistry, element anomalies detected on a broad, regional scale survey using media such as drainage samples (stream water, stream sediment), soils or rocks are identified for more detailed work. The aim is to 'home in' on the source of the anomaly which may be a mineral vein or other centre of mineralisation. This can be achieved, for example, by following a stream sediment or water anomaly upstream, or using a tighter grid of high-resolution soil sampling. Obviously, the type and extent of the anomaly depends on a number of factors such as the natural geochemical behaviour of the element(s) of interest, the host mineralogy, the geology and hydrogeology, and the local environment (including soil type, rainfall and other climate variables) and past geological processes such as glaciation.

With more detailed surveys and a knowledge of the dispersion patterns, and allowing for the 'confounding' variables mentioned above, accurate location of the 'target' mineralisation is possible. For the 'natural analogues' work in this report, the reverse of the exploration technique is required, in that the target or source is already known, along with important information such as the source mineralogy and chemical speciation, and it is the dispersion trends and surface-environment behaviour which are to be determined. In a sense, the use of pathfinder elements in exploration, i.e. the use of relatively abundant elements as tracers for rare elements, e.g. using As, Bi and Sb anomalies as indicators for potential gold mineralisation, also mirrors the natural analogues approach and relies on a knowledge of element associations and common behaviour patterns.

As with natural anomalies, anthropogenic ones (i.e. point-sources of contamination, from mine spoil or factory waste, for example) can also provide information on element dispersal patterns. In this case the source may or may not be known. Mine spoil and waste tips are physically fairly obvious, even where their chemistry and mineralogy may not be well characterised, but illegally-dumped chemical waste, historic contaminated land or leaking landfill sites provide more of a 'forensic' challenge. Again the experience of 'natural anomaly' element behaviour can be applied to such cases to explain and predict (in some cases) the patterns of contaminant dispersal.

In addition, backing up simple geochemical concentration determinations with 'extras' such as, for example, speciation tests using sequential extractions, or the determination of different isotopes and their ratios, can provide vital additional data on the source, mobility and dispersion patterns of 'contaminant' elements. Extra sampling media, such as plant material, soil organisms and aquatic biota enable the pathways of element transport from the geosphere to the biosphere to be studied, but such biogeochemical surveying on a regional scale is logistically difficult and expensive both in terms of collection and analysis. Consequently such surveys have only been attempted on a low sampling density, for example in the FOREGS Project (Salminen, 2005; De Vos and Salminen, 2006) or for very local studies (e. g. Breward, 1990). G-BASE lacks the resources to do such sampling, so unfortunately the 'transfer term' cannot be deduced from this data.

6. Examination of geochemical anomalies and dispersion patterns – various examples of both simple and multielement systems.

6.1a Barium: The Collingham - Bramham barium anomaly. (Yorkshire, UK).

High levels of barium in soils and stream sediments are present over the Permian limestone outcrop to the north-east of Leeds, Yorkshire, around the villages of Collingham, [^{4}39, ^{4}46] and Bramham [^{4}43, ^{4}43].

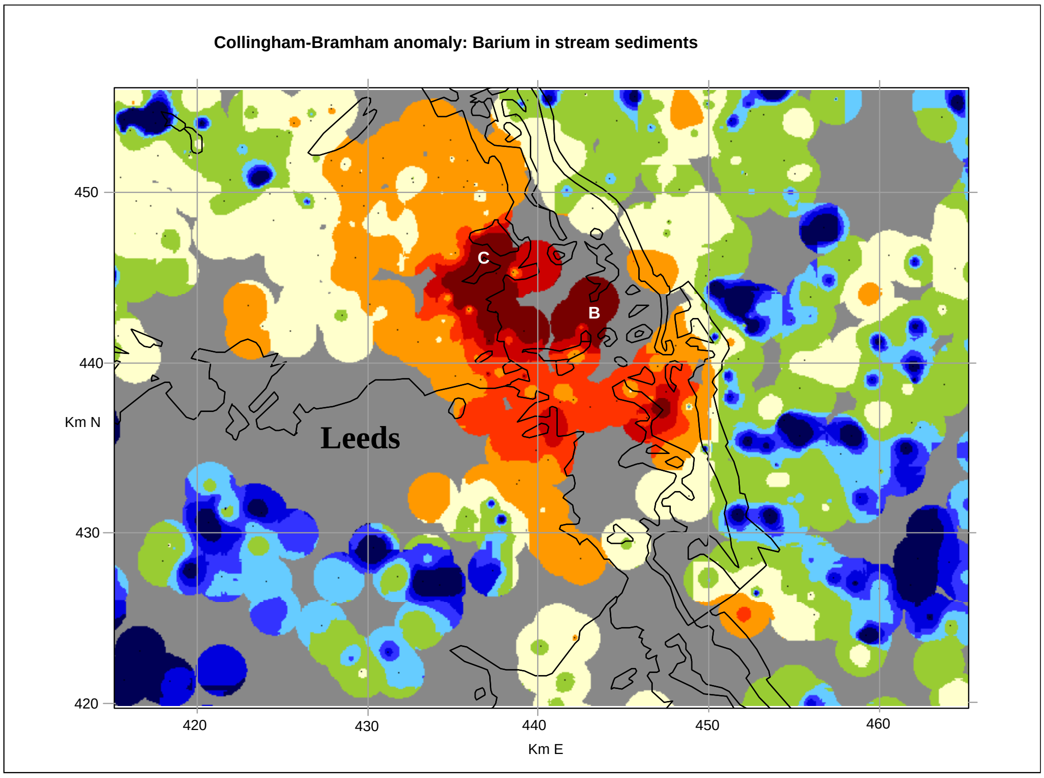
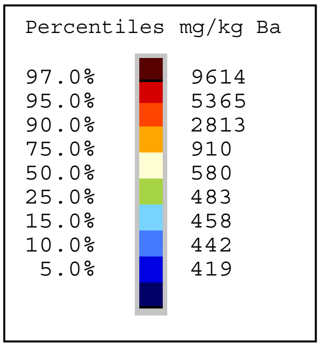


Figure 6a. The Collingham–Bramham Ba anomaly. Barium in stream sediments.1:625000 geology lines. B = Bramham, C = Collingham. Gridded at 50m per pixel.



Percentiles	mg/kg Ba
97.0%	9614
95.0%	5365
90.0%	2813
75.0%	910
50.0%	580
25.0%	483
15.0%	458
10.0%	442
5.0%	419

Figure 6b. Data distribution - sediments

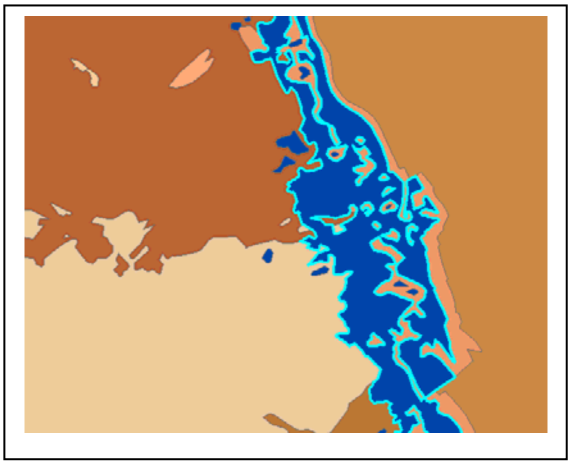


Figure 6d. Geology showing Permian Limestone source rock, outlined in blue. Carboniferous (Namurian and Westphalian) rocks outcrop to the west, Triassic sandstones and mudstones to the east.

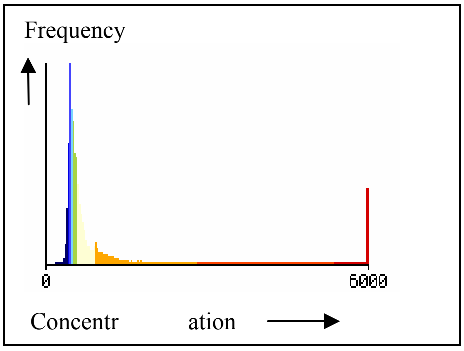


Figure 6c. Data histogram - sediments

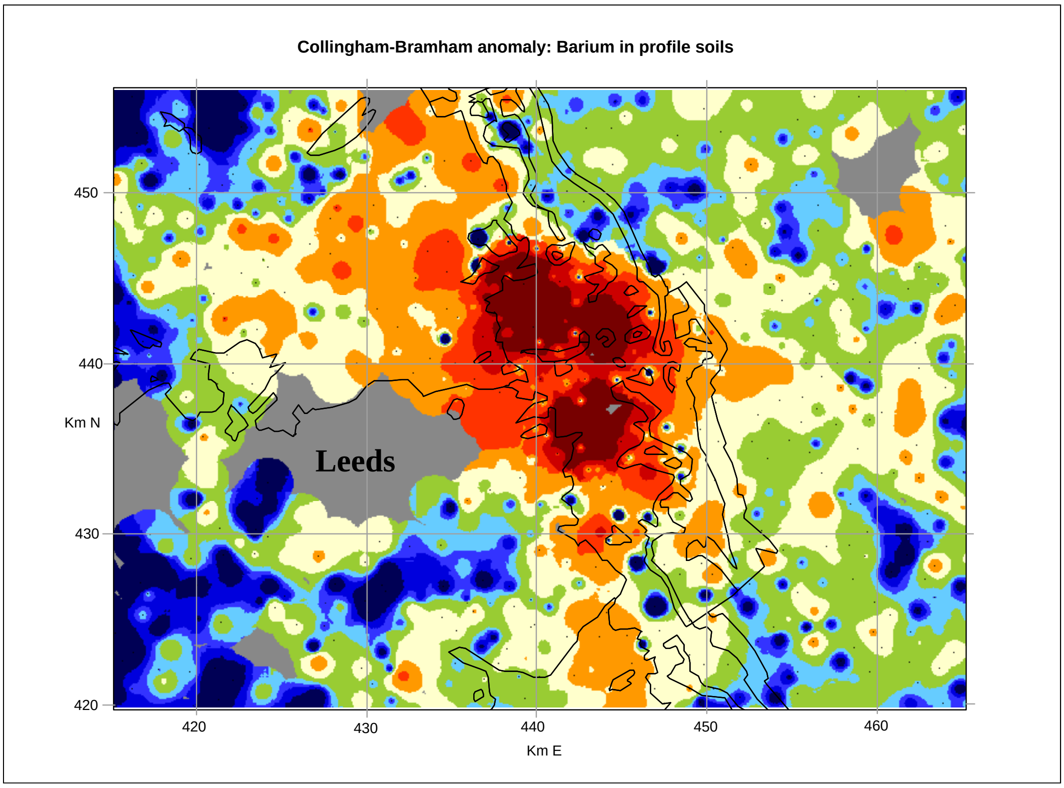
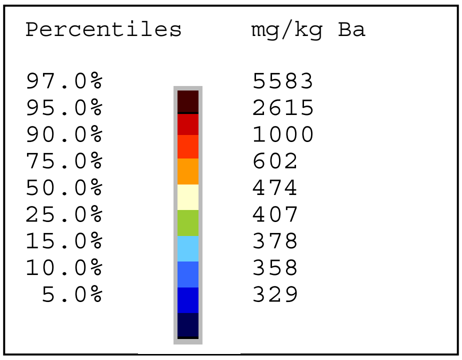


Figure 7a. The Collingham-Bramham Ba anomaly. Barium in profile soils (30-45 cm depth). 1:625000 geology lines. Gridded at 50 m per pixel.



Percentiles	mg/kg Ba
97.0%	5583
95.0%	2615
90.0%	1000
75.0%	602
50.0%	474
25.0%	407
15.0%	378
10.0%	358
5.0%	329

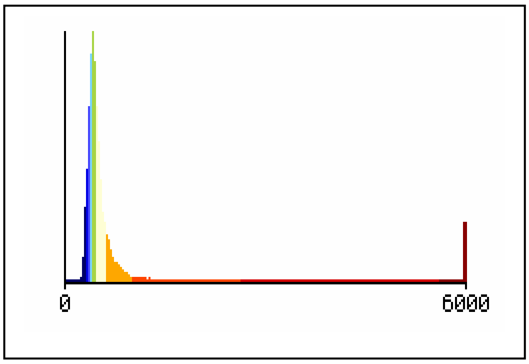


Figure 7b. Data distribution – profile soil

Figure 7c. Data histogram – profile soil

Despite the intensity of this anomaly, with Ba values reaching 61,400 mg/kg in stream sediments and 104,000 mg/kg in soils, there little reference to it in the literature. Occurrences of Ba were noted in cavities in the Magnesian Limestone on Forest Moor, Knaresborough, immediately to the north of the area by Wilson et al. (1922) – " lumps of barite up to one foot in diameter, with some celestine crystals'. The Leeds (Sheet 70) Memoir (Edwards et al., 1950) briefly notes barite as 'nodular lumps up to several pounds in weight' at Bramham, but there appear to be no mining records, economic or even academic interest in this deposit.

The anomaly appears to be restricted to the Cadeby Formation (Lower Magnesian Limestone) with some physical spread onto the Namurian to the west. The Cadeby Formation forms a scarp some 60 m high in this area so down-slope movement of Ba-rich debris will have been significant. There is little superficial Quaternary cover over the Permian ridge, but glacial and fluvioglacial deposits occur over the Carboniferous ground to the west. Head deposits may be present on the lower part of the scarp and no doubt contain derived barite.

Such high levels of Ba in stream sediments and soils suggest that levels in the associated stream waters might be raised, and these are shown in Figure 8a. Levels are indeed elevated over the anomaly, with up to 0.325 µg/L against a background median level of 0.07 µg/L, though the spatial pattern is less marked than for the solid media. Barium mobility is theoretically controlled by the low solubilities of both the sulphate and carbonate, and in the case of a barite deposit on limestone, Ba mobility in these waters should be low. Sulphate concentrations in these waters are near median background levels (50-100 mg/kg SO_4) and bicarbonate levels are moderate to high; 100-1000 mg/kg HCO_3^- but there seems to be little direct correlation with the Ba levels, as higher Ba levels in waters occur elsewhere, without any association with high soil or sediment values.

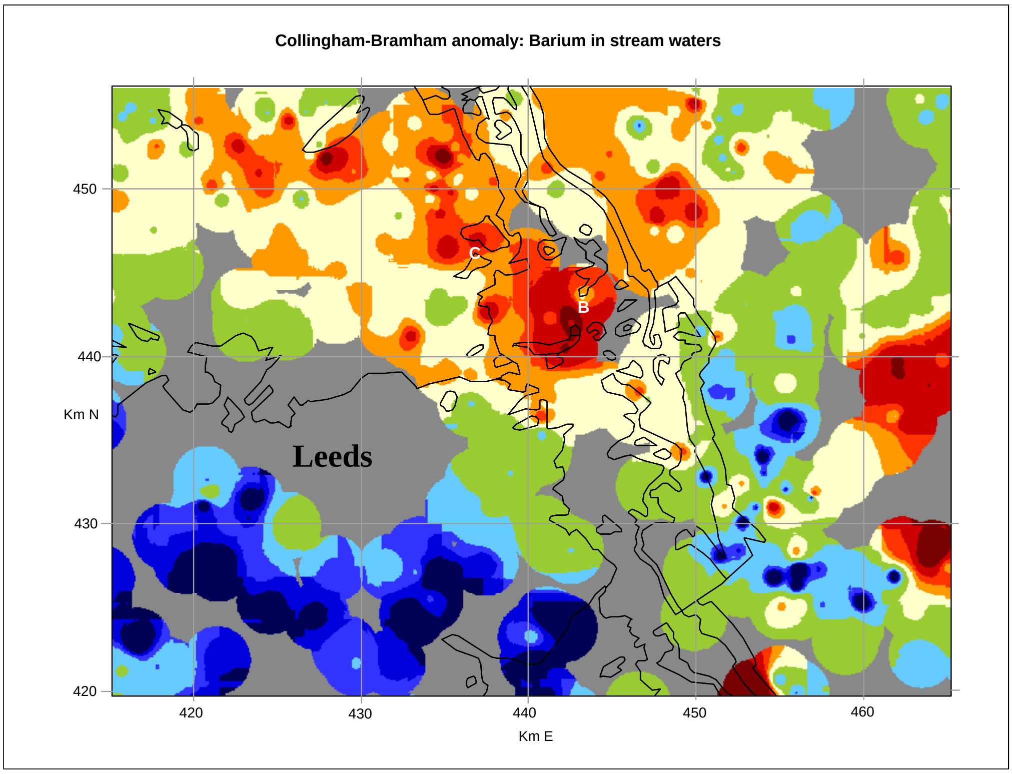
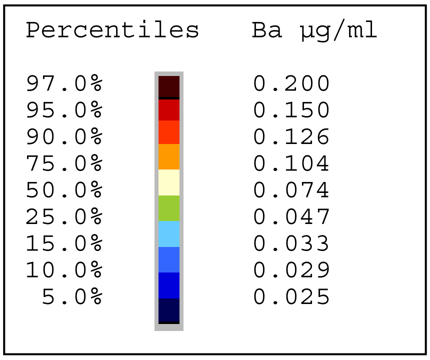


Figure 8a. The Collingham-Bramham Ba anomaly. Barium in stream water. 1:625000 geology lines. Gridded at 50 m per pixel.



Percentiles	Ba µg/ml
97.0%	0.200
95.0%	0.150
90.0%	0.126
75.0%	0.104
50.0%	0.074
25.0%	0.047
15.0%	0.033
10.0%	0.029
5.0%	0.025

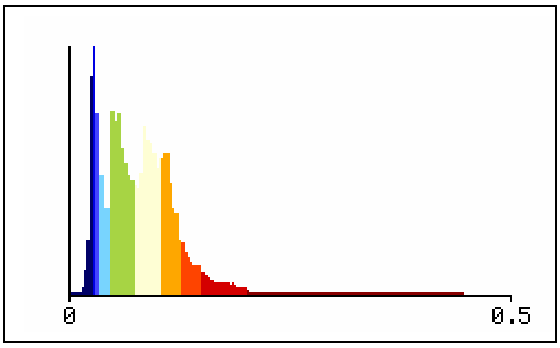


Figure 8b. Data distribution – stream waters

Figure 8c. Data histogram – stream waters.

In this case then, with a barite anomaly within a limestone host, it would appear that Ba (and by analogy, Ra) is of low mobility under these conditions. However, it is instructive to compare the Ba anomaly over the Old Red Sandstone outcrop of the Welsh Borders, and other Ba anomalies in Wales, such as in Pembrokeshire; and at Buith Wells and Llandridod Wells.

6.1b Barium over the Welsh Borders Old Red Sandstone outcrop.

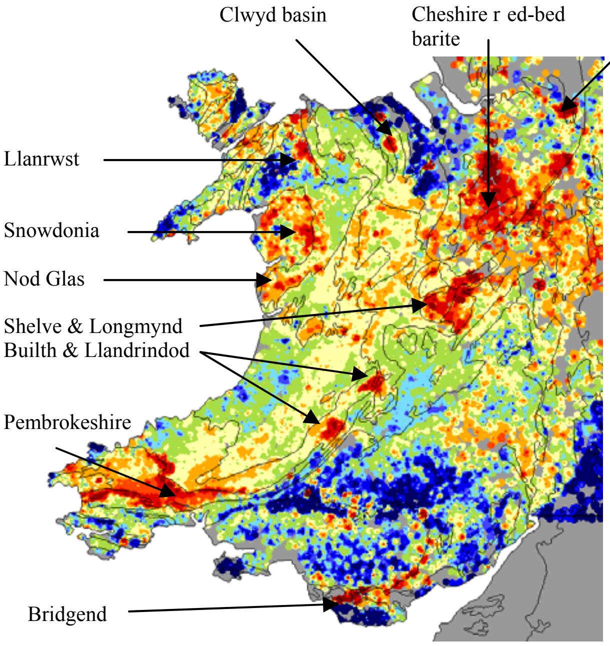


Figure 9a. Barium in Stream Sediments

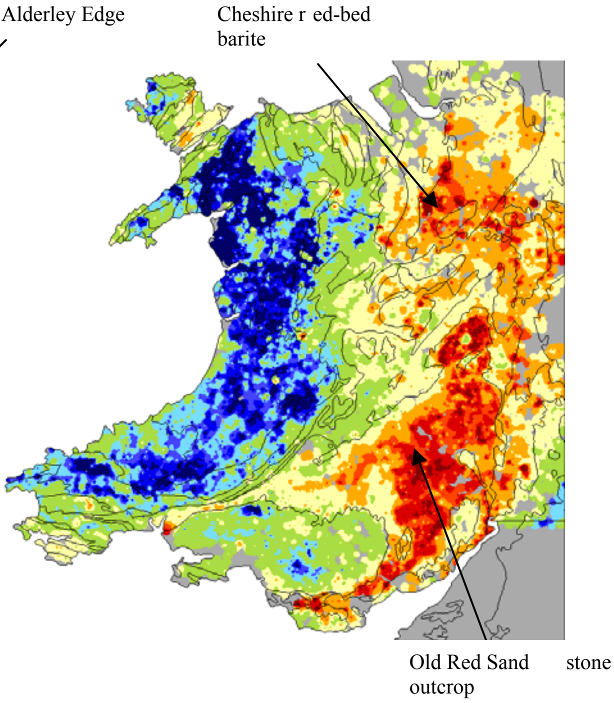


Figure 9b. Barium in Stream Waters

The Old Red Sandstone outcrop shows very high levels of soluble Ba in stream waters, even though the levels of Ba in stream sediments are unremarkable. The origin of these high Ba values is uncertain, since it implies the presence of a readily-soluble Ba mineral which is impersistent in the stream sediment environment. Neither of the common Ba minerals barite ($BaSO_4$) or witherite ($BaCO_3$) has these characteristics, as both are theoretically highly insoluble in the neutral to alkaline waters over the Old Red Sandstone outcrop. One possible explanation is that the dissolved Ba may be derived from fracture coatings in the sandstones which would make a much greater contribution to the stream water that to the sediments. Also, the stream waters in this area are strongly bicarbonate-dominated and relatively low in sulphate, so Ba may be being carried in solution as a bicarbonate complex and, therefore, it is much more mobile under these conditions. This also perhaps illustrates the dangers of relying on theoretical thermodynamic models of element mobility, when the reality of field conditions can lead to unexpected behaviour.

