

## **ENVIRONMENTAL GEOCHEMISTRY AND HEALTH - GLOBAL PERSPECTIVES**

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### **Abstract**

There is increasing concern about the effect of chemicals in the environment on the health of man, animals, crops and the sustainability of the Earth's surface life support systems. Concern centres on heavy metals, arsenic, fluoride, radioactive substances and persistent organic pollutants (POPs). In humans such potentially harmful substances (PHSs) have been associated with various diseases including cancer. There is also increasing recognition that changes in the chemistry of the Earth's surface as a result of human activity are having an impact on the environment at the global scale.

In the context of these concerns, there is a serious lack of monitoring and information on the concentration and distribution of PHSs in the environment and little information on associated exposure and effects on people and ecosystems.

High-resolution systematic digital geochemical maps are of value for addressing such problems at the national to local scale. Typically, a range of potentially harmful elements, radioactive elements and essential trace elements has been determined. The resulting data facilitate the understanding of complex environmental geochemical problems.

Unfortunately, the geochemical data currently available have been obtained mainly in the absence of any international standards and there have been considerable differences in survey methodologies. To address these problems, the IUGS and IAGC have established a Global Geochemical Baselines Working Group. The aims are to prepare a standardised global geochemical baseline, to document environmental problems and to provide a means of monitoring future changes in surface geochemistry. Such information can be used to refine, develop and validate models for the interaction of man and the environment at the local to global scale.

### **Introduction**

Geochemistry is the study of rock chemistry, and may appear far removed from human health. However, rocks are the fundamental building blocks of the planet surface and different rock mineral assemblages contain the 92 naturally occurring chemical elements found on Earth. Many elements are essential to plant, animal and human health in small doses. Most of these elements are taken into the human body via food and water in the diet and in the air we breathe. Through physical and chemical weathering processes, rocks break down to form the soils on which the crops and animals that constitute the food supply are raised. Drinking water travels through rocks and soils as part of the hydrological cycle and much of the dust and some of the gases contained in the atmosphere are of geological origin. Hence, through the food chain and through the inhalation of atmospheric dusts and gases, there are direct links between geochemistry and health (Figure 1).

Geochemists have been studying the links to health for over 50 years with growing importance in the last 20 – 25 years (for example, Nriagu, 1981; Bowie and Thornton, 1985; Thornton, 1986; Thornton, 1988; Lag, 1989; Fergusson, 1990; Appleton et al., 1996). There is increasing concern about the effects of chemicals on the health of man, animals and crops and the sustainability of the Earth's surface life support systems. There is also an awareness that man is influencing the environment at the global scale.