Curiously, the other Ba anomalies identified on the stream sediments map show very different solution-dispersion patterns in the stream waters. The barite mineralisation in the Triassic sandstones of the Cheshire Basin, for example at Alderley Edge, and also in the Clwyd Basin, does give rise to elevated Ba levels in waters. However, neither the Snowdonia mineralisation, Llanrwst or the Nod Glas or Pembrokeshire black shales, which give strong stream sediment anomalies, show much evidence of enrichment in solution in the stream waters, though this may be due, in part, to the high rainfall in these areas. In contrast, barite mineralisation in the Shelve Mining Field and the adjacent Longmynd, and in the Carboniferous Limestone at Bridgend, is associated with elevated Ba concentrations in the stream waters, whereas the mineralisation at Builth and Llandrindod Wells is not. This reinforces the observation that both the source speciation and mineralogy, plus the immediate geochemical environment, are vitally important in understanding the dispersion pattern of an element.

Many other examples of barite mineralisation a occur in the UK, notably in Scotland, the Lake District and the northern Pennines, but we lack reliable Ba in stream water data for these areas.

6.2 Black Shale lithologies as multi-element sources.

Black Shales are typically fine-grained sediments rich in partially decomposed organic matter, hydrocarbons and sulphides; and are the products of slow anoxic sedimentation in closed sedimentary basins. They can occur at any geological horizon if the sedimentary conditions are appropriate, but are rarely major deposits, as the conditions required for their formation are unstable and tend to be short-lived. Consequently, black shales tend to occur in fairly thin bands interspersed with more normal sediments. The geochemistry of black shales is often distinctive, with enrichments in ‘normal’ mudrock-facies elements such as B and Ga being supplemented by elevated levels of chalcophile elements such as As, Se, Cu and Cd, and rarer elements such as Ba, Mo, Ni, V and U which may be associated with phosphates and organic complexes. This wide range of elements makes them especially useful for natural analogue studies. When considering the 'natural geochemical background' of a region with a view to defining a baseline with which to compare anomalies due to anthropogenic activity, it is clear that the underlying bedrock lithology and its consequent geochemistry must be taken into account. However, sedimentary rocks with a 'black shale' component are often not mapped separately as such, and are only well defined by their characteristic geochemical signature as a result of regional geochemical surveys. The outcrop area of late Visean and early Namurian basin-facies sediments in north-east Staffordshire and south Derbyshire centred on the town of Ashbourne is shown in Figure 10 as an example.

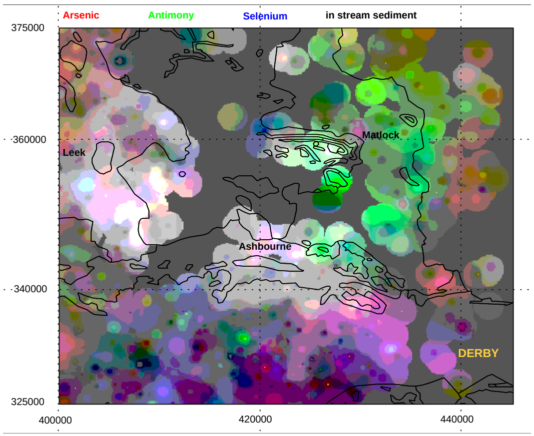


Figure 10a. Ashbourne area: Arsenic, Antimony and Selenium in stream sediments. RGB composite image, 1:625000 geology

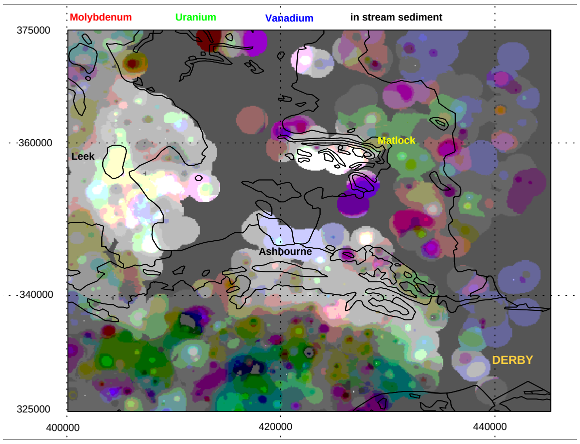


Figure 10b. Ashbourne area: Molybdenum, Uranium and Vanadium in stream sediments. RGB composite image, 1:625000 geology

(In RGB composite images, which use colour-addition techniques where an element is assigned a primary colour, i.e. red, green or blue, high levels of all three elements chosen show up as areas of white or pale grey).

In north-east Staffordshire and south-west Derbyshire, running approximately from Leek, through Ashbourne to Derby with an outlying patch near Matlock, the basinal sedimentary facies of the Carboniferous (the Widmerpool Formation - used here in its broad sense) shows a very distinctive 'Black Shale' geochemical signature. The Widmerpool Formation is of similar age (Visean to Namurian), and lithology to the Bowland Shale of the Craven Basin, and likewise shows high levels of many elements such as As, Sb, Se, Mo, U, V, Cd, Cu and Ni. The similarity of the anomalies is shown by the pale grey and white areas on these images (Figure 10).

The influence of the black shales is such that the anomaly extends over the Triassic rocks to the south, where it is based partly on Quaternary deposits derived from the nearby Widmerpool Formation exposures. However, the greatest influence on stream sediments and stream waters is in the catchments of the rivers Hamps, Manifold and Dove to the north and west of Ashbourne, and on the Longford Brook catchment to the southeast. Stream water pH values in the area are generally neutral to mildly alkaline, typically 7.5-8.5 over the main black shale outcrop. Under these conditions, 'normal' heavy metals such as Pb and Zn are likely to have low mobility, whereas elements such as U and Mo may be more soluble.

On the three-component stream sediment maps (above), the main limestone outcrop of the Derbyshire Dome, with its purer platform limestones, is shown in dark grey due to the absence of surface drainage, and hence the lack of stream sediment samples. BGS soil samples from the wider area show a generally similar pattern to those of the stream sediments, with much greater concentrations of elements such as As, Se and Mo over the Widmerpool Formation than over the main limestone outcrop. However, metals more associated with sulphide vein mineralisation, such as Pb, Zn and Cd, are widespread in soils over both the limestones and Widmerpool Formation outcrops.

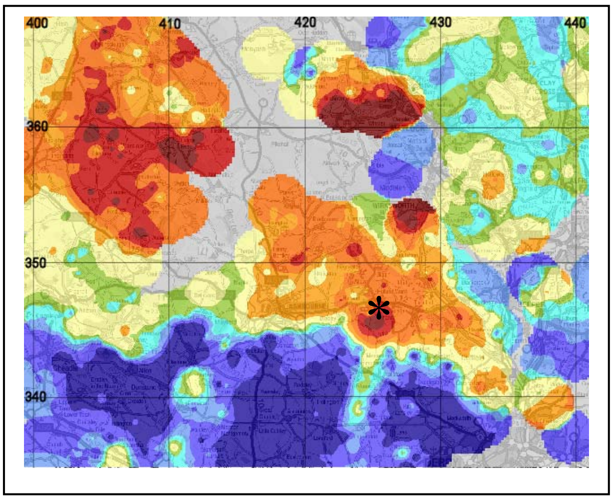
Within the anomalous area, the maximum concentration and range of concentrations of the remaining top ten stream sediments sites are as follows:

Element	Maximum value, mg/kg	Remaining top ten sites, mg/kg	Regional median, mg/kg
As	136	50-95	13
Se	43.6	11-15	0.6
Sb	31	13-23	3.5
Mo	46.6	30-40	2.5
U	20.5	10-17	2.7
V	395	260-370	99

These clearly show a substantial degree of enrichment relative to the 'background' values. Copper mineralisation is also present locally, most notably at Mixon [^{4}04, ^{3}57] and Ecton Hill [^{4}10, ^{3}58], and this is also related to the metal-enriched source rocks of the Widmerpool Formation (*s.l.*).

These geochemical anomalies are due to natural geological/geochemical occurrences, but some of them show levels of potentially toxic trace elements which are similar to, or even exceed, levels associated with anthropogenic contamination. Indeed, many of the concentrations observed in these 'black shale' anomalies significantly exceed the recommended maximum levels of the Contaminated Land Exposure Assessment (CLEA) model supported by DEFRA, the Environment Agency and SEPA (DEFRA, 2001). These areas are also notable for a high incidence of hypocuprosis, a copper-deficiency disease in cattle induced by high soil Mo levels (Thornton, 1977).

It is useful to compare individual stream sediment and water patterns side-by-side where reliable water data are available. Soil data generally shows similar patterns to those of stream sediments.



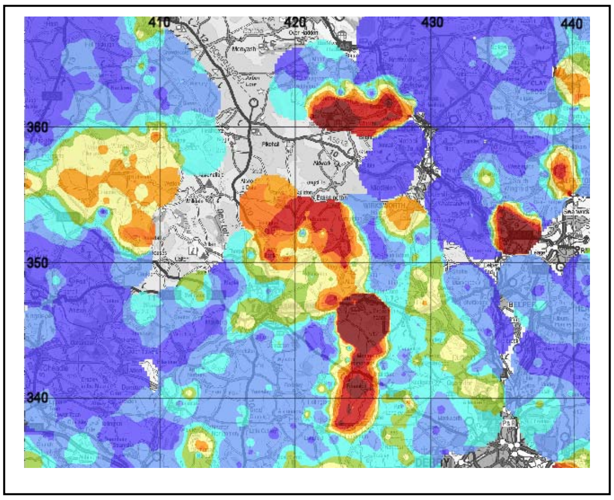
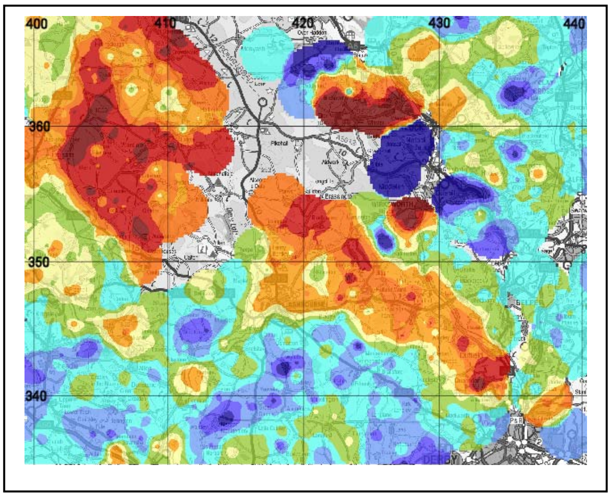


Figure 11a. Ashbourne area: Molybdenum in stream sediments

Figure 11b. Ashbourne area: Molybdenum in stream waters

Molybdenum. Molybdenum is clearly mobile in solution under these conditions, at least over short distances, and a good example (* on Figure 11a) can be seen in the upper reaches of the Brailsford Brook – Longford Brook catchment. The stream sediment anomaly in the headstream near the junction of the Widmerpool Formation and the Sherwood Sandstone is isolated, so this acts as a point-source for Mo dispersion in solution. The source anomaly is complicated by the presence of a large cement works which may also be responsible for the high water pH (8.0). Very high levels of Mo in water (130 µg l^{-1}) are present at the corresponding site, and fall steadily downstream over a 5 km reach before declining to background levels (5 µg l^{-1}).



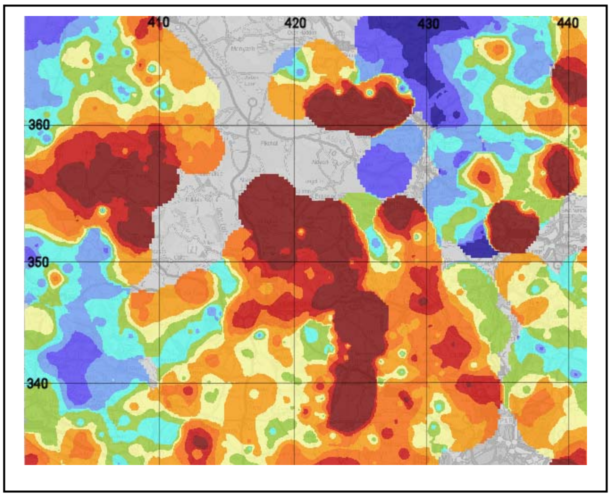
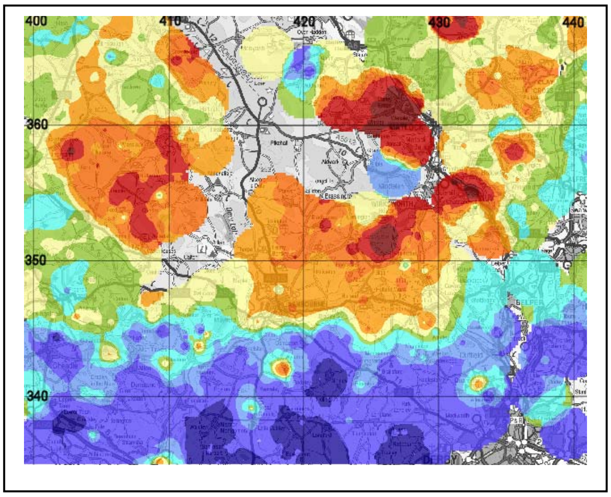


Figure 12a. Ashbourne area: Uranium in stream sediments

Figure 12b. Ashbourne area: Uranium in stream waters

Uranium. Uranium is also mobile in solution, though with a slightly different pattern. The highest U concentrations in sediments occur to the north-west of Ashbourne, but there is a another anomalous area north-east of Ashbourne, extending to Carsington Water and east to Hulland Ward, where many values in the 8-11 mg kg^{-1} range occur. The highest values in solution in the stream waters occur in the same area, notably in the Bradbourne

Brook catchment, and are typically 4 -6 µg L^{-1} at pH levels 7.5-8.5. Wherever several monitoring sites exist on the same stream, the indications are that U is mobilein solution for at least 2 km from source under these pH conditions.



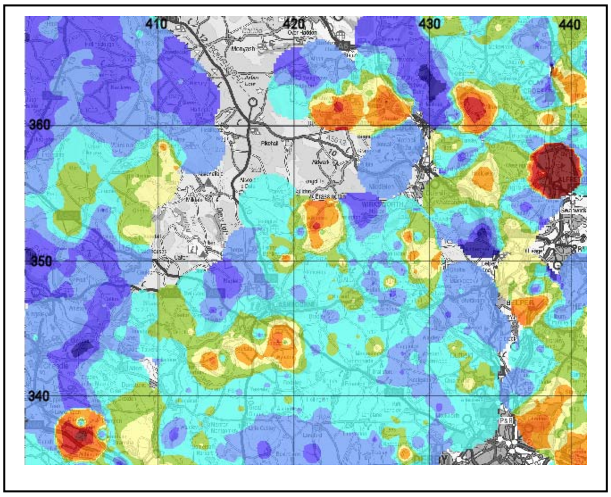
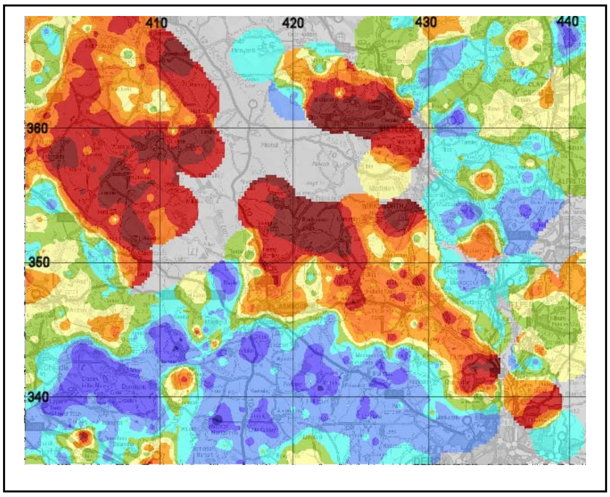


Figure 13a. Ashbourne area: Antimony in stream sediments

Figure 13b. Ashbourne area: Antimony in stream waters

Antimony. Despite anomalous levels in the soils and stream sediments, there is little evidence that Sb is mobile in solution under the prevailing conditions, Sb levels in stream waters being only slight elevated above the regional median over the area of the soil and stream sediment anomaly.



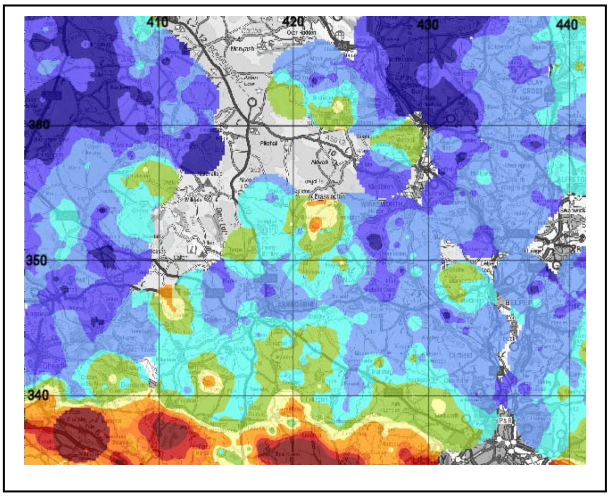


Figure 14a. Ashbourne area: Vanadium in stream sediments

Figure 14b Ashbourne area: Vanadium in stream waters

Vanadium is not a major component element of nuclear waste (other than in stainless steels and other alloys), but it may be a useful indicator, along with Mo, of the possible behaviour of elements such as Tc. The enhanced V concentrations over the Widmerpool Fm. Black Shale outcrop provides a potentially more soluble source for V than do the iron minerals, such as magnetite, with which it is usually associated. There is clearly some V mobilisation to stream water, but at relatively less elevated concentrations, and without showing such a clear pattern as was observed for Mo and U. The highest value for V in waters over the Widmerpool Fm. Black Shale outcrop is 5 µg L^{-1}, which is only ten times the background level, suggesting that less dissolution is taking place and/or that stronger sorbtion processes are operating. With V, Mo and U all at naturally elevated concentrations, their dispersion behaviour may be compared and contrasted.

Selenium concentrations are strongly anomalous in stream sediments over the black shales outcrop, with levels up to 43 mg kg^{-1} present compared with the regional mean of <1mg kg^{-1}. Unfortunately, analytical difficulties in the determination of Se in solution make it impossible to observe the dispersion pattern in stream waters.

Copper, although at elevated concentrations in sediments, copper seems to be immobile under these conditions, which is consistent with the theoretical low mobility of Cu under moderately high pH and in the presence of organic matter (see also section 6.11).

Silver is not notably enriched in this anomaly and is below the detection limit in stream waters (0.01 µg L^{-1}). Much higher Ag levels, up to 20 mg kg^{-1} in soils and sediments, are associated with the Pb-Zn sulphide vein mineralisation (galena-sphalerite) of the limestone areas, notably around Matlock to the east, but even there no Ag can be detected in stream waters so its dispersion trends cannot be assessed. Perhaps the observation that no data are above the 0.01 detection limit implies that little dispersion is taking place.