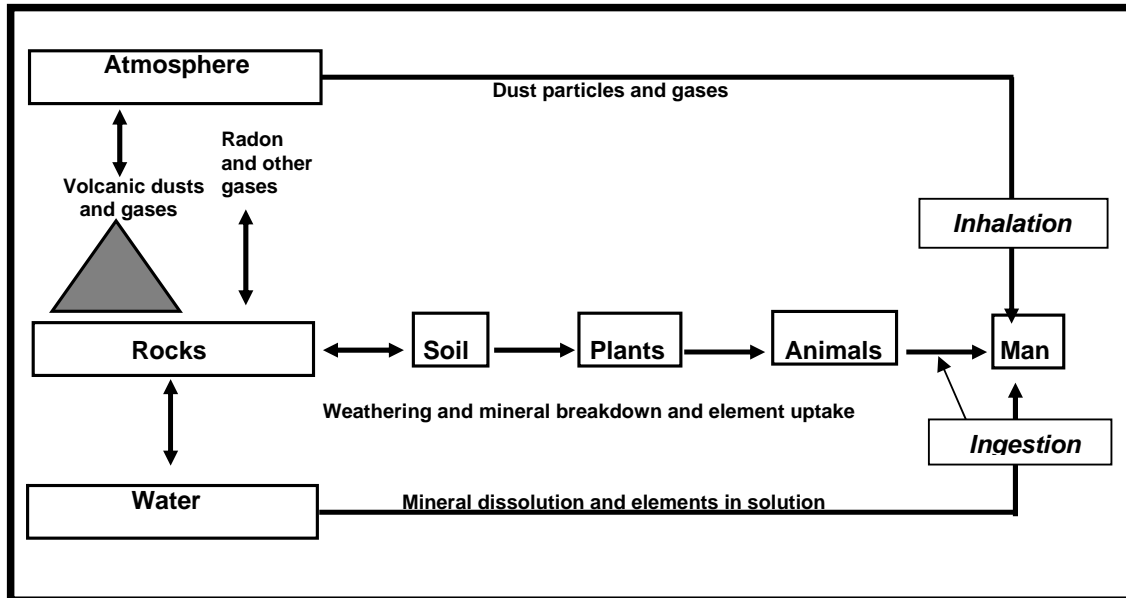


Figure 1. Simplified schematic diagram of the natural cycling of chemical elements from the geosphere into man.

It is important to realise that these chemicals can be natural or anthropogenic in origin (Figure 2). A number of geochemical factors such as soil and water pH, organic matter content, Eh conditions and the chemical form or speciation greatly influence the mobility and bioavailability of both natural and man-made chemicals in the environment. An understanding of these factors is necessary to remediate problems effectively.

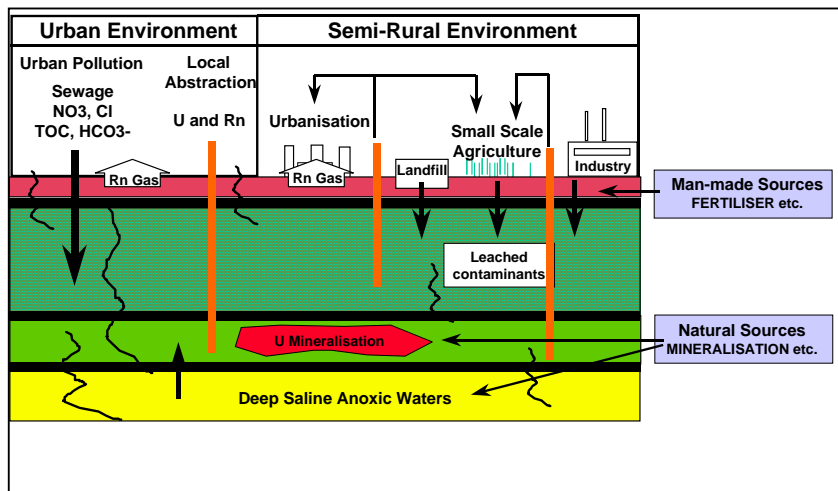


Figure 2. Schematic diagram illustrating potential natural and man-made contaminative processes (B Smith, pers. commun.)

## Natural Occurrences of Essential and Toxic Elements

The 92 naturally occurring elements are not distributed evenly across the surface of the earth and problems can arise when element abundances are too low (deficiency) or too high (toxicity). The inability of the environment to provide the correct mineral balance can lead to serious health problems. The links between environment and health are particularly important for subsistence populations who are heavily dependent on the local environment for their food supply.

Approximately 25 of the naturally occurring elements are known to be essential to plant and animal life in trace amounts, these include, Ca, Mg, Fe, Co, Cu, Zn, P, N, S, Se, I and Mo. On the other hand, an over-abundance of these elements can cause toxicity problems. Some elements such as As, Cd, Pb, Hg and Al have no/limited biological function and are generally toxic to humans (Mertz, 1986, WHO, 1996).

Most of these elements are known as trace elements because their natural abundances on Earth are generally very low (mg/kg concentrations in most soils). Trace element deficiencies in crops and animals are therefore commonplace over large areas of the world and mineral supplementation programmes are widely practised in agriculture (McDowell et al., 1993; Mills et al., 1985, Mertz, 1986). Trace element deficiencies generally lead to poor crop and animal growth, poor yields, and to reproductive disorders in animals. These problems often have greatest impact on poor populations who can least afford mineral interventions for their animals.

### *Iodine Deficiency*

Trace element deficiencies also affect man. In the case of iodine, the main environmental source is seawater and its abundance in most terrestrial environments is very low, normally a few mg/kg in most soils (Fuge, 1996). Low dietary intakes of iodine have been linked with a set of conditions known as iodine deficiency disorders (IDD). Iodine is involved in the processing of growth hormones in the thyroid gland and in most cases iodine deficiency manifests itself as goitre. Goitre is the enlargement of the thyroid gland as it attempts to compensate for insufficient iodine (Figure 3). Iodine deficiency in pregnant mothers can also lead to cretinism and impaired brain function in children. These are serious and debilitating consequences, as the capability of children is severely restricted and they become a burden on the family. The World Health Organisation currently estimates that over 1.6 billion people are at risk from iodine deficiency and that it is the single largest cause of mental retardation in the world today (WHO, 1996).



Figure 3. Woman suffering from iodine deficiency related goitre, Sri Lanka

The link between environmental iodine and IDD has been known for the last 80 years. During this time, many aid agencies and governments have attempted to solve the problem by increasing dietary intakes of iodine via the introduction of iodinated salt and iodinated oil programmes (Stanbury and Hetzel, 1980). Despite these interventions, IDD remain a major problem globally. It is likely that IDD are multi-causal diseases involving factors such as trace element deficiencies, goitre-inducing substances in foodstuffs (goitrogens) and genetics (Gaitan, 1996; Fordyce et al., 1998). Geochemists have an important role to play in determining the environmental cycling of iodine and its uptake into the food chain if levels of dietary iodine are to be enhanced successfully (Johnson, 1999).

#### *Selenium Deficiency and Toxicity*

The British Geological Survey (BGS) recently completed a study into Se deficiencies and toxicities in China funded by the UK Department for International Development (DFID). Selenium is an interesting element because the concentration range between deficiency (< 11 µg/day) and toxicity (> 900 µg/day) is very narrow. In the human body, Se forms part of the essential enzyme glutathione-peroxidase (GSH-Px) and acts as an anti-oxidant preventing tissue damage. Selenium deficiency has been linked to a heart disease called Keshan Disease, named after the Chinese district of Keshan where it was first discovered. The disease results in damage and enlargement of the heart muscles eventually leading to death. Keshan Disease (KD) occurs in a belt stretching from the north-west to the south-east of China and is coincident with remote populations living in areas of low environmental Se in soils and crops (Tan, 1989). Selenium toxicity is far less widespread, occurring in discrete areas, and results in hair and nail loss and nervous disorders in the local population (Figure 4).

In Enshi District, Hubei Province, these diseases occur within 20 km of each other, their incidence being controlled by geology. Sandstones, which contain low concentrations of trace elements including Se, underlie the north-west of Enshi District and KD is present in this area. Selenium toxicity, on the other hand, is associated with high environmental Se derived from coal-bearing strata in the centre and east of the District (Fordyce et al., 2000).



Figure 4. Man suffering hair loss due to selenium toxicity, Enshi, China

Studies into the relationship between low environmental concentrations of Se and the incidence of KD in Zhangjiakou District in northern China revealed some interesting results. Studies focussed on 15 villages, 5 with low/ no KD incidence, 5 with medium KD incidence and 5 with high KD incidence, all of which lie in a low Se environment. In each of these villages, soils, staple food-crops (wheat) and drinking water were collected and analysed as a measure of environmental Se. Selenium was also determined in human hair samples as an indication of human Se status.

It was anticipated that the highest disease incidence would occur in areas with lowest environmental Se. However, although Se in grain, drinking water and hair samples followed the expected trends, Se concentrations in soils were the opposite to that expected. Highest Se concentrations occurred in villages with the highest incidence of KD (Figure 5). Further investigations into the soils revealed that they had high organic matter contents and low pH. Selenium mobility is restricted at low pH and Se in the soil was also adsorbed onto organic matter making it less available for plant uptake.

This has important implications for the development of remediation strategies. Adding Se-rich fertiliser to the soil, for example, may not increase the Se contents of the plants, since the Se may remain trapped in the soil by the organic matter. A more appropriate approach may be to condition the soil with lime to increase the pH, making Se more mobile (Johnson et al., 2000).

These studies demonstrate why it is important to consider a broad range of controls on elements in the environment and to adopt a multi-element/ multi-factor approach. Determinations of the total concentration of Se in soils alone would not have provided sufficient information to predict areas at greatest risk from Se deficiency.