6.3 Lanthanides, Thorium and Zirconium.

The lanthanide elements (La-Lu) have been suggested as analogues for the actinides of most significance in nuclear wastes, but there are important differences in the geochemistry of the two series which makes this problematic, notably the tendency of most of the actinides (with the exception of actinium itself) to show stable oxidation states above the nominal +3 exhibited by most of the lanthanides, and a greater ability to form stable and soluble complexes, especially at these higher oxidation states. The typical +3 lanthanides tend to be relatively immobile due to the very low solubility of the phosphate, carbonate and hydroxide species over normal ranges of pH.

Ce and Th. On the other hand, the relatively abundant Ce and Th do show stronger similarities with the actinides owing to their common stable +4 redox state and the stability of the oxides CeO_2 and ThO_2 and, perhaps more importantly, the ability of both to substitute into phosphate minerals such as monazite ($(Ce,La)PO_4$), and also into 'group four' silicates such as zircon (Zr, *Ce,Th*)SiO_4. Recent G-BASE data from the Humber-Trent region gives a viable detection limit for both Ce and Th in filtered (0.45µm) stream waters of around 0.02 µg l^{-1}. Some 75% of the Ce data and 25% of the Th data lie above this limit so credible maps may be created and compared. The most significant patterns are those shown over the 'Millstone Grit' outcrops in the Pennines, where high levels of both Ce and Th are present in stream sediments, and in a smaller subset of the same area east of the watershed where elevated levels in stream waters coincide with very low pH values (<4.0) and drainage from upland peat deposits. This suggests mobilisation of both elements is occurring despite the essentially resistate mineral source in the sediments. The mainly drift-covered Lias outcrop shows elevated levels in sediments but a less clear pattern in waters. In the case of Ce, mobilisation may involve reduction to Ce^{3+}, but this is less likely for Th which is probably transported in colloidal form as the hydrous oxide $Th(OH)_4$ or $ThO_2.2H_2O$. In this, Th shows some similarity to Zr, and it is worth noting that recent advances in analytical chemistry are showing that such elements, previously regarded as 'insoluble' or 'immobile', do have a limited solution chemistry, albeit at very low concentrations.

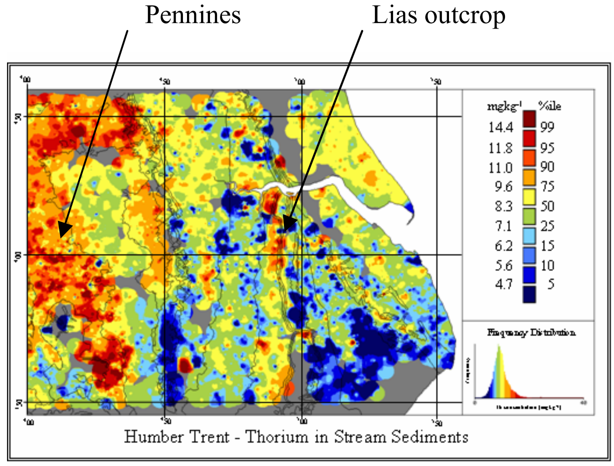


Figure 15a. Humber-Trent area: Thorium in stream sediments

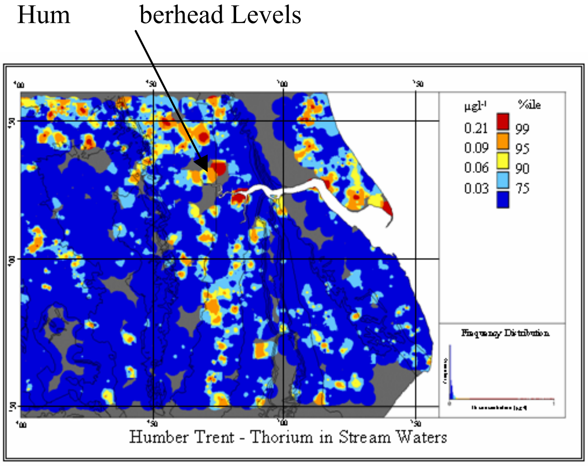


Figure 15b. Humber-Trent area: Thorium in stream waters

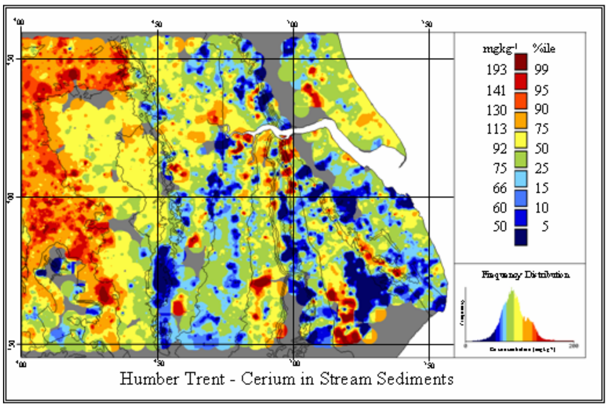


Figure 16a. Humber-Trent area: Cerium in stream sediments

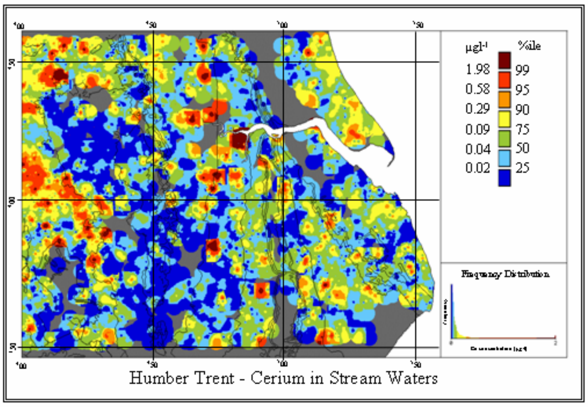


Figure 16b. Humber-Trent area: Cerium in stream waters.

The other prominent area of elevated Th in stream waters is at the head of the Humber, where Holocene peat deposits overlie glacial sands and gravels and also give rise to low-pH stream waters. Humic acids may therefore be playing an important role in Th mobilisation, probably as colloidal humic complexes, and allowing stabilisation in solution.

Zirconium. Examination of stream water pH, and Zr maps for sediments and waters, suggests that the behaviour of zirconium is very similar to that of Ce and Th. The collective similarity of Ce, Th and Zr suggests that these may be analogues for other +4 actinides such as Pu^{IV}, which also possesses a very stable low-solubility dioxide, PuO_2 but the analogy should be treated with caution, as the environmental stability of other species such as Pu PO_4 and possible Pu-humic acid complexes is not known.

Lanthanum (and **Yttrium**) shows a rather similar pattern to that of Ce and Zr, at least over the eastern Pennine watershed suggesting that the leaching effect of acid, humic-rich waters is also important for La. Uranium concentrations in this area are extremely low (below the 0.02 $\mu g\ l^{-1}$ detection limit) so there is no possibility of examining the validity of La as an analogue for the geochemically complex U in this area. However, La and americium (Am) may be more alike, except that Am also has a +4 redox state (cf. Ce) and their behaviour will therefore be different at higher values of Eh and pH (Brookins, 1988).

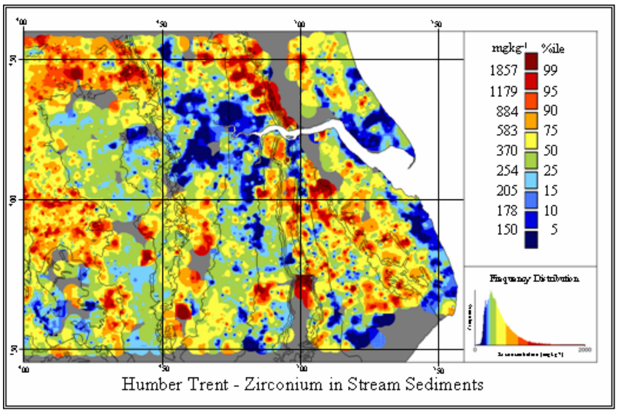


Figure 17a. Humber-Trent area: Zirconium in stream sediments

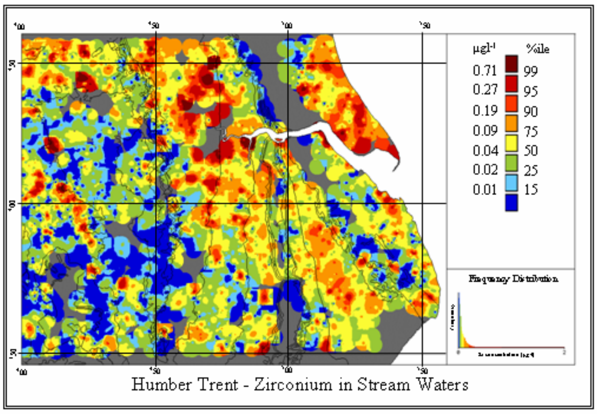


Figure 17b. Humber-Trent area: Zirconium in stream waters

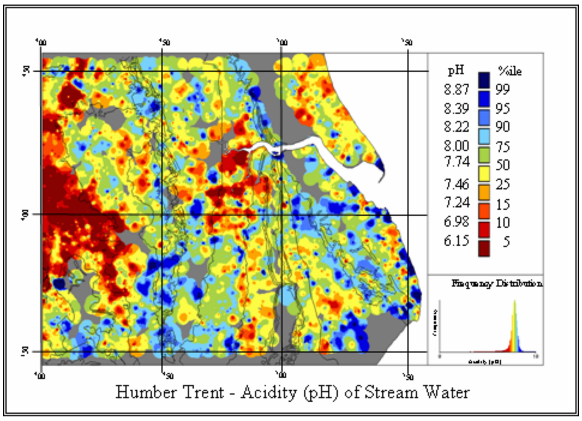


Figure 18. Humber-Trent area: Stream water pH

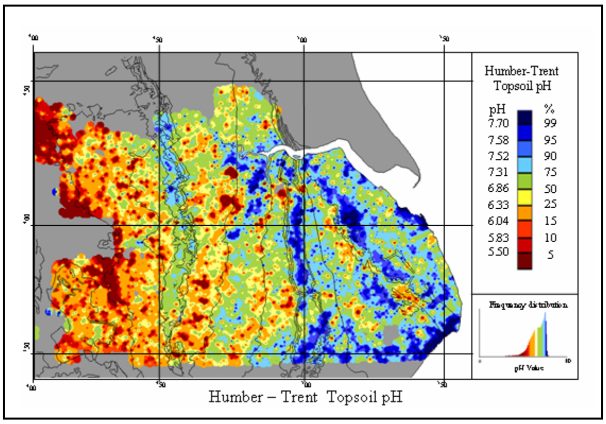
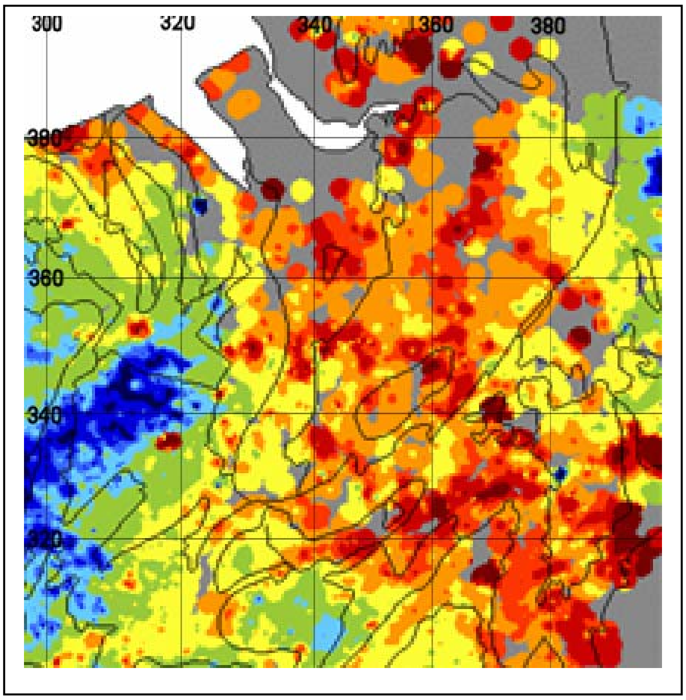


Figure 19. Humber-Trent area: Topsoil pH

6.4 Chloride in the Cheshire Basin – dispersion from rock-salt (halite) deposits.

Some studies of chloride behaviour in natural analogues of repository sites have examined buried marine sediments in currently-freshwater lakes, e.g. at Wastwater and Loch Lomond, to determine rates of seepage of brines through a clay cap. These studies are summarised in Miller et al. (1994) and presented in greater detail in Hooker et al., 1985 and Falck and Hooker, 1990. However, in the Cheshire Basin, drift-covered outcrops of halite provide a ready source of chloride to groundwater. The situation is complicated, as regards surface water anomalies, by the fact that the Mercia Mudstone Group also contains many thin halite bands in addition to the major salt units (the Wilkesley and Northwich halites), and the glacial deposits are also derived from Irish Sea outcrops of similar rock types. Thus there is a strong ‘dispersed anomaly’ in the source materials in addition to the obvious halite beds, which give rise to the rather dispersed pattern of chloride anomalies in stream waters (Figure 20a, b).

Chloride inputs in rainfall from marine spray sources are not a problem in central Cheshire, but anthropogenic inputs from landfill sites and road salting are an additional complication. However, the pattern of high Cl$^-$ values in stream waters over the Cheshire Basin suggests that Cl$^-$-rich groundwater is entering first-order streams and behaving in an entirely typical manner, i.e. being highly mobile and ‘conservative’ in its interactions with other elements and substrates irrespective of Eh, pH or any other parameter (though chloride and organic chlorine does concentrate in biota).



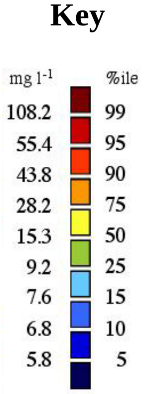


Figure 20a, b (key). Chloride in the Cheshire Basin – stream waters. Map extends from Merseyside south-east to near Birmingham

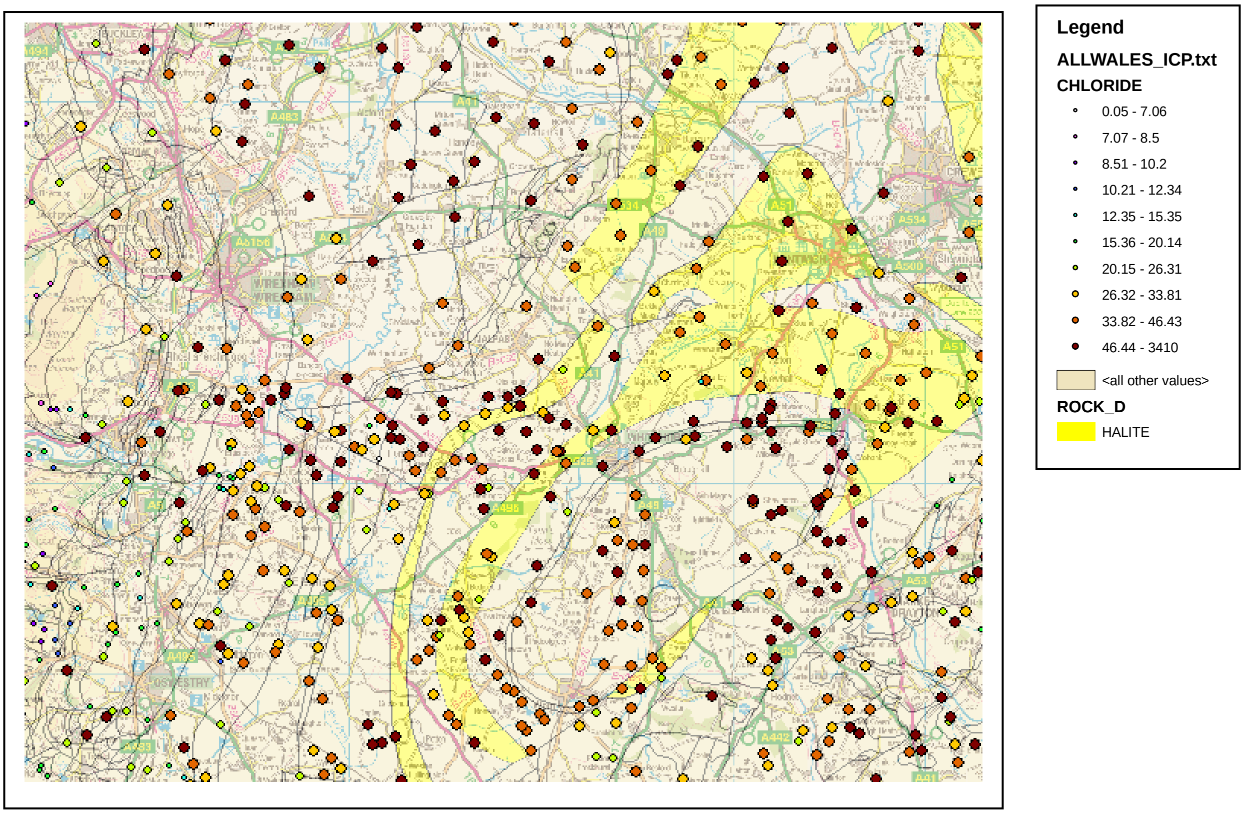


Figure 20c. Chloride in Cheshire Basin stream waters: detail centred on the town of Whitchurch, showing Halite beds (yellow) and colour-dot map of Cl$^-$ concentrations on the OS topographic map. High Cl$^-$ levels are not confined

to the outcrops due to the wide dispersion of saliferous deposits, both natural and anthropogenic, and the high solubility and conservative behaviour of chloride.

Other high-chloride waters have been observed over the Mercia Mudstone outcrops of the Stafford and Needwood Basins, and also may be derived from Coal-Measure brines leaking from abandoned mine workings, notably in the North Staffordshire and South Staffordshire coalfields.

6.5 Iodide in Eastern England.

Unlike chloride, iodine is not a 'conservative' element and may interact strongly with other elements and substrates in the environment, since it is biologically active and concentrates in biota, especially marine algae. The main input to stream waters may be via rainfall, which washes out volatile iodine from the atmosphere. Although the iodide ion I^- is the dominant species in solution over a wide range of Eh and pH, under oxidising conditions the iodate ion IO_3^- is stable.

Newly-available data for iodine as iodide I^- in topsoils for East Anglia reveals the strong affinity of iodine for organic materials of marine origin in the Fens, Norfolk Broads and the North Norfolk and Suffolk coastal strips. Bromine shows a near-identical distribution. Unfortunately, the determination of I^- and IO_3^- in stream waters is still somewhat problematical and it is not (yet) possible to routinely include this in the standard G-BASE aqueous analysis suite.

A very limited number of G-BASE water samples from the Fens were analysed and results are shown in Fig 21b (below right). It is not possible, on the basis of so few samples, to give a reliable assessment of I^- mobility in solution in stream waters, but a tentative good positive correlation with Br^- in solution (Fig. 22) suggests that the overall distribution pattern of I^- is similar to that of Br^- (Fig. 23).

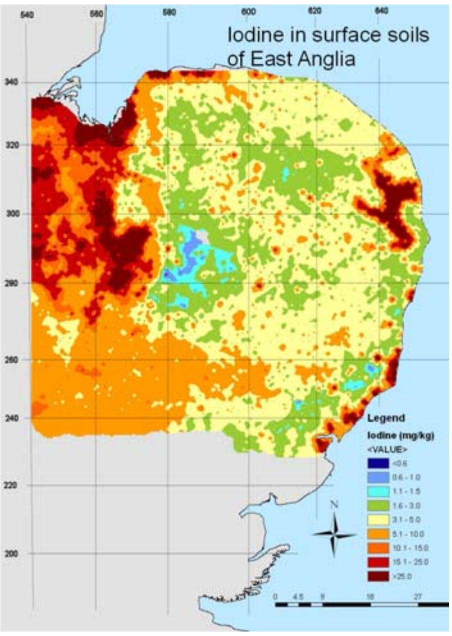


Figure 21a. Iodide in surface soils, East Anglia

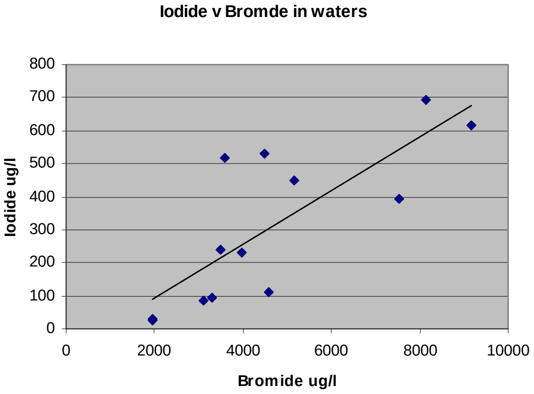


Figure 22. Iodide vs. Bromide correlation graph.