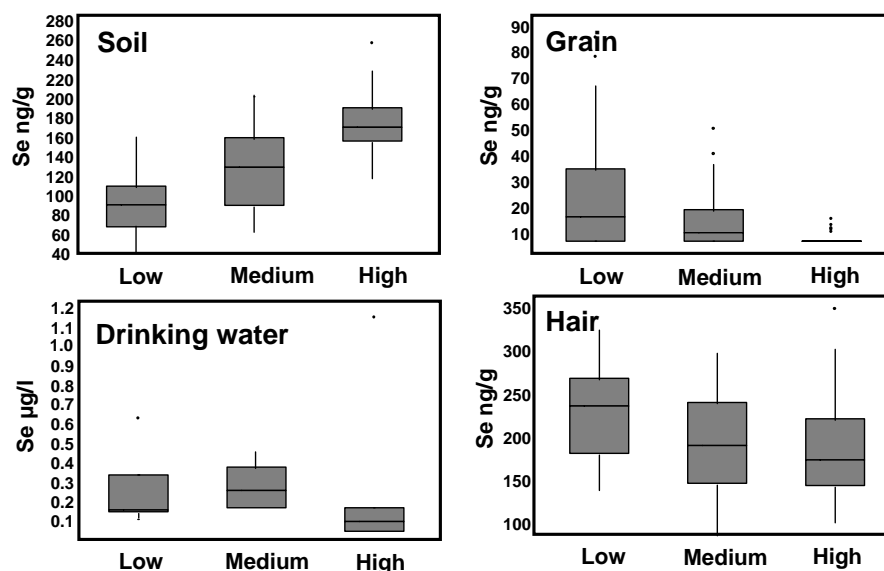


Figure 5. Box and whisker plots of 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup> and 90<sup>th</sup> percentile total selenium concentrations in soil, grain (wheat), drinking water and hair samples in villages with low, medium and high Keshan Disease incidence. Five villages were sampled in each disease incidence category. All villages lie in the low selenium environment of Zhangjiakou District, China.

### Anthropogenic Influences

In the last 200 years, the world population has undergone rapid economic and population growth often resulting in uncontrolled urbanisation and industrialisation with attendant migration and concentration of poor populations. These processes exert pressure on the natural environment leading to the destruction of natural ecosystems and over exploitation of aquifers. Even in non-urbanised areas, human activities adversely affect the environment. Mining, intensive agriculture and deforestation can lead to contamination, soil denudation and potential desertification.

The current problem with arsenic in groundwater in Bangladesh is an example of anthropogenic factors exacerbating a natural potential hazard.

#### *Arsenic in Groundwater, Bangladesh*

Inorganic arsenic is one of the oldest known poisons to man. Chronic arsenic exposure particularly affects the skin, mucous membranes, nervous system, bone-marrow, liver and heart (Mertz, 1986; WHO, 1996). Arsenic toxicity is strongly dependent on chemical form. The arsene gas state exhibits the greatest toxicity, whereas the more commonly occurring forms decrease in toxicity by approximately an order of magnitude through each stage of the sequence As(III)>As(V)>methyl-As .

In most animals, As (III) toxicity results from reactions with thiol (HS-) groups to form stable thio-As derivatives. Many key cellular proteins contain free thiol groups and reaction with As (III) can lead to a loss of protein function. Arsenate (As IV) toxicity is manifested via reduction to As (III), and through substitution for phosphate in normal cellular reactions (Abernathy et al., 1997). The role of As exposure in the development of bladder, liver and kidney and skin cancers has been highlighted through clinical (e.g. Sasieni and Cuzick, 1993) and epidemiological (e.g. Chen, 1992) studies and is often associated with arsenic in groundwater (Fordyce et al., 1994).

In terms of the population exposed, Bangladesh has the most serious arsenic problem in the world. The contamination occurs in groundwater from the alluvial and deltaic sediments that make up much of the country. The arsenic is of geological origin and has probably been present in the groundwater for thousands of years. Problems are only apparent now because it is just within the last 20-30 years that groundwater has been extensively used for drinking water in the rural areas (Kinniburgh and Smedley, 1998).

Over the last 20 - 30 years, aid agencies etc. have constructed many deeper wells and boreholes to avoid surface waters contaminated with disease and to meet the demands of a huge explosion in population and agriculture. Unfortunately, the geochemical characteristics of water from these deeper aquifers was not considered. It is estimated that 200 000 people have developed As poisoning including skin and internal organ cancers and that 20 – 30 million people are drinking water which exceeds the Bangladesh toxicity limit (0.05 mg/l) (Kinniburgh and Smedley, 1998).