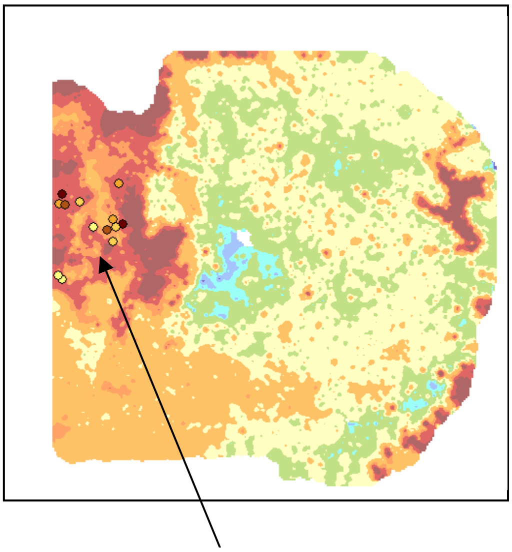


Figure 21b. Iodide in Water data, East Anglia. Max. 693 μg l^{-1} (dark=high). *(The background map is I^- in surface soils, as in Fig.21a).*

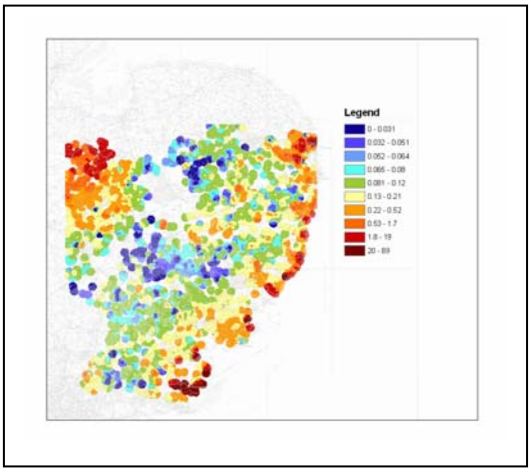
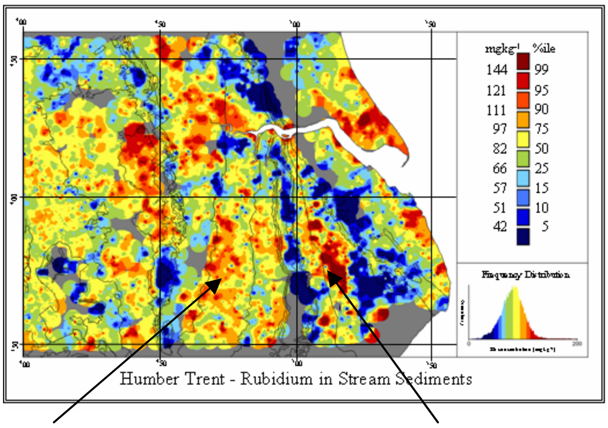


Figure 23. Bromide in waters (same area as in Figure 21a).

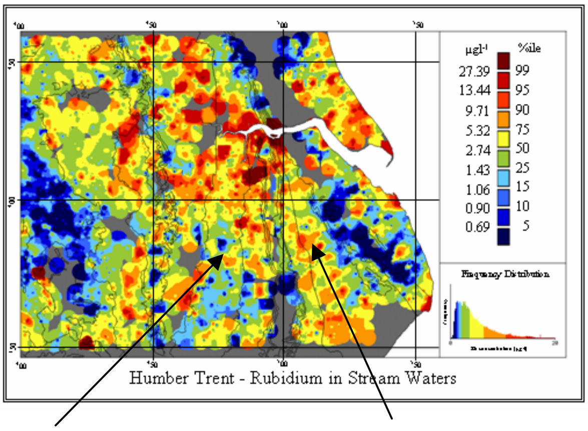
6.6 Rubidium and Caesium

Rubidium generally shows its customary affiliation with potassium, in that it is less mobile in the surface environment than its theoretical ionic solution (Rb^+) chemistry might suggest. The main reason for this appears to be the strong affinity both metals have for binding to clay minerals. The equilibrium between free solvated Rb^+ and clay-mineral bound Rb appears to be very much towards the latter, and this can be seen over the central Mercia Mudstone Group outcrop in the Humber-Trent region. High Rb levels in stream sediments are not reflected in the stream waters over this outcrop; neither is the Rb anomaly in sediments over the Jurassic and Quaternary clays of the River Witham fens to the east of Lincoln shown as a significant enrichment by the Rb in waters map. Rubidium should therefore be regarded as a low-mobility element where a substantial proportion of clay minerals are available for binding.



Mercia Mudstone Group Outcrop Witham fens

Figure 24a. Humber-Trent area: Rubidium in stream sediments



Mercia Mudstone Group Outcrop Witham fens

Figure 24b. Humber-Trent area: Rubidium in stream waters

Caesium has only recently been added to the range of elements routinely determined by G-BASE, and is available only for soils and stream sediments for East Anglia at present. Both theoretically and in practical observations relating to the fallout from the Chernobyl nuclear accident (e.g. Smith, 1999, 2000), Cs has been shown to have an even greater affinity for binding to clay minerals than does Rb, so in a clay-rich environment under normal pH conditions, Cs is expected to have a low mobility (Cremers et al., 1988). The map for Cs in East Anglian topsoils (below) also shows a strong affinity for the marine organic-rich silts and clays of the Fens and Norfolk Broads, and as such is somewhat similar to the distribution of Br and I. Again this implies (but does not prove) a low environmental mobility for Cs.

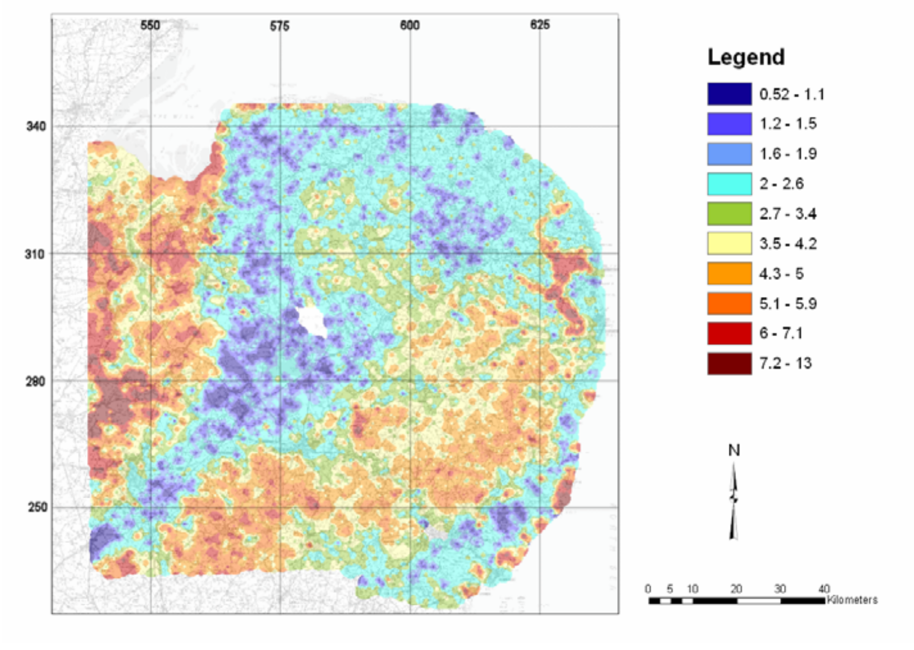


Figure 25. Caesium in topsoil, East Anglia. Values in mg kg^{-1}. Note the similarity in distribution to iodine (Fig. 23).

6.7 Strontium

Theoretically, Sr should be immobile in the surface environment, in waters above about pH 4, because of the low solubility of its sulphate and carbonate (Brookins, 1988). The reality is very different, as even in the presence of high dissolved SO_4^{2-} and HCO_3^- concentrations, Sr can be highly mobile. A good example of this can be seen over the Mercia Mudstone Group (MMG) outcrop in the Humber-Trent region where a mudstone based Sr-rich source rock, also containing gypsum and calcite, gives rise to stream waters in which high concentrations of Sr, SO_4^{2-} and HCO_3^- co-exist at moderately high pH levels (7.5-8.0). Strontium must therefore be considered a highly mobile element under these conditions, though its pattern of dispersion away from its source in the MMG is less clear. There is obviously a dynamic solution-sorption process operating with Sr – in places away from the source, sorption to clay minerals and coprecipitation as sulphate or carbonate is probably dominant. It is worth noting, however, that the area of the MMG outcrop of the Vale of York and Humberhead Levels – thickly covered with Quaternary deposits such as glacial gravels and peat – also shows high Sr concentrations, implying that the groundwater feed to the streams in this area is rich is dissolved Sr derived from the buried MMG.

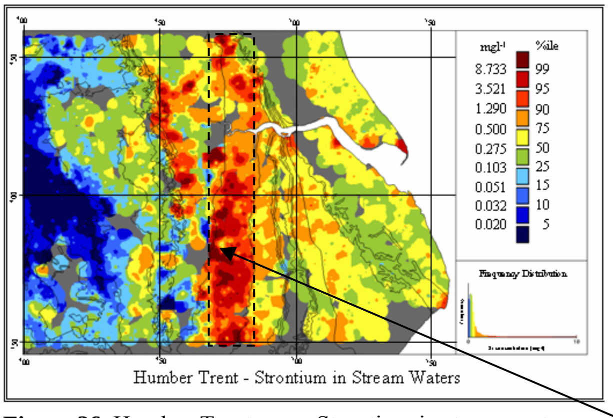


Figure 26. Humber-Trent area: Strontium in stream waters

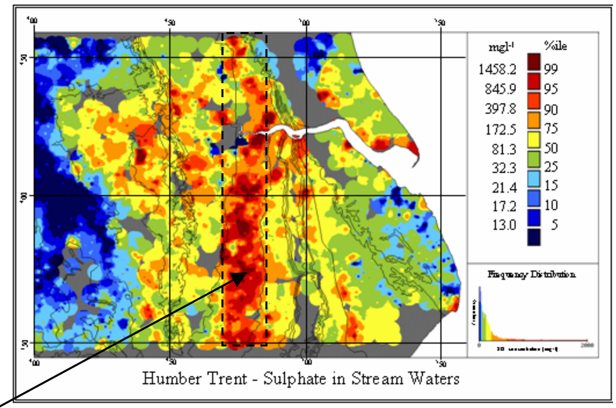


Figure 27. Humber-Trent area: Sulphate in stream waters

Mercia Mudstone Group outcrop (Approx.)

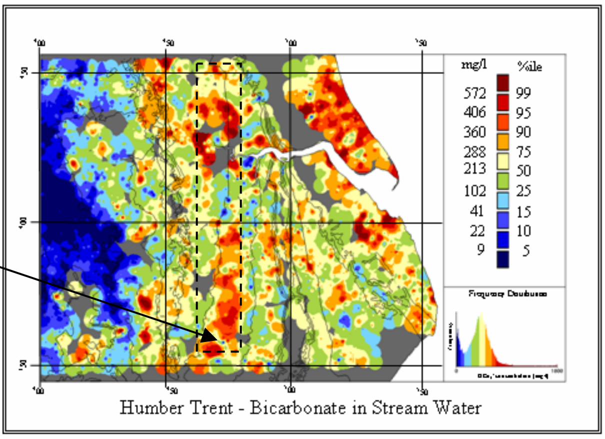


Figure 28. Humber-Trent area: Bicarbonate in stream waters

6.8 Chromium, Tin, Titanium and Niobium.

Chromium (Cr), Tin (Sn) and titanium (Ti) have long been part of the G-BASE element suite for stream sediments and soils. Despite great improvements in analytical technology however, the determination of these elements in stream waters is still extremely difficult as the levels likely to be encountered are very low. Some Cr in waters data are available, but not enough for a reliable assessment of mobility. For Sn and Ti, although there is no such thing as an 'insoluble' element, these two must be regarded as essentially immobile until further improvements in detection limits allow more data to be gathered to confirm or disprove this.

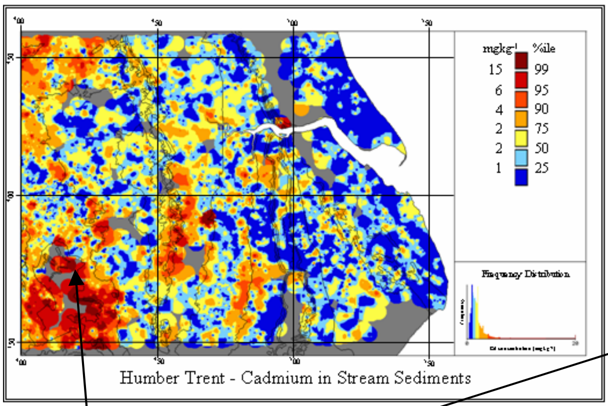
A similar position applies to niobium (Nb). As a 'group five' heavy metal with a highly stable and nominally 'insoluble' oxide Nb_2O_5, and neither an anionic or cationic species stable within the stability field of water at normal temperatures, the theoretical geochemistry would imply an extremely low mobility in the surface environment (Brookins, 1988), and this is supported by analytical observations. Although good regional datasets for Nb in soils and stream sediments exist, typically in the 10-20 mg kg^{-1} range, no reliable data for Nb concentrations in stream waters are available in the UK.

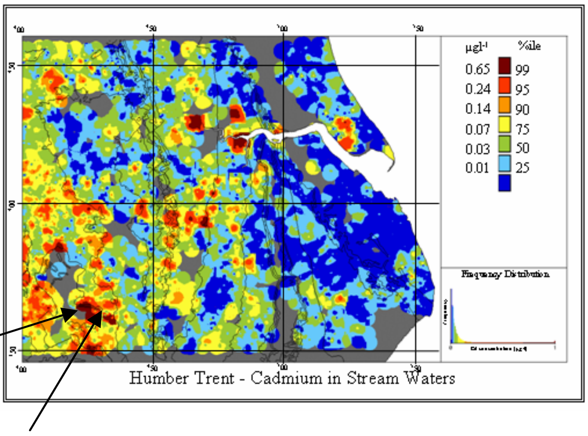
6.9 Lead and Cadmium (and a note on Bismuth).

There are numerous examples of Pb, Zn and Cd anomalies in the UK for which dispersion trends may be examined, mostly derived from sulphide vein mineralisation in which the source minerals are galena (PbS) and sphalerite, (Zn,*Fe*,*Cd*)S. The host rocks are often limestones, but may also be quartzose.

Lead. Generally, Pb from a sulphide source, especially in limestone, has a low mobility due to the very low solubility of the sulphate and carbonate weathering products at pH levels above 5, and strong sorption of any mobilised soluble Pb^{2+} by secondary iron oxides in soils and stream sediments. High concentrations of Pb in stream waters rarely persist for more than a few hundred metres downstream from a lead mine, for example. In a repository, much of the lead may be in metallic form and its behaviour may be different, but, under alkaline conditions, mobility is unlikely.

Cadmium is much more soluble and therefore potentially mobile, but is strongly adsorbed to clay minerals, often in 'exchangeable' form. Until recently, the limit of detection for Cd in stream waters was well above its natural abundance so data were very limited and regional geochemical maps only showed high anomalies. An improvement of two orders of magnitude in sensitivity has allowed much more data to be resolved, and in the Humber-Trent area the Derbyshire Mining Field, stream sediment and water maps show that elevated concentrations in water are much less widespread than high concentrations in sediments, indicating that the dispersion of Cd in solution under these conditions is being limited by sorption.





Derbyshire Mining Field

Matlock

Figure 29a. Humber-Trent area: Cadmium in stream sediments.

Figure 29b. Humber-Trent area: Cadmium in stream waters.

However, values of up to 8 $\mu g\ l^{-1}$ Cd in stream waters in the area south and west of Matlock, in association with high concentrations of Zn, Pb and Ba from mining contamination, does imply at least short-range mobility (at least 1 km) and dispersion of Cd at fairly high concentrations, even in limestone areas with stream water pH typically >7.

A brief study was carried out on a Welsh stream heavily contaminated with Pb/Zn mining waste, as a small part of a PhD thesis (Breward, 1990). This showed that Pb was immobilised due to the relatively high pH for the catchment (6.0) induced by the predominately calcite gangue minerals, despite the very high Pb levels in the ores and waste dumps. However, the clay mineral fraction of the stream sediment was responsible for sorbing the more soluble Zn and Cd on the basis of cation exchange, as much of the 'available' (non-sulphide) metal could be extracted by leaching the sediment with dilute ammonium acetate solution. Although natural cation exchange is a rapid, short-term process, it is clearly effective at stripping metals from solution in stream water, provided the sorbtion capacity is not exceeded and the acidity is not excessive. However, a marked decrease in pH could potentially reverse the sorbtion process and re-release the sorbed metals to solution.

Bismuth data for UK stream sediments were examined, but unfortunately the low natural abundance of the element (< 0.2 mg kg^{-1}) and a detection limit of 1 mg kg^{-1} means that only anomalous values could be resolved. The absence of any reliable data for Bi in waters means that its dispersion trends cannot be assessed.

6.10 Cumbrian granites: Uranium and the importance of source mineralogy and speciation.

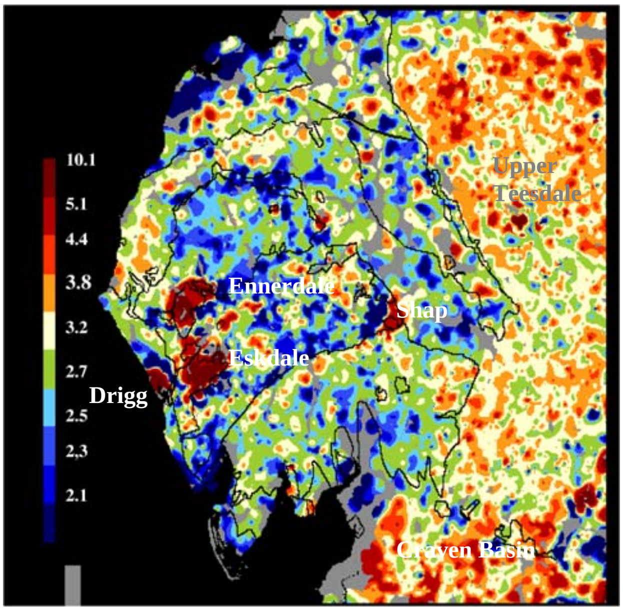


Figure 30a Lake District: Uranium in stream sediments

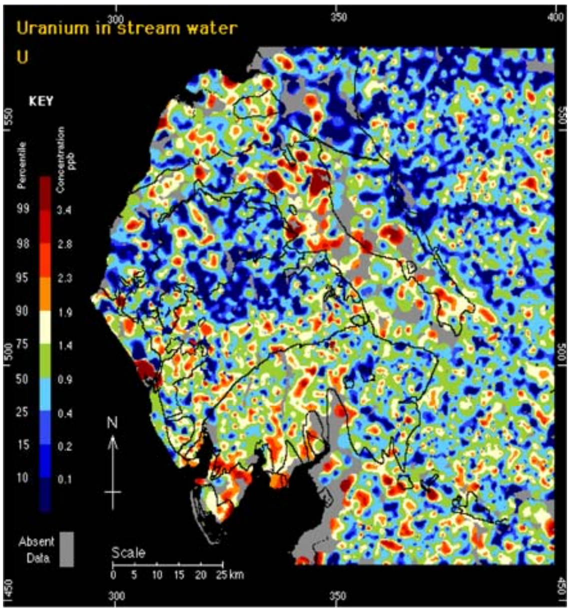


Figure 30b Lake District: Uranium in stream waters

Comparison of the regional geochemical maps for stream sediments and stream waters for uranium in the English Lake District is instructive when considering the effects of the source mineralogy and speciation of an element on its subsequent migration and dispersion. The map for stream sediments (left) is dominated by high U levels (many >25 mg kg^{-1}) over the outcrops of the magmatically-evolved granites of Eskdale, Ennerdale and Shap, with less prominent broader enrichments over the Carboniferous sediments of the Pennine blocks to the east and the Craven Basin to the south. There is one single-site natural high anomaly in Upper Teesdale, and an anthropogenic anomaly on the stream draining from the low-level radwaste disposal site at Drigg on the coast. In contrast, the stream waters map shows no elevation in U levels over the granites, which are indistinguishable from the background, and only a limited scatter of higher values over the Carboniferous of the Craven Basin-Forest of Bowland area. The most prominent natural anomalies are located near outcrops of the Carboniferous Limestone, for example in the Furness area and the margins of the Vale of Eden, where the more bicarbonate-dominated waters allow U to be held and transported in solution as carbonate complexes. However, the stream water U anomaly at Drigg exceeds these by at least an order of magnitude.

The U in the granites, and to a lesser extent in the Carboniferous sediments, is clearly in a form which is resistant to chemical weathering and solution. Such minerals as zircon and monazite are likely to be the resistate sources for U and Th in the granites and sandstones, possibly with more rather more soluble organic complexes in the mudstones of the Craven Basin. The speciation of U in the source for the Drigg stream is not known, but it is clearly much more soluble than the natural minerals of the bedrock.

6. 11 Uranium in Scotland

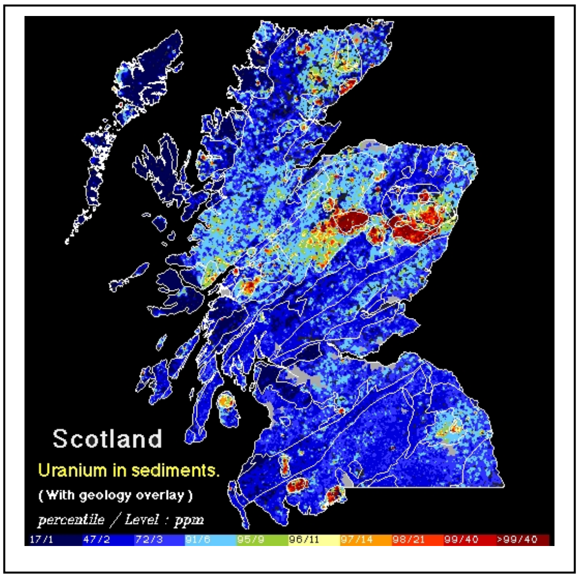
Useful comparisons and contrasts between the distribution of U in stream sediments and stream waters have also been observed in G-BASE data in Strathmore, Deeside, eastern Sutherland and Caithness, Scotland (BGS 1979, 1991).

In Strathmore, stream sediments over the Old Red Sandstone bedrock shows only a slight elevation in U concentrations compared to the regional mean (2 mg kg^{-1}), while the corresponding stream waters have significant enrichments (>6 µg L^{-1}) relative to the regional mean values (0.5 µg L^{-1}). Phosphatic horizons in the mudstone facies of the Old Red Sandstone are the most likely source for the U, with bicarbonate-rich waters being responsible for keeping the U in solution.

The major granite bodies of Deeside and the Cairngorms are rich in uranium, the Cairngorm and Ballater units especially so, with many stream sediment U values in the 200-500 mg kg^{-1} range and several > 1000 mg kg^{-1}. Although the U in stream waters draining from these granites is locally elevated, with some values > 6 µg L^{-1}, the degree of enrichment relative to the mean is nothing like as great as for the sediments. The source minerals hosting the uranium in these granites are simialr to those of the Cumbrian units and show low rates of weathering, while the acid stream waters further limit U dispersion.

On the east coast of Sutherland, the Helmsdale Granite is unusual in that it shows enrichment in both stream sediments and associated stream waters, as here, secondary uranium mineralisation is present in the granite and the country rock, and U from this source is more readily weathered and shows a higher mobility.

In Caithness and in the Black Isle area north of Inverness, some horizons of the Old Red Sandstone bedrock are phosphatic and rich in U, and these show similar solubility patterns and elevated concentrations as those shown in Strathmore.



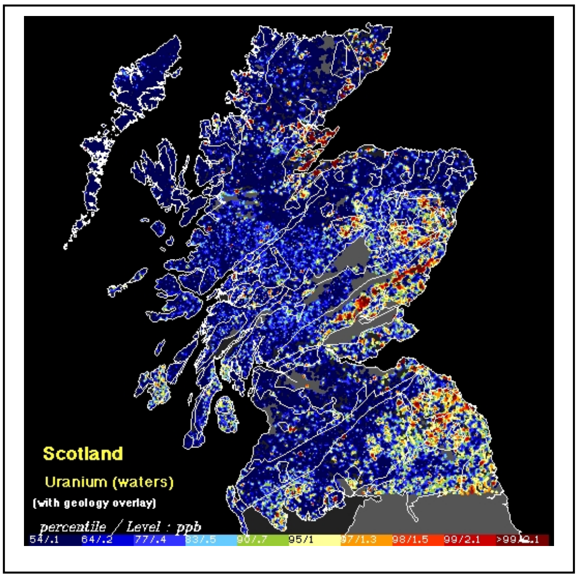


Figure 31a Scotland: Uranium in stream sediments

Figure 31b Scotland: Uranium in stream waters

6.12 Copper mineralisation, mobility and dispersion.

Copper mineralisation in the UK includes the volcanogenic massive sulphide deposit at Parys Mountain, Cu-Pb-Zn sulphides at Snowdon (North Wales), the Coniston area in the Lake District, Cu-Mo porphyry-style mineralisation at Coed–y–Brenin (North Wales), Red-bed style Cu-Ba mineralisation at (for example) Alderley Edge and Clive in the Cheshire Basin , and veins with in the Carboniferous Limestone at Llandudno (North Wales), Ecton Hill (Staffordshire) and Middleton Tyas (North Yorkshire). Extensive Cu mineralisation is also present in south-west England, and native copper has also been found at a few sites in Permian red-beds, such as in the Crediton Trough in Devon.

The behaviour of Cu is important in repository studies since, although it is not a radiogenic element, it may be present in containers, wire, fixings etc. As this is usually in metallic form, the behaviour of native Cu is of special interest, and archaeological studies of Cu have also been employed in the search for natural analogues (e.g. Tylecote, 1979; Johnson and Francis, 1980). Examples of Cu anomalies are given here, but the range of environmental conditions is rather limited for repository studies: most are sulphide-based and weather under oxic conditions to give acid effluents (especially at Parys Mountain). The behaviour of Cu under alkaline, reducing conditions ***may*** be that of low mobility, but it is difficult to categorically confirm this from the available data.

6.12a Parys Mountain, Anglesey, North Wales.

Parys Mountain was the site of a highly productive copper mine, a major world producer in its heyday in the late 18th century and, though long closed, still a site of considerable ore reserves at depth. The main pyrite - chalcopyrite Cu ore weathers to produce a highly acid effluent (in effect, metal-rich dilute sulphuric acid at pH=2) which strongly affects the local drainage, especially the Afon Goch stream catchment and its tributaries, which lies mainly to the south of the main ore-body and drains into Traeth Dulas. The situation is complicated by the presence of former precipitation ponds and the disturbed drainage around the old open-pit workings. The geochemical map (Fig. 32a) shows Cu concentrations in stream sediments while the graph (Fig. 32b) shows a downstream profile of the Afon Goch system with pH and Cu concentrations in water. Although both the Rhosybol and Penysarn branches show very high values for Cu in sediments, it is the very acid Penysarn branch that shows extremely high Cu concentrations in stream water. The near-neutral Rhosybol waters show high levels by regional standards, but those of the Penysarn stream are orders of magnitude higher.

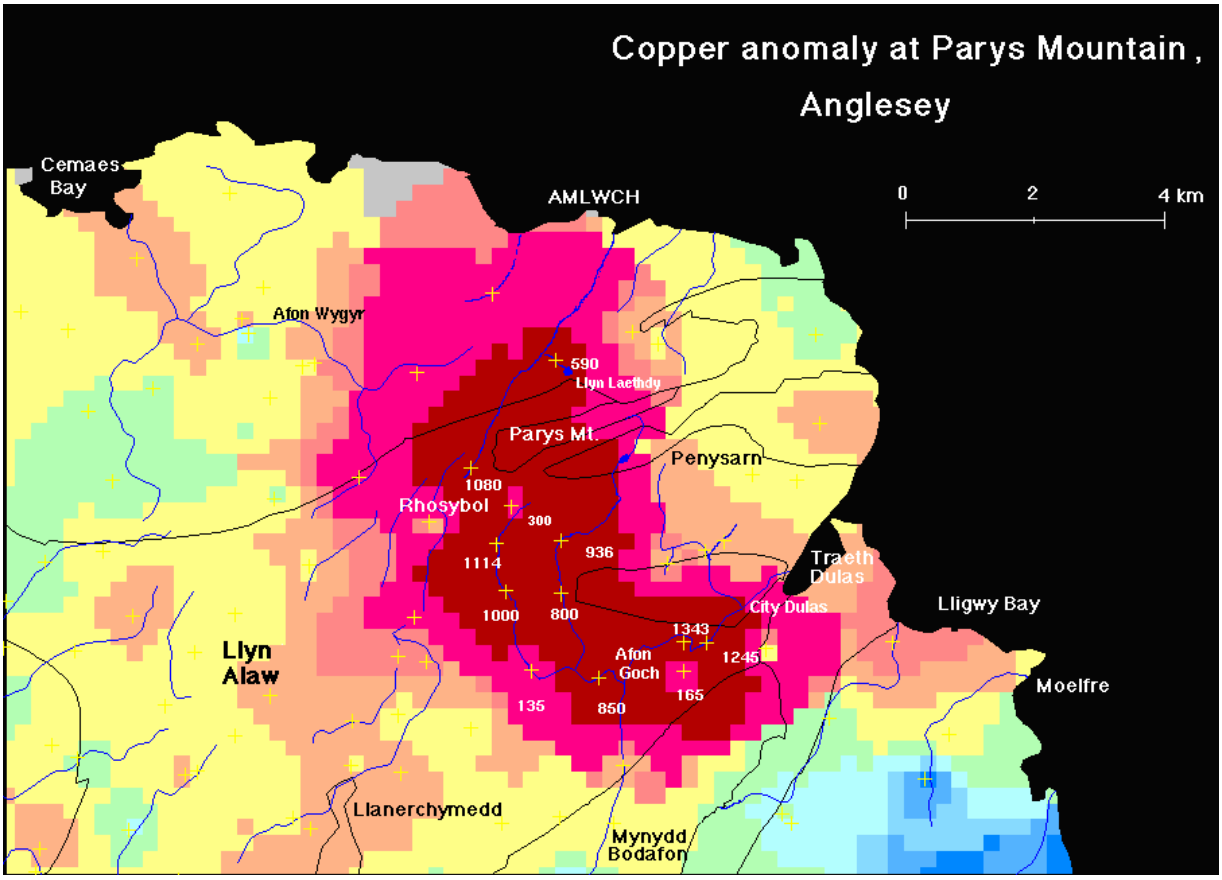


Figure 32a. Copper in stream sediments, Parys Mountain, Anglesey (North Wales). Copper values in mg kg^{-1}.

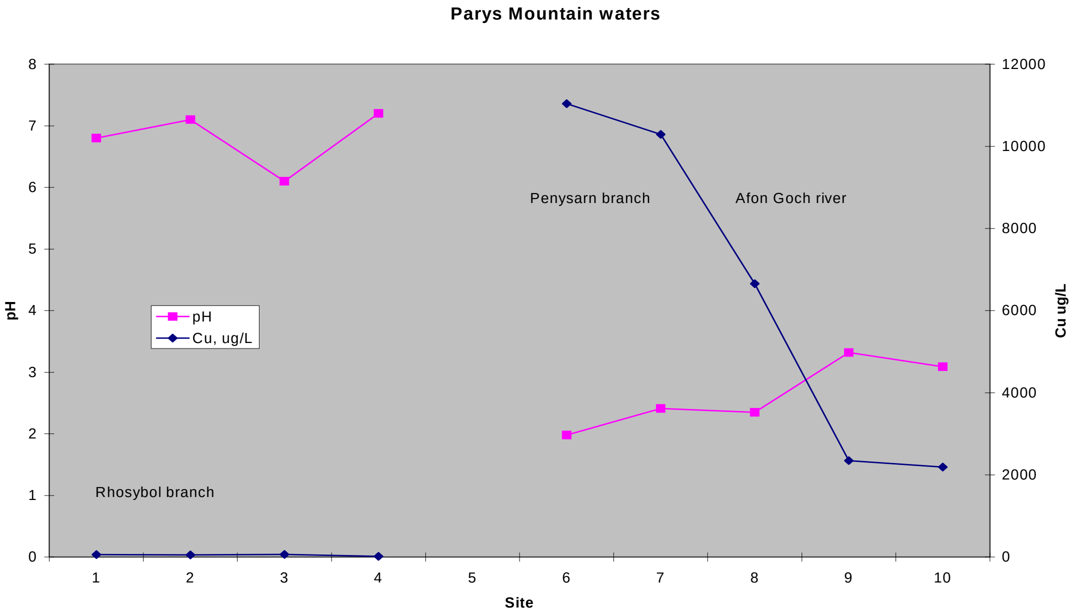


Figure 32b. Graphs of pH and dissolved copper in the Afon Goch stream system, Parys Mountain, Anglesy.

6.12b Snowdon Mining Field, North Wales

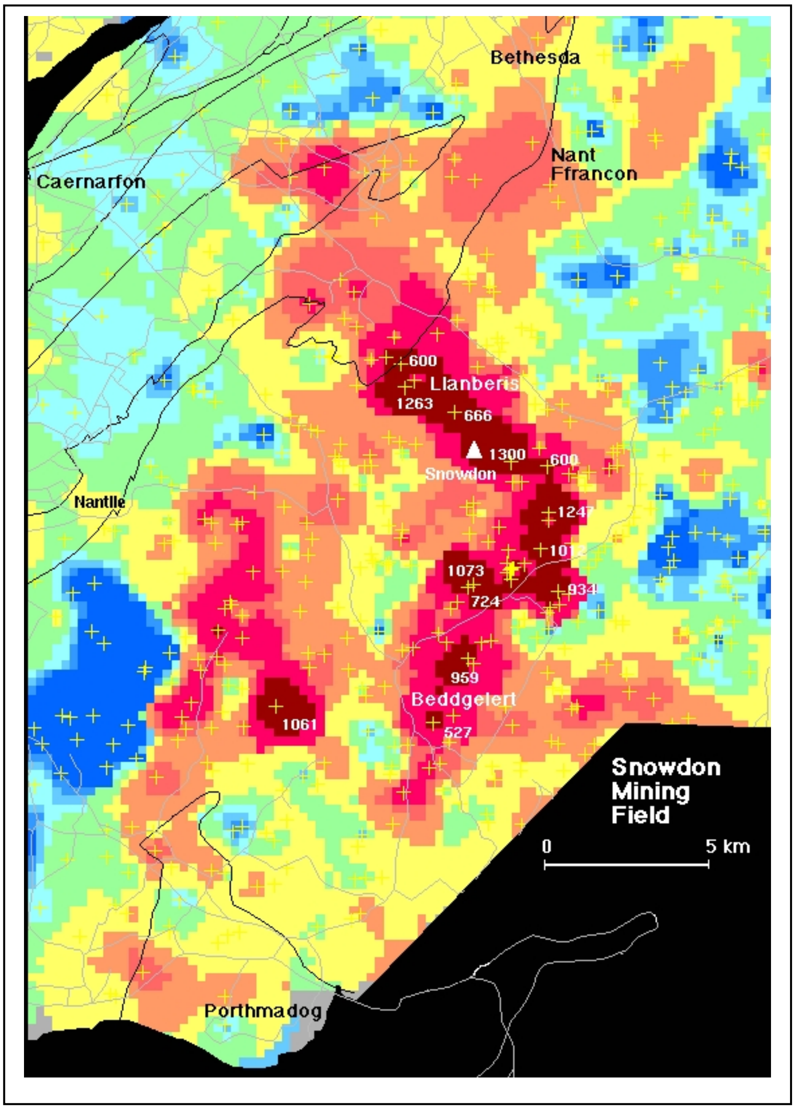


Figure 33. Copper in stream sediments, Snowdon, North Wales.

Copper concentration in mg kg^{-1}.

Multi-element vein sulphide mineralisation (Cu, Pb, Zn, Cd) in the Snowdon area gives rise to high Cu concentrations in sediments. Acidity is not so pronounced as at Parys Mountain, with pH values typically above 5.0, a background Cu level of 1-2 µg L^{-1}, and anomalous Cu concentrations in stream waters only of the order of a few tens of µg per litre, reaching a maximum of about 50 µg L^{-1} where the stream pH is 4.0 and sediment Cu is 1073 mg kg^{-1}. This reinforces the observation that, although Cu is mobile in acid, oxidising conditions, it requires pH values of <4.0 to substantially mobilise Cu to solution even when abundant Cu in sediments is present.

6.12c Ecton Hill, Staffordshire.

Ecton Hill was a substantial copper mine, working a sulphide (mainly chalcopyrite) pipe vein in Carboniferous Limestone, at its most productive in the late 18th and early 19th centuries (Porter and Robey, 2000). Examination of the copper anomaly here is worthwhile as it is a limestone-hosted system and should, therefore, have high-pH stream waters, where these occur. As it lies within the influence of the Widmerpool Formation black shale outcrop (see section 6.2), however, its influence on the local geochemistry is somewhat problematical. There is the additional problem that first-order streams on limestone are rare, and only one sampled stream site sampled by G-BASE, from just east of Ecton Hill, is directly affected by the mineralisation. This has a sediment Cu concentration of 300 mg kg^{-1}, but only 10 µg L^{-1} Cu in waters at a pH of about 8.5. About 5km to the west, the headstream of the River Hamps flows past another former mine site at Mixon, and while 600 mg kg^{-1} is present in sediments at one siteon this river, less than 10 µg l^{-1} Cu is present in the waters at a pH of 8.3. Again pH seems to be the deciding factor in mobilisation of Cu, mobility being low in these natural systems under mildly alkaline conditions.

6.12d. Drax power station, Yorkshire

However, some anthropogenic anomalies do not behave in such a predictable way. One example from the Humber-Trent regional dataset can be seen near the Drax power station, between Goole and Selby, Yorkshire (Figure 33). Here, Cu concentrationss in water exceed 319 $\mu g\ L^{-1}$ at one site (**1**) and 119 $\mu g\ L^{-1}$ at another (**2**), with pH values of 7.8 and 8.5 respectively. The upstream site (**3**) has 6 $\mu g\ L^{-1}$ Cu and a pH of 7.9, fairly typical of the area. The presence of high concentrations of Cu and other elements such as Ni and Zn in solution in an alkaline stream is anomalous, but contamination by run-off from coal tips and fly-ash settling lagoons is likely. Levels of metals in the stream sediments, however, are unremarkable; 40 and 60 $mg\ kg^{-1}$ Cu, only marginally above the local median values. The speciation of the Cu in solution is not known, but conductivity levels are very high, as are levels of chloride, sulphate and nitrate. Complexation (with chloride) and possibly binding to coal organics are, therefore, the most likely controls on Cu solubility here, and clearly these over-ride the pH limiting that would be expected at such a high pH. Although this site is anthropogenic and anomalous, in some ways it more closely resembles a repository in its alkaline nature than do many of the natural Cu anomalies examined. Alkaline regimes in repositories cannot therefore be totally guaranteed to immobilise Cu.

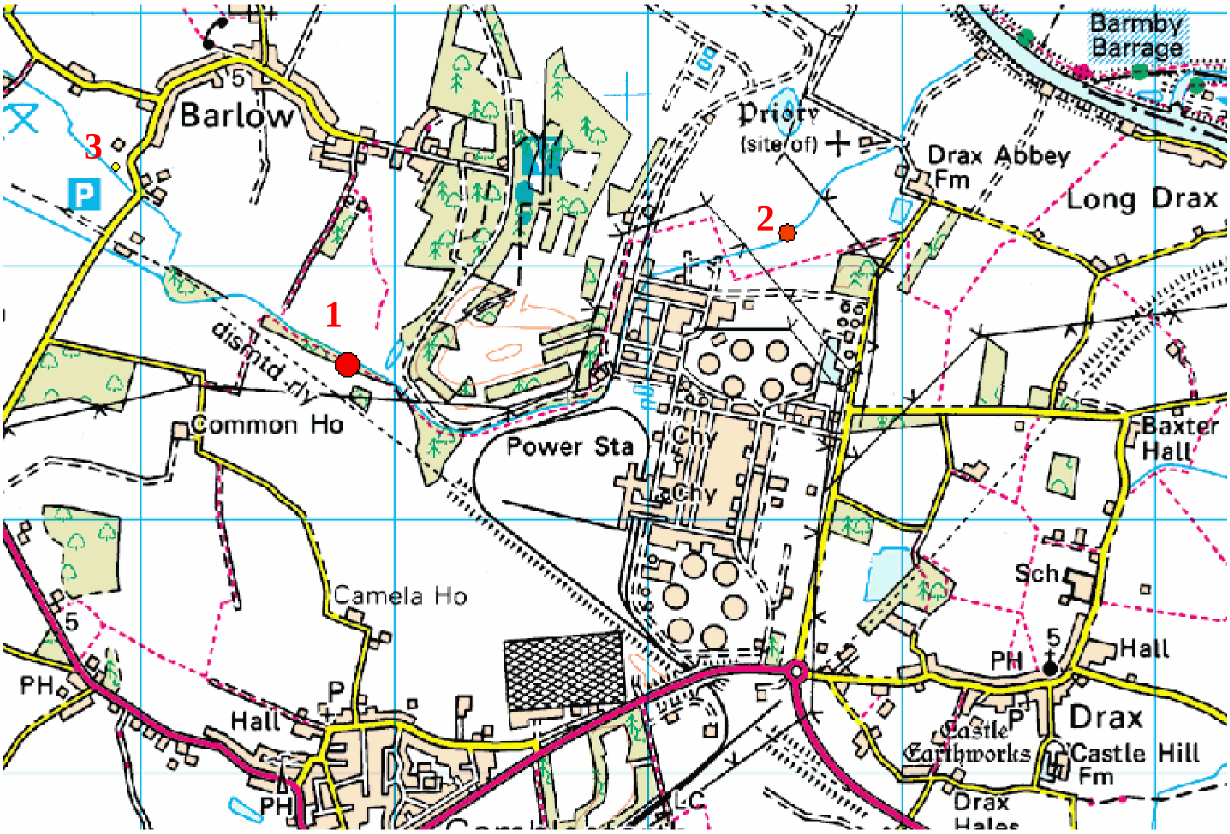


Figure 34. Anomalous water sample sites at Drax coal-fired Power Station. Background map: Ordnance Survey 1:50,000 topographic.