Geochemical investigations demonstrate that the groundwaters are anoxic and that a large proportion of the arsenic is present as the As (III) more toxic form. In terms of sources, there have been insufficient analyses of the alluvial sediments to provide a regional picture, but current data suggest that arsenic is usually in the range 2-20 mg/kg; only slightly greater than typical sediments (2-6 mg/kg). However, it appears that an unusually large proportion of the arsenic is present in a potentially soluble form adsorbed onto iron and other oxides/ oxyhydroxides. It is likely that there are multiple sources of As and that the relationship between the arsenic content of the sediment and that of the water passing through it is complex (Kinniburgh and Smedley, 1998).

The groundwater arsenic problem in Bangladesh arises because of an unfortunate combination of natural and anthropogenic factors:

- (i) a source of arsenic (arsenic is present in the aquifer sediments)
- (ii) mobilisation (arsenic is released from the sediments to the groundwater)
- (iii) transport (arsenic is flushed away in the natural groundwater circulation)
- (iv) human pressure to exploit these resources, exposing large populations to the hazard

#### **Exposure and Bioavailability**

In addition to understanding both natural and anthropogenic sources of harmful substances in the environment, it is also important to consider exposure and bioavailability. Exposure is the qualitative and/or quantitative description of total exposure to a given chemical substance via a range of pathways. Bioavailability is the proportion of a chemical available for uptake into the systemic circulation of a given target organism following a given mode of exposure (Smith et al., 2000).

Bioavailability directly influences exposure and therefore the effect and risk of health detriments. Large quantities of a potentially harmful substance may be present in the environment, but if it is in a non-bioavailable form, the risk to health may be minimal.

Furthermore, as demonstrated with the arsenic in Bangladesh example, a potential hazard only becomes a problem if there is an exposure route. The potential hazard of high arsenic groundwaters have existed for thousands of years but it is only in recent years with the sinking of deeper boreholes to access this water that an exposure route has been established and a health effect manifested. In the absence of exposure, there is no adverse effect.

Exposure pathways include diet (food, water, deliberate/inadvertent soil ingestion), dermal absorption and inhalation. In terms of ingestion, much emphasis has been placed on water, simply because it is an easy sample-type to analyse. However, soils and food stuffs are likely to be far more important dietary contributors because the concentrations of potentially harmful substances in soils are much greater (parts per million) than in water (parts per billion). Whether soil ingestion is inadvertent or via the deliberate eating of soil known as geophagia, this exposure route should not be under-estimated. For example, studies in Kenya have shown that 60 – 90% of children between 5 – 14 years of age practice geophagia and consume 28 g of soil per day (Geissler et al., 1997).

#### *Cerium in Uganda*

Investigations carried out by BGS under the DFID aid programme into high cerium and low magnesium in relation to a heart disease, endomyocardial fibrosis (EMF), in Uganda revealed the importance of understanding exposure pathways. Concentrations of Ce in the staple food stuff cassava were analysed. However, Ce concentrations in raw cassava were not that high (Figure 6). The processing of the food in Uganda is the responsibility of women. Once harvested, the cassava is lain on the ground to dry. Soil geochemistry investigations demonstrated that Ce is concentrated in the very finest (< 20 µm) dust particles. These particles stick to the cassava during the drying process and elevate the Ce content (Figure 6). Studies revealed that the Ce content of soil is four times greater than that of foodstuffs and that the deliberate and inadvertent ingestion of soil is the dominant exposure route for Ce and many other elements in the Ugandan diet (Smith et al., 1998).