6.12e. Coed - y- Brenin, North Wales, and others.

Coed-y-Brenin is a (currently) subeconomic copper-molybdenum porphyry-style mineral deposit in a forested area within the Harlech Dome area of North Wales, adjacent to the Dolgellau gold mineralisation belt. The site is significant in that it was not historically mined directly, but was a mining curiosity as it was worked on a small scale by digging peaty turf impregnated by copper absorbed from shallow groundwater, and burning it to release the metal (Andrews and Fuge, 1986). Three G-BASE sample sites in the area show high Cu concentrations in both stream sediments (up to 5000 $mg\ kg^{-1}$) and stream waters (up to 159 $mg\ l^{-1}$) along with high Mo levels, at near-neutral pH. The site was studied in greater detail as part of a survey of the Harlech Dome area by the MRP (Cooper et al., 1985) and could provide the basis for further natural analogue studies for both Cu and Mo. Other MRP studies on porphyry-type Cu deposits (often including Mo enrichment) include those at Llandeloy, south-west Dyfed, Wales (Allen et al., 1985), Ballachulish, Scotland (Haslam and Kimbell, 1981) and at Black Stockarton Moor, South-west Scotland (Brown et al, 1979). The MRP studies carried out at Middleton Tyas (North Yorkshire) could also form the basis of a further study on Cu dispersion (Wadge et al, 1982).

7. Element mobility: Summary and conclusions based on examples given in this report.

Antimony

Only the dispersed black-shale Sb enrichment in the Widmerpool Formation east of Ashbourne gives analytically-reliable, above-detection antimony data for waters as well as for soils and stream sediments. Here, locally elevated Sb stream water concentrations (3.9 µg L^{-1}) are found in close proximity to the mineral source, but dispersion appears to be less than 1 km downstream before sorption to components of the stream sediments (clays, iron oxides or organic matter) reduces the Sb concentration in solution to the regional mean levels (0.4 µg L^{-1}).

Barium

In general the low solubility of barium carbonate (Witherite) and sulphate (Barite) (solubility products: Log K_s = -8.56 and -9.97 respectively) would suggest that the transport of barium in solution in the biosphere should be severely limited. This is borne out for the localised barium mineralization in Snowdonia, the Nod Glas outcrop, Builth and Llandrindod Wells, and the dispersed black shale-hosted barium found in Pembrokeshire and the Widmerpool Formation. In contrast, barium mineralisation at Shelve and Bridgend, parts of Cheshire and the Clwyd basin are associated with elevated barium concentrations (>300 µg L^{-1}) in stream waters.

There are also elevated barium in stream waters concentrations over the Old Red Sandstone outcrop of the Welsh borders, but without obvious localised sources indicated by elevated stream sediment levels. This suggests that either the source remains unknown or is dispersed. These are bicarbonate-rich waters and it is most likely therefore that Ba is being held in solution and transported as bicarbonate complexes. In the Collingham barium anomaly, it is difficult to estimate how much of the dispersion of the bedrock anomaly is due to downslope soil movement as opposed to stream transport.

Cadmium

In the Derbyshire Mining Field, the presence of numerous point sources of cadmium associated with vein mineralisation and mine waste gives rise to a dispersed Cd anomaly in stream sediments, but this is not matched by equivalent broad anomalies in stream waters. Only very localised stream-water Cd anomalies are generated which, although they may be at significant concentrations in solution in close proximity to the mineral source (such as sphalerite), are very limited in their dispersion distance. This can be attributed to the high sorption affinity of Cd to clay minerals in the stream bed, especially in near-neutral and alkaline waters, which is also supported by the example from Wales.

Caesium

The available data for sediments and soils held by BGS is limited to the most recent G-BASE surveys, and no Cs in stream water data is yet available. Despite locally high Cs levels in soils and stream sediments (up to a maximum value of 13 mg kg^{-1}) , a critical visual examination of the available soil and stream sediment geochemical maps for East Anglia suggests that dispersion is limited by its strong degree of sorption to clay-rich and sediments, whereas it may be more readily leached from sandy, well-drained soils. This observation supports previous studies on Cs mobility and retention in UK soils carried out in the wake of the Chernobyl accident in 1986 (e.g. Wright et al, 2003).

Cerium- see lanthanides.

Chloride

Despite the presence of halite beds at subcrop and undergoing solution by groundwater within the Cheshire Basin, the complexity of the superficial Quaternary deposits and anthropogenic inputs gives rise to a delocalised source which results in a dispersed Cl anomaly. Chloride concentrations up to 3000+ mg L^{-1} are present in surface streams. The lack of available data for larger, high-order, streams in the G-BASE dataset make it difficult to follow anomalous Cl concentrations for a significant distance downstream, so the dispersion distance is hard to estimate, but will certainly be >5 km.

Chromium

Although good data for soils and stream sediments exists, the poor limit of detection relative to a very low natural concentration in the water data makes the assessment of mobility and dispersion trends for Cr uncertain, but suggests a very low mobility under normal conditions. Even over Cr-rich sediments in Wales with Cr concentrations >250 mg kg^{-1}, Cr levels in solution do not exceed the ICP-AES detection limit 16 µg L^{-1}. In spite of the great improvement in sensitivity achieved with ICP-MS analysis, only 20% of the Humber-Trent regional water data exceeds the detection limit of 0.4 µg L^{-1}. The generally resistate nature of most naturally-occurring Cr-bearing minerals, such as spinels, is a further barrier to Cr mobilisation and dispersion. In some cases of contaminated land where both soluble Cr^{III} and Cr^{VI} (chromate and dichromate) compounds may be present, mobility may be significantly greater.

Copper

Copper is relatively mobile in solution as Cu^{2+} under strongly acid conditions, but generally shows much lower solubility under normal pH ranges. However, the contaminated stream at Drax suggests that complexation may be a feature in some alkaline streams keeping Cu in solution when the pH regime would suggest otherwise. The strong affinity of Cu to form complexes with organic matter is well known, but the stream waters at the Drax site contain high levels of chlorides derived from the coal and waste-ash heaps, and therefore probably also contain chloro-complexes of copper in solution, such as $CuCl_4^-$. The effects of counter-ions acting as complexing ligands, where these are present at high levels, should always be taken into account when assessing mobility. In this case, as the Cl^- level falls with dilution, these complexes will probably break down quickly downstream and the Cu will also be lost from solution, probably by sorption to sedimentary organic matter.

Iodine

The concentration of iodine into organic-rich sediments implies a dispersed source, which in the case of iodine, probably includes atmospheric deposition via aerosols and rainfall as well as an input and controls from the parent material of the soils (i.e. the bedrock and superficial geology). The very limited I^- in water data available suggests a positive relationship with concentrations in surface soils, but is not conclusive. Consequently the mobility is difficult to assess directly, but the tight definition and sharp geochemical gradients which can be seen in the soil geochemical map for East Anglia imply limited dispersion.

Lanthanides (plus Y and Zr)

The lanthanides, Ce and La, show generally low environmental mobilities but cannot be regarded as being completely insoluble, as some credible patterns for their concentrations in stream water are present. Similar properties are shown by Y and Zr. The fact that these elements, long regarded as ‘insoluble’ and immobile, are now known to have sigificant, if low, solubilities due to improvements in analytical techniques, is an important observation. The relationship to the source mineralogy may be especially important in these cases. The suggested use of the lanthanides as analogues for the more geochemically complex actinides is questionable, as the latter show a greater variation in redox state and complex formation.

Lead

Examples from point sources (mineral veins containing galena, PbS, as the main lead carrier) suggest very limited mobility of lead in solution at normal ranges of pH. Strong sorption to the iron oxide fraction in stream sediments and soils will further limit mobility and bioavailability, if surface conditions do not radically alter.

Molybdenum

Elevated stream water Mo concentrations (up to 130 $\mu g\ L^{-1}$) are found in close proximity to the localised Mo mineralization in the Widmerpool Formation. The broader area of the Widmerpool Formation outcrop shows a more dispersed anomaly in stream sediments which is also reflected in the elevated stream water concentrations. It is difficult to give indications of maximum transport distances, which may be >5 km, as no samples are available for the larger high-order streams in the G-BASE dataset.

Niobium

Niobium is essentially immobile under natural conditions. Naturally-occurring concentrations of Nb in stream waters are well below the limits of detection of the ICP-MS analytical technique used for G-BASE samples.

Platinum Group elements

In the absence of suitable data, these can only be suspected of being largely immobile under natural conditions.

Rubidium

Dispersed geogenic sources of Rb giving rise to high Rb concentrations in stream sediments over the Mercia Mudstone Group outcrop are not reflected in elevated concentrations in stream waters. This indicates a high partition coefficient of rubidium onto clay minerals in stream sediments relative to waters, and this is clearly a major limiting process for Rb dispersion.

Selenium

Although good data for soils and stream sediments exist, the absence of water data makes assessment of mobility and dispersion trends impossible using this data. However, numerous studies on the health impacts of selenium deficiency and excess (Fordyce, 2007; Fordyce et al; 2005, Fordyce and Green, 2000, Broadley et al., 2006) have shown that Se uptake to food plants from soils can be significant.

Silver

Limited data for soils and stream sediments exist, albeit with a high detection limit relative to its low abundance, but the absence of water data makes assessment of mobility and dispersion trends impossible. The low solubility of many of its compounds would suggest a limited mobility, but as ever, complexation reactions may be important.

Strontium

Strontium is a highly 'mobile' element within the area of the Mercia Mudstone Group outcrop, showing a clear spatial relationship between stream sediments and stream waters. It is unclear whether this mobility extends away from the Mercia Mudstone Group outcrop which provides the Sr source, or that equilibrium with the low-solubility carbonate and sulphate is achieved.

Technetium

Technetium does not occur naturally. Molybdenum is a useful 'first-order estimate' analogue element, as there are similarities between TcO_4^- and MoO_4^{2-}, and between MoS_2 and TcS_2.

Tellurium

Insufficient data are available for a reliable assessment of its mobility.

Thorium

Dispersed Th mineral sources in the east Pennine Millstone Grit give rise to localised enhanced Th concentrations in the low-pH stream waters. Note, however, that in the Humberhead Levels, Th solubility also appears to be enhanced, perhaps due to the lower pH and / or the presence of organic colloids. There are also units within the Lias that show enriched Th in sediments with associated localised stream water enrichment. Thus Th has a greater solubility and potential mobility than might be expected from its typically resistate mineralogy and high field strength element geochemistry.

Tin and Titanium

Tin is low-abundance trace metal, titanium an abundant metal, but both must be regarded as essentially immobile, as water data are unavailable due to the very low natural levels in solution being below the currently-achievable detection limits.

Uranium

Elevated stream water U concentrations (up to 6 $\mu g\ L^{-1}$) above the dispersed uranium mineralization in the Widmerpool Formation generally show less than 2 km of downstream migration. Stream sediments above the southern Lake District granites show high concentrations of uranium derived from the underlying granites. However, this is not reflected in uranium enrichment in the associated stream waters. This is most probably due to the low solubility of the resistate uranium-bearing mineral phases within the granites.

Vanadium

Moderately elevated V stream water concentrations (up to 5 $\mu g\ L^{-1}$) are found in a rather weak association with the dispersed black shale V enrichment in the Widmerpool Formation, as shown by concentrations in the stream sediments, but the maximum dispersion distance seems to be <2 km. The lack of a strong spatial correlation between the stream sediment and stream water enrichment patterns implies a limited mobilisation of V in this area. Higher V concentrations in waters present over the River Tean - Dove Valley floodplain sediments to the south of the Widmerpool outcrop are curious and in need of further examination.

Yttrium- see lanthanides

Zirconium- see lanthanides

8. Conclusions.

The examination of natural and, indeed, anthropogenic geochemical anomalies as a means of understanding element mobility, and extrapolating this to the behaviour of elements from a repository source, is potentially of considerable relevance to post-closure safety assessment, but is a complex and far-ranging topic for investigation.

This preliminary study has examined a handful of UK sites in moderate detail. It has been restricted to the most readily-available datasets i.e. G-BASE. The smaller-scale MRP and other BGS data have only received a cursory examination and it is likely that additional information could be extracted. Data from BGS overseas projects has not been examined in detail and nor have academic theses.

However, to be useful, high-quality spatially-related combined sediment, soils and stream water datasets for the required elements are necessary, and these are not widely available.

As noted above, a thorough appraisal of the factors influencing the transfer of elements from the geosphere to the biosphere should include the biogeochemical aspects of weathering and mobility studies, including such aspects as uptake of elements by plants. These aspects are not usually covered in BGS data. Further work should focus on these data for a more complete examination of natural element dispersion processes.

9. Glossary of terms

Acidity (pH)

The concentration of hydrogen ions in a water-based solution. It is measured by the logarithmic term pH which is defined as: $pH = -\log_{10}[H^+]$. It is a principal variable in aqueous geochemistry.

Chalcophile element

An element having a strong preferential affinity for sulphur, forming stable sulphide minerals.

Fission products

Elements produced by the splitting-apart of the atomic nuclei of heavy elements such as uranium and plutonium.

Humic and fulvic acids

High molecular weight organic acids produced during the decay and breakdown of vegetation.

Lithophile element

An element having a strong preferential affinity for silicate rock-forming minerals.

Mobile elements

Those which will readily dissolve and migrate from their source minerals to enter the hydrosphere and biosphere.

Radiogenic nuclides (radionuclides)

Those formed by radioactive decay, or other nuclear processes such as fission or neutron capture.

Radiolysis

The dissociation of molecules by intense radioactivity.

Redox

The state of oxidation or reduction of an element, depending for example on the availability of oxygen in the system. Changes in redox state can strongly influence element solubility, mobility and toxicity. Along with pH it is one of the principal variables in geochemistry.

Resistate elements

Those elements which are generally immobile and form minerals that are strongly resistant to chemical and physical weathering.

Speciation (geochemical)

The chemical form in which an element is found. This includes its redox state, the other elements with which it is combined, and the overall electrical charge on dissolved ions.

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Appendix 1. Theoretical Geochemistry of the elements used in this report.

Antimony Sb

Antimony (Sb) has an approximate atomic mass of 122, three main oxidation states (-3, +3, and +5) and two naturally occurring stable isotopes, ^{121}Sb and ^{123}Sb. It is a low-abundance chalcophile element forming several rather rare minerals including stibnite (Sb_2S_3), a variety of sulphosalts, valentinite (Sb_2O_3) and kermesite ($2Sb_2S_3.Sb_2O_3$). However, it is more usually present at trace levels in minerals such as ilmenite, magnesium-olivine, galena, sphalerite and pyrite.

Antimony shows low environmental mobility, especially under reducing conditions. Under very low (below pH 3.0) or very high pH (above pH 10.0) values, antimony converts to the $Sb(OH)_2^+$ cation and $Sb(OH)_4^-$ anion respectively (McBride, 1994). Antimony adsorbs strongly to Fe hydrous oxides, and under less extreme pH conditions ionic Sb usually hydrolyses to low-solubility basic salts and complexes with clay minerals.

Antimony is a non-essential element, and, at high concentrations, it is more toxic than either arsenic or lead; Sb^{3+} compounds being more toxic than Sb^{5+} compounds. It has no known function in living organisms (Mertz, 1987). Anthropogenic sources of antimony include copper-lead smelters, coal combustion and car exhaust fumes (Reimann and de Caritat, 1998). With its low natural abundance, it is a useful indicator of industrial contamination in regional geochemical surveys.

Barium Ba

Barium (Ba) has an approximate atomic mass of 137, one main oxidation state of (+2) and seven naturally occurring stable isotopes, ^{130}Ba, ^{132}Ba, ^{134}Ba, ^{135}Ba, ^{136}Ba, ^{137}Ba, and ^{138}Ba. It is a lithophile element forming several minerals including barite ($BaSO_4$) and witherite ($BaCO_3$), but is widely distributed as an accessory element in such minerals as apatite, K-feldspars, micas and calcite.

Barium usually has low environmental mobility; the more toxic soluble barium salts in water are often rapidly converted to insoluble carbonate and sulphate salts, which precipitate. Under suitable conditions, Ba^{2+} readily substitutes for K^+ in some minerals such as felspars, due to the similar ionic radii of the two elements (McBride, 1994). It can be immobilised by precipitation with sulphate or carbonate, or by co-precipitation with Fe/Mn oxides, at low salinities (Coffey *et al.*, 1997). Manganese oxides seem to have a particular affinity for absorbing Ba, and this can give rise to mixed-oxide secondary minerals such as psilomelane ($(Ba,H_2O)_2Mn_5O_{10}$. This behaviour also appears to be followed by Ra (Milodowski et al., 1999) and this may be an important mechanism in the control of both Ba and Ra dispersion.

Barium may be essential for some organisms, but generally its soluble compounds are toxic to humans, animals and plants, although the very low solubility of barium sulphate limits its toxicity. However, the dietary intake should not exceed 20µg/g. It has been shown that very high barium concentrations (10 mg/kg) in water can cause high levels of cardiovascular mortality (Mertz, 1987). Anthropogenic sources of barium include lead mining, paper and paint manufacturing.

Bismuth Bi

Bismuth (Bi) has an approximate atomic mass of 209, two main oxidation states of (+3 and +5) and one naturally occurring stable isotope, ^{209}Bi. It is a low-abundance heavy chalcophile element forming several rare minerals including bismuthinite (Bi_2S_3) and bismite (Bi_2O_3) but is more widely distributed as a trace element in galena, where a coupled substitution of silver and bismuth replaces lead. Other possible host minerals for bismuth include chalcopyrite, sphalerite and a variety of sulphosalts. To a limited extent, bismuth can also display lithophile tendencies, replacing calcium in apatite (Angino and Long, 1979).

Bismuth has low mobility under most environmental conditions. It shows similar chemical behaviour to arsenic and antimony, and also to a more limited extent to lead, germanium and tin (Feldmann *et al.*, 1999). Bismuth is usually found with lead–zinc–copper sulphide mineralisation, and has been used as a pathfinder element for rarer metals such as gold (Li and Thornton, 1993). It becomes concentrated in stream sediments and soils as the pH increases from 5.0 to 8.0 (Li and Thornton, 1993). It has been suggested that methylated bismuth compounds occur in the environment, similar to those of arsenic, but this is yet to be confirmed.

Bismuth is considered non-essential for organisms. It is a relatively non-toxic element, and is found in low quantities in human tissues. The normal daily intake is around 5µg/ day (Mertz, 1987). It can bind to Zn^{2+} and Fe^{3+} in the human body, and toxic side effects include burning and itching of the eyes and headaches (Feldmann *et al.*, 1999). Anthropogenic sources of bismuth include lead, copper, gold and silver smelting, waste water and sewage sludge (Reimann and de Caritat, 1998).

Cadmium Cd

Cadmium (Cd) has an approximate atomic mass of 112 and has one main oxidation state of (+2) and eight naturally occurring stable isotopes, ^{106}Cd, ^{108}Cd and ^{110}Cd to ^{116}Cd. It is a low-abundance chalcophile element forming several minerals including greenockite (CdS) and the rare octavite ($CdCO_3$) and monteponite (CdO) (Reimann and de Caritat, 1998), but is most commonly found in trace amounts in other sulphides, especially sphalerite where it substitutes for zinc, and also silicates such as biotite and amphiboles.

Cadmium is very soluble and mobile at low pH values and can substitute for calcium and manganese. Cadmium compounds in stream sediments are easily re-dissolved during sediment disturbance, for example, flooding. The majority of cadmium in stream sediments is of a carbonate fraction, with smaller proportions as Fe/Mn oxides, bound to clays, and organics (Curtis and Walker, 1994). Excess magnesium and calcium added to streams can inhibit the release of many metals from sediments, such as iron, but it may increase the soluble cadmium content, due to the competition for adsorption sites on clays by cations (Curtis and Walker, 1994). In comparison with Pb and Zn there is little uptake of Cd^{2+} on to amorphous $Fe(OH)_3$ below pH 6.0 (O'Day *et al.*, 1998), sorption by clays being more important.

Cadmium is biologically non-essential, and is toxic to humans through inhalation of dust causing lung damage, and may cause cancer from long-term exposure (WHO, 1996). The maximum tolerable intake of cadmium is regarded as 7µg/kg of body weight per day (WHO, 1996). Plants can accumulate cadmium via their roots, and fungi such as mushrooms, and plants such as spinach and wheat may concentrate cadmium. Anthropogenic sources of cadmium include zinc and copper smelters, electroplating, fertilizers and sewage sludge.

Cerium Ce

Cerium (Ce) has an approximate atomic mass of 140, two main oxidation states of (+3 and +4) and four naturally occurring stable isotopes, ^{136}Ce, ^{138}Ce, ^{140}Ce and ^{142}Ce, of which ^{140}Ce comprises 88.5% of the total mass. It is a lithophile metallic element, the most abundant of all the Rare Earth Elements (REE`s). It forms several minerals including the common monazite ($(Ce,La,Nd,Th)(PO_4SiO_4)$) and rarer bastnaesite ($(Ce,La)CO_3(F,OH)$) and cerite ($(Ce,La)_9(Mg, Fe)Si_7(O,OH,F)_{28}$), but is also widespread as an accessory element in apatite, feldspars, sphene, fluorite and zircon.

The elemental mobility of Ce is very low, mainly due to the stability and low solubility of $CePO_4$ and CeO_2 (Brookins, 1988). It is associated with the 'resistate' group of elements which includes Zr, Hf and Th. In stream sediments derived from high grade metamorphic rocks and granites, the trace element REE`s are controlled by the heavy mineral fractions such as monazite and garnet (Chandrajith and Tobschall, 2001). Cerium, along with heavy REE`s, if released as Ce^{3+} in solution during weathering, always absorbs strongly onto Fe oxides (Leleyter *et al.*, 1999).

Cerium is considered biologically non-essential. It can replace Ca in the bone structure of the human body, which may cause skeletal problems. It can certainly cause pneumoconiosis due to inhalation of Ce-bearing dusts, and it has also been implicated in endomyocardial fibrosis disease in Africa (Smith, 1998). Anthropogenic sources of cerium include glass and ceramic dust and the steel industry (Reimann and de Caritat, 1998). Recently, Ce has become widely used in a fuel-borne catalyst (Eolys) to facilitate the regeneration of diesel particulate filters, which may increase the ambient levels of Ce in the environment.

Caesium Cs

Caesium is the heaviest member of the alkali metals group (which includes Li, Na, K and Rb) apart from the ultra-rare radioactive Francium, having an atomic number of 55 and a mass of approximately 133. Typically for the alkali metals there is only one oxidation state, +1. There is one stable isotope -^{133}Cs – and important radioisotopes in ^{134}Cs, ^{135}Cs and ^{137}Cs, the latter being of particularly interest (half-life 30.1 years) and an important component of nuclear fallout from accidents such as Chernobyl. Caesium is a low-abundance lithophile element (typically 3 mg kg^{-1} in continental crust) which forms few minerals of its own other than pollucite ($(Cs,Na)_2Al_2Si_4O_{12}.H_2O$), but is hosted by micas such as biotite, muscovite, zinnwaldite and lepidolite, plus beryl and K-felspar. It is, therefore, more abundant in granites than in basic igneous rocks, though it is still more abundant in shales and mudstones due to its affinity with clay minerals, to which it binds strongly.

Although the Cs^+ ion in solution closely resembles K^+ in its solubility, its much stronger tendency to bind to clay minerals and soil organic matter is a distinguishing feature, and limits its mobility. Thus, Cs from Chernobyl fallout can still be detected, with only partial attenuation, in soils in some high-rainfall upland areas in the UK twenty years after the accident. Thus K is not a good analogue element for Cs; Rb is closer, but there are still differences in sorbtion characteristics. However, there are abundant data on Cs mobility, so the use of analogues in this case is hardly necessary.

Caesium has a relatively low chemical toxicity although it has no known biological function and cannot replace K in biochemical activity. Unlike radiotoxic elements such as ^{131}I, Cs is not concentrated in specific organs and tissues of the body.

Chlorine Cl

Chlorine is the most abundant element of the halogen group which also includes F, Br and I. Its atomic number is 17, its atomic mass 35.5 with two stable isotopes (^{35}Cl and ^{37}Cl) and oxidation states of -1, 1, 3, 5 and 7, of which -1 (chloride) is by far the most important in the natural geological and surface environment. It is a lithophile/atmophile non-metal which forms several important minerals such as halite (NaCl), sylvite (KCl) and carnallite ($KMgCl_3.6H_2O$), which are typically evaporite minerals, and others such as the rarer sodalite ($Na_4Al_3Si_3O_{12}Cl$) and eudialite ($Na_6ZrSi_6O_{18}Cl$). Other host minerals include biotite, apatite and sphene, especially in fluid inclusions in these minerals, and Cl is more abundant in acid than in basic igneous rocks.

Chlorine as the chloride ion Cl^- is essentially a very soluble and mobile species, largely unaffected by naturally-occurring ranges of Eh and pH, and is a dominant anion in the hydrosphere and biosphere. It is an essential major element in all organisms. The oceans and saline groundwaters are a major reservoir for the element, as are evaporite deposits. Chloride is a ‘conservative’ ion, that is, it is reluctant to bind to other substrates which would remove it from solution. Few metal chlorides are insoluble, and these are rare (e.g. AgCl). Only evaporation is a major removal mechanism of Cl from solution, but Cl may also be removed from the hydrological cycle by the burial of marine sediments with entrained brines, though these may be removed and remobilised during diagenesis and play a subsequent part in mineralisation, for example.

Evaporation of chloride-rich waters used in irrigation systems has led to salinisation of soils and consequent loss of productive agricultural land in some arid and semi-arid parts of the world. Many anthropogenic Cl compounds, especially organochlorines, are highly toxic and include such pesticides as DDT and compounds such as PCBs and dioxin.

Chromium Cr

Chromium (Cr) has an approximate atomic mass of 52, three main oxidation states of (+2, +3, +6,) and four naturally occurring stable isotopes, ^{50}Cr, ^{52}Cr, ^{53}Cr and ^{54}Cr of which ^{53}Cr contributes 84% of the total mass. It is a lithophile metallic element forming several minerals including chromite ($FeCr_2O_4$) and the rare crocoite ($PbCrO_4$), but is present as an accessory element in several others such as spinels, amphiboles, micas, pyroxenes and garnets. It is, therefore, much more abundant in basic and (especially) ultrabasic rocks than in granitic rocks and sediments derived from them.

Chromium is a low mobility element, especially under moderately oxidising and reducing conditions and near-neutral pH values. Cationic Cr^{3+} is the main form of chromium in the environment, though it is rarely present as the free hydrated ion. Anionic Cr^{VI}, as the chromate ion CrO_4^{2-}, rarely occurs except in industrial waste waters, and is reduced naturally to Cr^{3+} in stream sediments over time (Whalley *et al.*, 1999). Cr^{3+} readily substitutes for Fe^{3+} in minerals, and precipitates as insoluble $Cr(OH)_3$ at moderate to high pH values. Organic matter reduces chromium (VI) and binds to the Cr^{3+} produced, making it stable (McBride, 1994).

Chromium, once thought to be non-essential, is now known to have at least one important biological function (Frausto da Silva and Williams, 1991). Chromium has varying toxicity depending on it’s oxidation state and speciation in the environment. Soluble Cr^{3+} is considered relatively harmless at levels normally encountered, but Cr^{6+} is highly toxic (causing liver and kidney damage) and is a carcinogen. However, chromium is needed by the human body in small amounts for insulin action and metabolism of proteins and carbohydrates (WHO, 1996). Anthropogenic sources of chromium include copper smelting, metal electroplating, tanning, the chemical industry, engineering and waste incineration (Reimann and de Caritat, 1998).

Copper Cu

Copper (Cu) has an approximate atomic mass of 63.5 and has two main oxidation states (+2 and +1) and two naturally occurring stable isotopes, ^{63}Cu, and ^{65}Cu. It is a chalcophile element forming several minerals including chalcopyrite ($CuFeS_2$), covellite (CuS), and malachite ($Cu_2CO_3(OH)_2$). However, it is more widely dispersed at trace levels in biotite micas, pyroxenes and amphiboles, thus showing a greater affinity for basic than for acid igneous rocks.

Copper is mobile under oxidising, acidic conditions. However, Cu has a strong binding affinity for organic matter such as humic acid and this is, therefore, important in controlling copper speciation; once buried, and reducing conditions are established, the copper is rapidly converted to sulphides, for example, chalcopyrite (Parkman et al., 1996). Copper is especially stable in solution at pH values of 5.0 – 6.0. Copper, along with silver and lead, is often bound to the coarser sediment fraction, but copper being more soluble is often transported further downstream (Lottermoser et al., 1999). At low pH values, copper and zinc are preferentially adsorbed to lead and silver; at higher pH values, co-precipitation of copper and zinc occurs in the presence of Fe hydrous oxides (Lottermoser et al., 1999).

Copper is an essential trace element for all organisms; humans can tolerate very high levels of copper (up to 12 mg/day: - WHO, 1996), unlike cattle and sheep which are vulnerable to poisoning. However, copper can be toxic at extremely high levels, for example, poisoning of small children from drinking water has been reported (Reimann and de Caritat, 1998). Anthropogenic sources of copper include copper mining and smelting, agriculture, sewage sludge and steel works. Although Cu metal is not attacked by non-oxidising acids, it will readily corrode in acidic, oxidising conditions.

Iodine I

Iodine is a halogen element, along with F, Cl and Br. The element has an atomic number of 53, an atomic mass of 127, five oxidation states (-1, +1, +3, +5 and +7) and one naturally occurring stable isotope (^{127}I). Although most radioactive isotopes of iodine have very short half-lives, ^{129}I has a half-life of 15.7 million years. ^{131}I has a half-life of only 8.1 days but it is very radioactive and hazardous in the immediate aftermath of nuclear events as it concentrates in the human thyroid gland. Nuclear power plants can be significant sources of both isotopes, particularly when accidents such as the one that occurred at Chernobyl result in the release of large amounts of radioactive iodine into air.

Although iodine is the least abundant of the halogen elements (other than the ultra-rare radioactive astatine), ^{127}I is ubiquitous throughout the Earth's surface at approximately 0.5 mg kg^{-1}. The rare iodine minerals are sub-divided into two distinct groups: insoluble iodides, e.g. iodembolite Ag(Cl,Br,I); and soluble iodates, e.g. schwartzembergite $Pb_5IO_3Cl_3O_3$ (Fleischer, 1966). Fluid inclusions within minerals may be a primary source of iodine (Wedepohl, 1978) while substitution of chloride ions by iodide ions in some mineral groups is also thought to occur (Kogarko and Gulyayeva, 1965).

Iodine concentrations in common rock-forming minerals range from <20 µg kg^{-1} to 1,200 µg kg^{-1} and similar low concentrations are recorded for igneous and magmatic rocks ranging from <20 µg kg^{-1} to 1,900 µg kg^{-1} (Fuge and Johnson, 1986). It is thought that the large ionic radius of iodine, its chalcophilic character (Fuge and Johnson, 1984) and its possible occurrence in non-ionic form in melts are all factors controlling the distribution of iodine in igneous rocks (Wedepohl, 1978). Iodine concentrations in clastic rock types are thought to be relatively low but with a higher range than for igneous and magmatic rocks. Organic-rich rocks have the highest concentrations of iodine - Cosgrove (1970) reported high levels in samples of Kimmeridge shale (mean 17 mg kg^{-1}. Elevated levels of iodine have also been described in sandstones containing argillaceous material; probably resulting from adsorption of iodine onto the clay surfaces (Becker et al., 1972).

Marine waters form an important reservoir of iodine with concentrations of 0.06 mg l^{-1} (Hem, 1992), whereas iodine levels in non-marine surface waters are very variable, typically in the range 0.1 to 18 µg l^{-1}. Surface environments in coastal regions will have higher iodine concentrations than areas more distant from the sea because of a greater wet and dry deposition of iodine. Iodine is easily oxidised, but about 90% of all iodine found in natural freshwaters occurs as the anion I^-. Iodine is a volatile element and atmospheric migration is a peculiar feature of iodine geochemistry, volatilisation of the iodine being influenced by biochemical activity.

Iodine is an essential trace element in the diet of humans and animals and has therefore received considerable attention. It was the first element for which an association association between human health and a trace element in the environment was recognised. Iodine provides a substrate for the synthesis of thyroxide hormones and is essential to normal human growth and development. Lack of iodine in the human diet causes a number of medical conditions collectively known as iodine deficiency disorders (IDD). The most obvious manifestation is an enlarged neck caused by a swollen thyroid gland and referred to as a goitre. A more widespread and more significant effect is the mental impairment and cretinism that can afflict populations over large regions of the world. IDDs affect over 740 million people worldwide (WHO, 2002).

Lanthanum La

Lanthanum (La) has an approximate atomic mass of 139, one main oxidation state (+3) and two naturally occurring stable isotopes, ^{138}La and ^{139}La, of which ^{139}La contributes 99.9% of the mass. It is a lithophile element forming several minerals including the relatively common monazite ((Ce, La, Nd, Th)(PO_4)) and rarer cerite ((Ce, La)$_9$(Mg, Fe)Si_7(O, OH, F)$_{28}$), though it is widely dispersed at trace levels in several rock-forming minerals such as biotite, apatite, pyroxenes and feldspars. Consequently La is much more abundant in acid and intermediate than in basic or ultrabasic igneous rocks.

Lanthanum has very low mobility under most environmental conditions, mainly due to the very low solubility of the phosphate ($LaPO_4$). As a light REE, it is preferentially adsorbed onto organic matter (Leleyter et al., 1999) compared with heavier REEs.

Lanthanum is considered biologically inactive and non-essential, and is believed to have a low toxicity. Inhaled REE`s as dusts probably cause pneumoconiosis, and ingested REEs can accumulate in the skeleton, teeth and liver. Anthropogenic sources of lanthanum include mining and processing of alkaline rock, but natural sources are generally more abundant than anthropogenic ones (Reimann and de Caritat, 1998).

Lead Pb

Lead (Pb) has an approximate atomic mass of 207, and has two main oxidation states (+2 and +4) and four naturally occurring stable isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. It is a chalcophile metallic element forming several important minerals including galena (PbS), anglesite ($PbSO_4$), cerrusite ($PbCO_3$) and minium ('Red Lead', Pb_3O_4) but is also widely dispersed at trace levels in common minerals which include K–feldspar, plagioclase, micas, zircon and magnetite, and as such is more abundant in acid than in basic igneous rocks. In nuclear waste repositories, much Pb may be present in metallic form or as Pb-glass because of its use in radiation shielding.

Lead mobility in the environment is limited, mainly by the low solubility of its sulphide, sulphate and carbonate compounds, and also by the strong affinity of lead for sorption by secondary iron and manganese oxides and (to a lesser extent) by organic matter. Sulphides such as galena may be oxidised to sulphate at high E_H but the sulphate produced is itself highly insoluble and may form a protective crust on the galena grains. Below pH 5.2 Pb becomes mobile in non-calcareous soils, but is adsorbed preferentially before copper and zinc on iron oxides (O'Day et al., 1998) and, therefore, does not migrate readily to groundwater (Martinez and Motto, 2000). Around 35 % of lead in steam sediments is found in the sand fraction, but the majority is found in the silt and clay fractions, associated with feldspar and micas, and secondary iron oxide precipitates. Thus most of the lead is transported in the finer fractions, hence being carried further from the source than that held on the coarser sediment fractions (Song et al., 1999).

Lead is biologically non-essential and is well known for its toxic properties. It can cause mental impairment in young children, causing neuropathy and hypertension in adults, and may be lethal at high levels (over 25µg/kg of body weight: - WHO, 1996). Anthropogenic sources of lead include aerosols from car exhausts, (although this has decreased somewhat due to the introduction of lead-free petrol), old lead-based paints, pottery glazes, steel works, sewage sludge and smelting.

Molybdenum Mo

Molybdenum (Mo) has an approximate atomic mass of 96, five main oxidation states (+2, +3, +4, +5 and +6) and seven naturally occurring stable isotopes. It is a chalcophile or siderophile metallic element forming several minerals including molybdenite (MoS_2), wulfenite ($PbMoO_4$) and powellite ($Ca(Mo, W)O_4$). It is more likely to be associated with 'evolved' granites than with other igneous rocks. However, it is more widely present at trace levels in association with organic matter and sedimentary sulphides, notably in black shales. It also occurs in the rare tungsten minerals scheelite and wolframite, but it does not readily substitute into silicates.

Molybdenum is mobile under oxidising, acidic, neutral or alkaline conditions. Molybdenite (MoS_2) slowly oxidises under acidic weathering conditions to form ferrimolybdate or molybdenum-bearing iron hydroxides (Cook, 2000). Molybdenum is often associated with copper mineralisation (in Cu-Mo porphyry-type deposits); but it differs from copper in that it is more mobile in alkaline conditions. It forms the soluble molybdate (MoO_4^{2-} and $HMoO_4^-$) anions over a wide range of pH values, but MoS_2 is stable and insoluble under reducing conditions, rendering Mo immobile where it forms (Brookins, 1988). Stream and lake sediments usually contain molybdenum derived from a hydromorphic source (Cook, 2000). It is then fixed by organic matter, and secondary iron and magnesium oxides. This is more common at low pH values (Cook, 2000).

Molybdenum is considered essential for all organisms (25 µg/ day is needed by the human body (WHO, 1996)). However, it can be toxic at high levels especially to cattle and sheep. In plants, it has a role in nitrogen fixation. Symptoms of deficiency include coma and night blindness. Molybdenum intoxication reduces the uptake of copper in the human body, and leads to skeletal deformities (WHO, 1996). Anthropogenic sources of molybdenum include molybdenum mining and smelting, oil refining, phosphate fertilizers and sewage sludge (Reimann and de Caritat, 1998).

Niobium Nb

Niobium (Nb) has an approximate atomic mass of 93, two main oxidation states of (+5, and +3) and one naturally occurring stable isotope ^{93}Nb. It is a lithophile metallic element forming several rather rare but economically important minerals including pyrochlore ((Na,Ca)$_2$(Nb,Ta)$_2$O$_6$(OH,F)) and columbite-tantalite ((Fe,Mn)(Nb-Ta)$_2$O$_6$)), but is more widely present at trace levels in rock-forming minerals such as biotite, rutile, sphene, cassiterite and zircon.

Theoretically, Nb displays very low mobility under all but the most extreme environmental conditions, due to the high stability and very low solubility of the oxide Nb_2O_5 and niobates derived from this (Brookins, 1988), thus exhibiting 'resistate' type behaviour in the surface environment.

Niobium is considered non-essential, but it is present in living organisms and can affect biological mechanisms. Niobium levels in the body are comparable to those of copper, and (of the heavy metals) are exceeded only by iron and zinc (Mertz, 1987). However, little is known about its chemical speciation and toxicity. Anthropogenic sources of niobium include nuclear fuel production, welding and steel production (Reimann and de Caritat, 1998).

Platinum Group elements (Ruthenium, Ru; Rhodium, Rh and Palladium, Pd)

These elements have very low natural abundances but are relatively common fission products in nuclear waste. Collectively they are part of the Platinum group, along with osmium, iridium and platinum, and all have broadly similar chemistries, though with some individual and important variations. However, the environmental geochemistry of these elements is still not fully understood. They all appear to have very low environmental mobility, mainly due to the high stability and low solubility of the native metals, the disulphides (not Rh) and the oxides over the normal ranges of Eh and pH (Brookins, 1988).

Rubidium Rb

Rubidium (Rb) has an approximate atomic mass of 85, one main oxidation state (+1) and two naturally occurring stable isotopes, ^{85}Rb and ^{87}Rb, the former contributing 72% of the mass. It is a lithophile metallic element forming no 'pure' minerals of its own but is present in several common minerals replacing potassium, for example in K-feldspar, muscovite and biotite and also occurs in rarer minerals such as lepidolite, carnallite and pollucite (replacing Cs). Consequently, it is more abundant in acid igneous rocks than in intermediate or basic varieties.