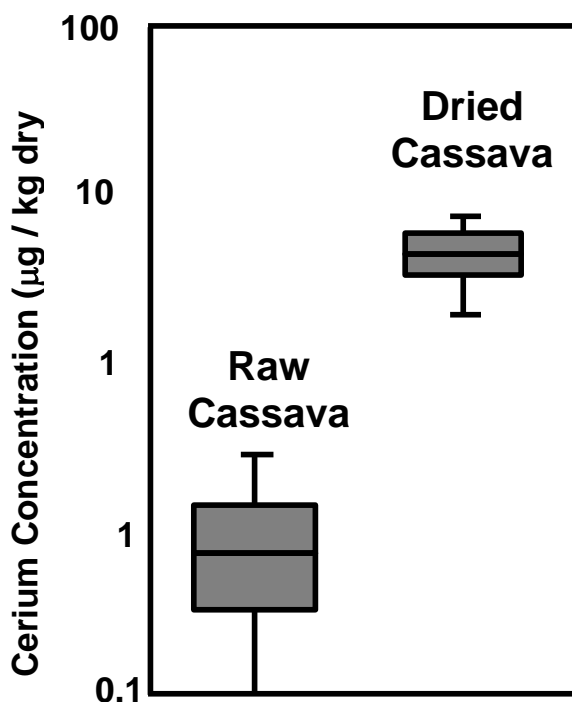


Figure 6. Box and whisker plots of 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup> and 90<sup>th</sup> percentile total cerium concentrations in raw cassava and cassava dried on the ground, Uganda (Smith et al., 1998).

The populations studied have a preference for eating soils derived from termite mounds. In vitro bioavailability (or strictly bioaccessibility) studies known as Physiologically Based Extraction Tests (PBET), were applied to different soil types. These tests mimic conditions in the human gut, and results revealed that several elements were more bioaccessible in termite soils than ordinary soils. The

bioaccessibility of beneficial elements such as magnesium and iron was enhanced in addition to potentially toxic substances such as Ce. No relationship between high Ce and low Mg with EMF was found in Uganda perhaps due, in part, to the greater availability of Mg in the Ugandan diet (Smith et al., 2000).

#### *Multi-disciplinary Approach to Risk Assessment*

As demonstrated in the Ugandan example, studies of exposure, bioavailability and risk are extremely complex and require a multi-disciplinary approach to problem solving. However, geoscientists have an important role in these issues. Hazards may be physical (including geological), chemical (including geochemical) or biological; exposure assessments may require nutritional, geochemical, mineralogical, biological and sociological information and determination of the health effects requires medical, sociological, epidemiological and chemical (including geochemical) knowledge.

### **Potentially Harmful Substances (PHSs) and Regulation**

Clearly there is a link between the cycling of chemical substances through the natural environment and adverse human health outcomes. These problems literally affect billions of people world-wide, many of whom are the poorest in society. Substances of particular concern include the heavy metals (such as copper, chromium, nickel, lead and zinc), selenium, fluoride, radioactive substances (natural and man-made) and persistent organic pollutants (POPs). PHSs have been linked to a host of human health effects including cancer, allergies, damage to the central and peripheral nervous systems, diseases of the immune system, heart disease, reproductive disorders and interference with child development. Accumulation of these pollutants in the environment has also been the cause of significant environmental damage and a loss of biodiversity. There is an obvious need to monitor these substances in the environment.

Throughout the developed world, PHSs are subject to increasingly stringent regulation, with particular emphasis on the progressive and substantial reduction in chronic exposure. Because of concern that the hazards, particularly to sensitive groups such as children, can be serious and irreversible and can take a long time to appear, governments are tending to legislate to reduce exposure without waiting for specific proof of harm (the precautionary principle).

In the context of these concerns there is a serious lack of monitoring and information on the concentration and distribution of potentially harmful substances in air, water, stream sediment, soil and food and little information on associated exposure and effects on people and ecosystems. Moreover, current toxicity risk assessments are based mainly on single substances, although people and ecosystems are generally exposed to complex mixtures. There is also a general lack of understanding that PHSs can occur naturally.

### **Geochemical Mapping**

High-resolution systematic digital geochemical maps (Figure 7) have been shown to be of value for addressing such problems at the national to local scale. Many countries already possess these data-sets. Typically, a range of trace elements including potentially harmful elements, radioactive elements and essential trace elements have been determined (although few if any geochemical maps include information on the distribution of POPs). The resulting data, usually in digital form, enable complex environmental geochemical problems to be identified in the context of natural background levels of chemical substances, which can be highly variable.

The data collected during these surveys represent the background geochemical condition of the environment for the time at which the samples were collected, i.e. a “snapshot” of the environment. As such, they cannot be used directly to monitor short-term changes in the environment but they are vitally important because they represent a starting point from which sensitivity to change, and future longer-term changes, can be recognised and prioritised. Without a detailed understanding of the background geochemistry it is meaningless to monitor change and also to set realistic regulatory guidelines that lead to sustainable development with minimal environmental impact.



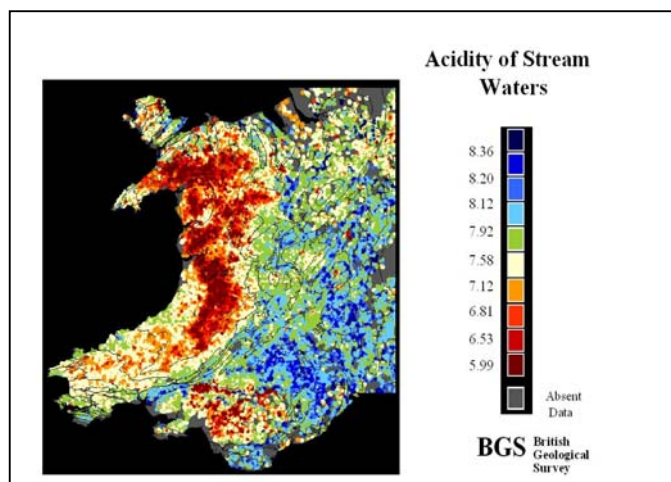


Figure 7. Geochemical map of stream water pH in Wales, UK

Unfortunately, the geochemical data currently available have been obtained mainly in the absence of any international standards and there have been considerable differences in the methods used to collect and analyse samples from a wide variety of sample types. Hence it is difficult to integrate and compare the data to assess environmental geochemical problems, including those which are of significance to human health at the international to global scale. This is a particular problem in developing countries where geochemical mapping has normally been carried out for mineral exploration.

#### **IUGS/IAGC Working Group on Global Geochemical Baselines**

To address these problems, a Working Group was established by the International Union of Geological Sciences (IUGS) and the International Association of Geochemists and Cosmochemists (IAGC), following the successful International Geological Correlation Programme (IGCP) 259 and 360 projects led by Dr A. Darnley of the Geological Survey of Canada. The final report of IGCP 259 (Figure 8) presents the issues which are important for such an undertaking and recommends the establishment of a Global Reference Network (GRN) of a 5000 point geochemical sampling grid around the globe (Figure 9).

The aims of the project are to prepare a standardised global geochemical baseline, to document environmental problems and to provide a means of monitoring future changes in surface geochemistry.

More than one hundred countries including Brazil, China, Colombia, India, Russia, Korea, Canada, USA, South Africa, Morocco, Ecuador, Botswana and the Co-ordinating Committee for Coastal and Offshore Geoscience Projects in East and South-east Asia (CCOP) countries are participating and over 60 national correspondents are listed for the project. Regional centres act as foci for co-operation and may be aid agencies, international organisations or collaborations of national or international bodies.

In Europe, activities are co-ordinated by the Forum of European Geological Surveys (FOREGS). Over 20 countries are collaborating in the preparation of a European GRN by collecting and analysing suites of geochemical samples by standardised methods. This activity is a model for other international projects. Detailed sampling, analytical and data interpretation methods to improve and standardise data quality have been agreed and published (Figure 8). The methods and resulting data are being disseminated to all participating countries through the project web-site as they become available.

These data can be used with other spatially related data-sets to identify potential hazards from harmful chemicals in surface and groundwater, soils, sensitive ecosystems and human populations. Such information can be used to refine, develop and validate models for the interaction of man and the environment at the local to global scale. Also, the data and their analyses can be used to demonstrate

the distribution and extent of environmental problems to decision-makers, stake holders and individuals in a readily understood and attractive format using geographical information systems (GIS).

To this end, IUGS/IAGC Working Group is keen to develop links and contacts with other international initiatives and to combine these data-sets with information not normally associated with geochemistry.