Rubidium displays relatively low environmental mobility, despite the stability and solubility of Rb^+ and most of its compounds, mainly due to its very strong sorbtion by clay minerals such as illite. Rubidium is more strongly sorbed by clay minerals than is potassium, and Rb may, therefore, be enriched relative to K_2O in mudstones.

Rubidium is considered biologically non-essential and non-toxic. It behaves very similarly to potassium in the human body, and may replace it if potassium levels are low (Mertz, 1987). There is also some evidence that rubidium may be involved with neuro-pathway mechanisms (Mertz, 1987). It is rapidly and highly absorbed by the human body. Anthropogenic sources of rubidium include glass dust, but geogenic sources are more important than anthropogenic ones (Reimann and de Caritat, 1998).

Selenium Se

Selenium (Se) has an approximate atomic mass of 79, four main oxidation states of (-2, 0, +4 and +6) and six naturally occurring stable isotopes, ^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, and ^{82}Se. It is a low-abundance chalcophile non-metallic element forming several rare minerals including crookesite ((Cu, Tl, Ag)$_2$Se), berzelianite (Cu$_2$Se) and tiemannite (HgSe), but is more widely present as an accessory element replacing sulphur in more common sulphide minerals such as pyrite, chalcopyrite, pyrrhotite and sphalerite.

Selenium is highly mobile under oxidising, acidic, neutral and alkaline conditions, although it's mobility decreases with decreasing pH (Gondi *et al.*, 1992) and it is immobile under reducing conditions. Its solution chemistry is principally anionic with selenite and selenate (Se IV and Se VI) corresponding to sulphite and sulphate, although elemental Se is also stable over a wide pH range under reducing conditions (Brookins, 1988).

Selenium is a biologically active element and is essential for many organisms. Selenium is needed for growth and fertility in animals, while deficiency in humans leads to Keshan and Kashin-Beck diseases, affecting the heart and bones respectively (Mertz, 1987). Some 30 – 40 µg/ day is needed for adult humans (WHO, 1996) but it has a narrow optimal intake range and can also be toxic at higher levels, causing hair and nail loss, skin disorders, nerve damage and abdominal cramps (Mertz, 1987). Anthropogenic sources of selenium include coal combustion, smelters, vulcanised rubber, waste water and some phosphate fertilizers (Reimann and de Caritat, 1998).

Silver Ag

Silver (Ag) has an approximate atomic mass of 108, three main oxidation states of (+1, 0, and +2) and two naturally occurring stable isotopes, ^{107}Ag, and ^{109}Ag. It is a rare chalcophile metallic element that forms several minerals including argentite (Ag_2S), silver arsenide (Ag_3As), and native silver, although it is more widely present as a trace element in sulphide minerals such as galena, sphalerite, tetrahedrite and chalcopyrite.

Silver is mobile under acidic, oxidising conditions, and Ag^+ can form aqueous complexes with chloride. However it has a relatively low solubility, and is deposited from solution as the pH rises above 4.0 (Lottermoser *et al.*, 1999). At higher pH values (between 4.0 and 8.0 (Jones, 1986)), silver and lead will be preferentially adsorbed onto Fe hydroxides, compared to copper and zinc (Lottermoser *et al.*, 1999). Native silver and silver sulphide are stable and insoluble under reducing conditions over a wide pH range (Brookins, 1988).

Silver is biologically active but is non-essential for all organisms. It is toxic to fish and many micro-organisms, but its toxicity to humans is low. It occurs naturally in very low concentrations in soil, plants and animal tissues (Mertz, 1987). Silver interacts metabolically with copper and selenium, preventing uptake of those elements in the human body (Mertz, 1987). Anthropogenic sources of silver include copper, zinc, tin and lead smelters and sewage sludge (Reimann and de Caritat, 1998).

Strontium Sr

Strontium (Sr) has an approximate atomic mass of 88, one main oxidation state (+2) and four naturally occurring stable isotopes, ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr, of which ^{88}Sr is the most abundant at 82.6% of the total mass. It is a lithophile metallic element which forms several minerals including strontianite ($SrCO_3$) and celestite ($SrSO_4$). It is widely present substituting for Ca in several common rock-forming minerals such as feldspars, gypsum and, especially, calcite and dolomite, which are the main sources of Sr in stream waters. It is generally more abundant in acid-intermediate igneous rocks than in other varieties, some granodiorites being especially enriched in Sr. Some substitution for Ba also takes place in barite ($BaSO_4$) and witherite ($BaCO_3$).

Strontium, as Sr^{2+}, is mobile under most environmental conditions, despite the relatively low solubility of the carbonate and sulphate at neutral to high pH levels (Brookins, 1988). It does not precipitate in many secondary phases (Martin and McCulloch, 1999), other than by co-precipitation with calcium carbonate in limestones.

Biologically, strontium is considered to be a non-essential element. However, it can substitute for Ca^{2+} in living organisms, causing concern over radiogenic forms of strontium in the environment, such as the highly radiotoxic ^{90}Sr. Strontium, like calcium, is absorbed more effectively in the presence of vitamin D, lactose, and some amino acids (Mertz, 1987), while magnesium deficiency reduces the absorption of strontium. Long-term toxicity causes “strontium rickets” where the skeleton fails to mineralise, even when there is adequate calcium and vitamin D (Mertz, 1987). Anthropogenic sources of strontium include zinc refineries and radiogenic strontium from nuclear tests (Reimann and de Caritat, 1998).

Technetium, Tc

Technetium is notable in that it is the lightest element (atomic number 43) to have no stable isotopes and does not occur naturally, except perhaps in extremely low levels in uranium ores as a result of spontaneous fission of ^{235}U. Despite the artificial nature of Tc, its relatively long-lived radioisotopes such as ^{97}Tc and ^{99}Tc and its abundance in fission products have allowed its chemistry to be well characterised, but its environmental geochemistry is not quite so well understood, despite a history of low-level releases from nuclear reactors and reprocessing plants. Technetium has found an important use in medicine as a low-toxicity mildly radioactive tracer and imaging agent.

Chemically it is very similar to the naturally-occurring but extremely rare rhenium (Re) and some authors have consequently used Re as an analogue for Tc behaviour (Brookins, 1986). However, Re is much too rare to be routinely determined in geochemical surveys. Brookins (1988) gives Eh-pH diagrams for Tc in simple systems, which suggest that Tc as TcO_4^- (the pertechnate anion) is the likely soluble phase in oxidising conditions irrespective of pH, but reducing conditions can immobilise Tc as the insoluble oxide or sulphide. The much more abundant (than either Re or Tc) Mo shows some close similarities of behaviour in the solubility of the molybdate $HMoO_4^-$ and MoO_4^{2-} ions and insolubility of the sulphide MoS_2 under reducing conditions, though Tc apparently lacks the cationic MoO_2^+ aqueous ion produced by Mo under acid, oxidising conditions. Molybdenum is, therefore, considered to be a viable natural analogue for Tc in this study.

Tellurium Te

Tellurium is the heaviest member of the chalcogen group which includes O, S and Se, other than the ultra-rare and radioactive polonium. It has the atomic number 52 and an atomic mass of 127.6, with numerous stable isotopes, and some very long-lived radioisotopes, of which ^{128}Te and ^{130}Te are the most abundant. Tellurium is a low-abundance strongly chalcophile metalloid element, though showing a more metallic character than its group co-member Se, and has redox states of -2, 2, 4 and 6, of which +4 is the most important. Although it forms a few rare 'pure' minerals such as tellurite (TeO_2) it is more widely dispersed in more common sulphides such as pyrite, molybdenite, chalcopyrite and pentlandite; and also in gold and silver deposits. Tellurium is one of a very few elements which form stable compounds with gold. Much of the Te produced commercially is recovered from the processing and refining of nickel and porphyry copper ores.

The environmental geochemistry of Te is not well understood, though the element and its compounds are widely used in steel alloys and the electronics industry. Its general mobility appears to be very low, even though Brookins (1988) shows potentially mobile cationic and anionic forms are thermodynamically stable in solution along with low-solubility elemental Te and TeO_2 over the normal range of Eh and pH values. However, the simple system illustrated is unlikely to be realistic for Te.

Tellurium has no known biological function and is believed to have a relatively low toxicity, although ingested Te is metabolised and converted to volatile methyl tellurides before excretion or exhalation. However, some Te compounds such as H_2Te are known to be highly toxic, and, therefore, Te compounds should be treated with caution.

Thorium Th

Thorium (Th) has an approximate atomic mass of 232, one main oxidation state of +4, and one naturally occurring long-lived isotope, ^{232}Th. It is a weakly radioactive lithophile metallic element forming several minerals including monazite ((Ce, La, Nd, Th)(PO_4, SiO_4)) and the rarer thorite ($ThSiO_4$) and thorianite (ThO_2). However, it is more widely dispersed as an accessory element in zircon, sphene, epidote and uraninite, and as such is more abundant in acid than in basic igneous rocks.

Thorium has low mobility under all environmental conditions, mainly due to the high stability of the low-solubility oxide ThO_2 and the strongly resistate nature of its carrier minerals such as monazite and zircon ((Zr, Th)SiO_4). The soluble species $Th(SO_4)^{2+}$ may form below pH 3 and under oxidising conditions (Brookins, 1988), for example in acid mine waters. However, the behaviour of Th under natural surface conditions is not yet fully understood. It is thought to be bound to suspended particulates in river water, and does not occur readily as a dissolved ion. Scavenging of thorium by Mn oxyhydroxides has also been reported (Andersson *et al.*, 1995). In comparison, Th is much less mobile than uranium, as it is not readily oxidised or reduced and lacks a species analogous to the stable and soluble U^{VI} species UO_2^{2+}.

Thorium is considered biologically non-essential; it is chemotoxic, radiotoxic and a carcinogen. It behaves similarly to REE`s (especially Ce) in the environment, substituting for calcium in bones and teeth. Anthropogenic sources of thorium include fertilizers, uranium mining and processing, and coal combustion (Reimann and de Caritat, 1998).

Tin Sn

Tin (Sn) has an approximate atomic mass of 119, two main oxidation states of (+4 and +2, though the latter is rare under normal surface environment conditions) and ten naturally occurring stable isotopes, ^{110}Sn, ^{114}Sn to ^{120}Sn, ^{122}Sn and ^{124}Sn. It is a rather low-abundance siderophile metallic element forming several minerals including cassiterite (SnO_2) and the rarer stannite (Cu_2FeSnS_4), but may also present as an accessory element in biotite, muscovite, amphiboles, sphene and rutile. It is much more abundant in granites, especially highly 'evolved' ones, than in other igneous rocks.

Tin shows a low mobility under most environmental conditions, mainly due to the high stability of the oxide SnO_2 and, theoretically, the insoluble sulphide SnS_2 under reducing conditions (Brookins, 1988). Tin is often found in stream sediments as cassiterite (SnO_2) which, being a heavy resistant mineral, often has a slow transport rate in streams (Fletcher and Loh, 1996). The man-made organotin pesticide Tributyltin readily adsorbs onto suspended particulate material, and, therefore, it increases in concentration as sediment grain size decreases (De Mora and Phillips, 1997).

Tin is considered possibly essential for some organisms (for example, humans), but many of its compounds are toxic to lower organisms. Examples being the well-documented cases of shell abnormalities in shellfish and imposex in gastropods caused by tributyltin in anti-fouling paints for ships (De Mora and Phillips, 1997). Inorganic tin toxicity can cause growth depression and anaemia in humans, it also interferes with the metabolism of zinc, copper and calcium (WHO, 1996). Fortunately, however, it is poorly absorbed by the human body. Anthropogenic sources of tin include tin plate, coal and wood combustion, waste incineration and sewage sludge (Reimann and de Caritat, 1998).

Titanium Ti

Titanium (Ti) has an approximate atomic mass of 48, three main oxidation states of (+4, +2 and +3) and five naturally occurring stable isotopes, ^{46}Ti, ^{47}Ti, ^{48}Ti, ^{49}Ti, and ^{50}Ti, of which ^{48}Ti contributes 74% of the total mass. It is an abundant lithophile metallic element which forms several minerals including ilmenite ($FeTiO_3$), rutile, brookite, anatase (all TiO_2) and sphene ($CaTiSiO_5$). It is also found as an accessory element in pyroxenes, amphiboles, micas and garnets. It is relatively more abundant in basic igneous rocks than in intermediate varieties or granites.

Titanium has very low mobility under almost all environmental conditions, mainly due to the high stability of the low-solubility oxide (TiO_2) under all but the most acid conditions ($pH<2$) (Brookins, 1988). It behaves as a refractory element during weathering, but relatively little is known about its behaviour in natural waters (Skrabal, 1995). It only exists in water above $pH > 2$ as a fully hydrated form $TiO(OH)_2$ and is therefore transported in a colloidal state rather than as a dissolved ion. Concentrations of 'dissolved' titanium generally decrease with increasing salinity. However, it has higher concentrations in organic rich waters (Skrabal, 1995) providing further evidence of colloidal transport. Methods of titanium removal from waters include flocculation of colloidal material, adsorption and scavenging by precipitation of Mn and Fe oxides (Skrabal, 1995).

Titanium is biologically non-essential and non-toxic, due to it's poor absorption and retention in living organisms (Mertz, 1987). No evidence has been suggested that titanium performs a necessary role in the human body (Mertz, 1987). Anthropogenic sources of titanium include paint pigments and alloys, although geogenic sources are more important than anthropogenic ones (Reimann and de Caritat, 1998).

Uranium U

Uranium (U) has an approximate atomic mass of 238, five main oxidation states of (+2, +3, +4, +5 and +6, of which +6 and +4 are most common in nature) and three naturally occurring isotopes, ^{234}U, ^{235}U and ^{238}U, of which ^{238}U contributes 99% of the total mass. It is a lithophile metallic element present in several minerals including uraninite (UO_2), brannerite ($(U,Ca,Ce)(Ti,Fe)_2O_6$) and carnotite ($K_2(UO_2)_2(VO_4)_2.3H_2O$). It is also present as an accessory element in more common minerals such as zircon, apatite, allanite and monazite. Consequently it is enriched in granites, especially 'evolved' varieties, relative to other igneous rocks. Uranium also forms complexes with organic matter and phosphates, so it is relatively enriched in coals, black shales and phosphatic sedimentary ironstones.

Uranium displays high mobility under oxidising, acidic, neutral and alkaline conditions. Under acid, oxidising conditions the main species in solution is the uranyl ion UO_2^{2+}, whereas under neutral to alkaline oxidising conditions, soluble uranyl-carbonate complexes such as $UO_2(CO_3)_2^{2-}$ predominate (Brookins, 1988; Duff *et al.*, 1997, Rose, 1994). Under reducing conditions, the insoluble U^{IV} oxide UO_2 is formed. Hexavalent U^{6+} is known to be reduced to U^{4+} by SO_4-reducing bacteria and Fe-reducing bacteria in the laboratory (Duff *et al.*, 1997) and this mechanism almost certainly operates in anoxic sediments. The chemistry of U^{4+} is very similar to Th^{4+}, in that they both strongly adsorb to iron oxides and organic matter. However, as soon as the conditions become oxic, uranium is rapidly mobilised, and becomes soluble (Duff *et al.*, 1997), whereas Th remains immobile.

Uranium is a non-essential element, it is chemotoxic, radiotoxic and a carcinogen. The radioactive decay of uranium releases radon gas, which is itself radiotoxic and highly mobile. Anthropogenic sources of uranium include uranium mining and milling, phosphate fertilizers and coal combustion (Reimann and de Caritat, 1998).

Vanadium V

Vanadium (V) has an approximate atomic mass of 50 and has three main oxidation states (+3, +4 and +5) and two naturally occurring isotopes, ^{50}V, and ^{51}V, of which ^{51}V forms 99.8% of the total mass. It is a lithophile metallic element forming several minerals including vanadian magnetite ($(Fe,V)_30_4$), vanadinite ($Pb_5(VO_4)_3Cl$), and carnotite ($K_2(UO_2)_2(VO_4)_2.3H_2O$). It is also present as an accessory element in dark micas, apatite, pyroxenes and amphiboles, so it shows more affinity with basic than acidic igneous rocks.

Vanadium is a highly mobile element, under high or low pH, and shows both cationic character under acid conditions as the vanadyl VO^{2+} and VO_2^{2+} ions, and anionic character under less acid to alkaline conditions as the vanadate HVO_4^{2-} or $H_2VO_4^-$ ions (Brookins, 1988). V^{4+} and V^{5+} are the most soluble forms in nature, and their complexes with fluoride, sulphate and oxalate may act to increase vanadium solubility under oxidising conditions (Wanty and Goldhaber, 1992). V^{4+} is reduced to V^{3+} under a variety of conditions, one of which may involve hydrogen sulphide (H_2S), especially in pyritic ore deposits (Wanty and Goldhaber, 1992). V^{5+} is reduced to V^{4+} in reducing conditions associated with organic matter. The reduced forms of V are more likely to be sorbed by clay minerals and organic matter, thus being removed from solution.

Vanadium is biologically active and is an essential nutrient for many animals. Its precise biochemical function is still in some doubt (WHO, 1996) but Frausto da Silva and Williams (1991) suggest a role in peroxidase enzymes. Vanadium toxicity (over 10 mg/day for adults) greatly depends on speciation and oxidation state, usually occurring by intake of airborne anthropogenic vanadium (WHO, 1996). Vanadium can accumulate in some vegetables, including mushrooms, potatoes and radish. Anthropogenic sources of vanadium include oil and coal combustion, steel alloy tool production and traffic.

Yttrium Y

Yttrium (Y) has an approximate atomic mass of 89, one main oxidation state of (+3) and one naturally occurring stable isotope, ^{89}Y. It is a lithophile metallic element which forms several minerals including xenotime (YPO_4) and yttrialite ($(Y,Th)_2Si_2O_7$) (Reimann and de Caritat, 1998), but is also present as an accessory element in biotite, feldspars, pyroxenes, garnets and apatite. It is slightly more abundant in granites, especially sub-alkaline varieties, than in basalts, but there is not a strong fractionation. In sedimentary rocks, mudstones tend to have higher concentrations than sandstones or carbonates.

Yttrium displays very low mobility under all environmental conditions. Although not itself a lanthanide element, in most cases it can be treated as a trivalent REE (van Middlesworth and Wood, 1998) and like the REEs, many of its carrier minerals are resistate. Although theoretically the Y^{3+} ion is soluble under acid conditions, the low solubility of the phosphate, hydroxide and possibly carbonate species negates this (Brookins, 1988). REEs in river waters are often in the form of suspended particles or colloids rather than in dissolved form, and they are thought to co-precipitate with $Fe(OH)_3$ (van Middlesworth and Wood, 1998). The light REEs are also thought to adsorb to organic matter (Leleyter et al., 1999).

Yttrium is considered to be non-essential for living organisms. Its toxicity is regarded as low, but it is more toxic than some REEs. Anthropogenic sources of yttrium include REE mining and ceramic dust (Reimann and de Caritat, 1998).

Zirconium Zr

Zirconium (Zr) has an approximate atomic mass of 91, one main oxidation states (+4) and five naturally occurring stable isotopes, ^{90}Zr, ^{91}Zr, ^{92}Zr, ^{94}Zr and ^{96}Zr, of which ^{90}Zr contributes 51.5% of the total mass. It is a lithophile metallic element which forms several minerals including the common zircon ($ZrSiO_4$) and rarer baddeleyite (ZrO_2), and is also present at trace levels in pyroxenes, amphiboles, micas, garnets and ilmenite. Acid igneous rocks are generally richer in Zr than basic varieties, but not greatly so, and some evolved granites may be particularly low in Zr.

Zirconium displays very low mobility under most environmental conditions, mainly due to the very high stability of the principal host mineral zircon and the low solubility of the hydrate $Zr(OH)_4$. However, as analytical methods have improved, a realistic detection limit for Zr in stream waters has been achieved by ICP-MS and shows that Zr does have a genuine aqueous soluble or colloidal geochemistry, albeit at very low concentrations. Given the extremely resistate nature of Zircon (it may be preserved through several geological cycles of orogeny and erosion lasting hundreds of millions of years), minerals other than zircon are likely to be the source of this mobile Zr. Zirconium displays some similar geochemical characteristics to titanium and tin; these elements are also only slightly mobile, and co-precipitate from colloidal suspension with iron and calcium. Colloidal zirconium is readily adsorbed by organic matter, macroplankton and siliceous material (Smith et al., 1978).

Zirconium is a non-essential element, having no known biological role. Little is known about its toxicity; however, it is regarded as being a low risk (Mertz, 1987). Anthropogenic sources of zirconium include nuclear fallout and ceramic dust; however, geogenic sources are considered to be more important than anthropogenic ones (Reimann and de Caritat, 1998).