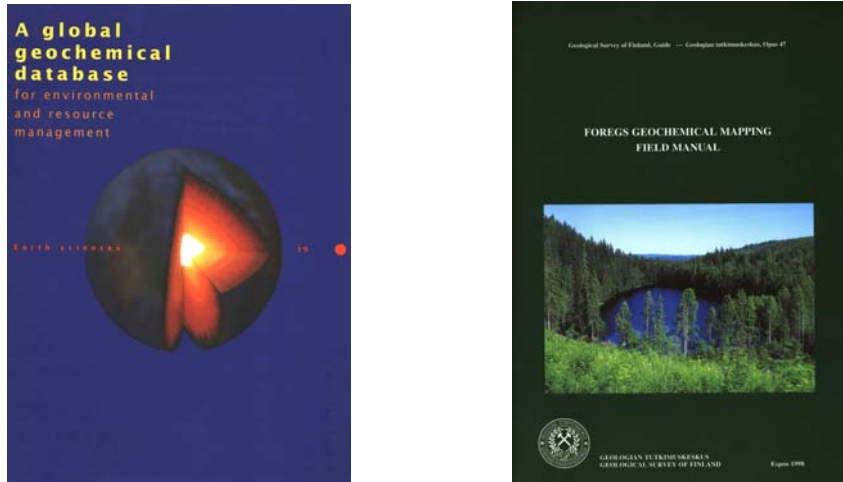


Figure 8. IGCP 259 Final Report (Darnley et al., 1995) and the FOREGS Geochemical Field Manual (Salminen et al., 1998).

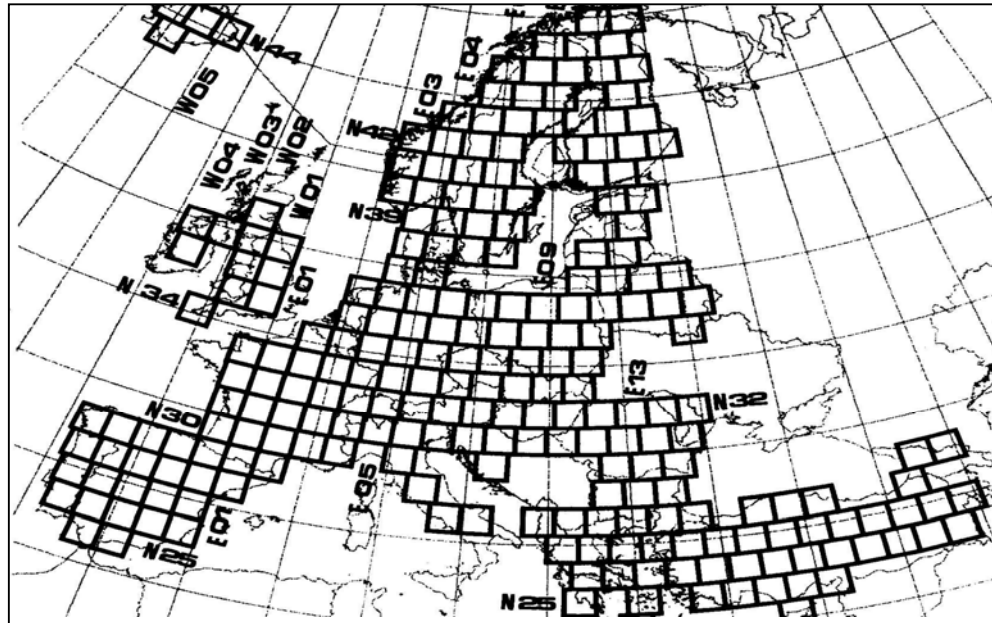


Figure 9. GRN for Europe. This diagram illustrates the sampling grids, five random sampling sites are selected from each grid. At each of these sites, a suite of geochemical samples is collected, including stream water, stream sediment, soils, floodplain samples and humus samples.

## Conclusions

1. Chemicals and other substances whether man-made or natural, can have adverse effects on human health. These health outcomes affect billions of people around the globe.
2. Geochemical mapping is a systematic way of studying the surface of the Earth and can be used to identify global environmental problems. Geochemical investigations not only show the abundance and sources of potentially harmful substances in the environment, but elucidate the likely migration, exposure pathways and bioavailability of these substances to given targets such as man.
3. Environment and health interactions are complex, involving linkages between physical, chemical and biological systems. Study of any of these systems uniquely without reference to these linkages will lead to a narrow view of the problem. There is therefore a need for greater collaboration between research disciplines.
4. There are many international monitoring projects organised by different research disciplines: ecosystem projects, air quality projects, soil monitoring projects etc. Currently there are no links between these different international programmes and it is difficult to compare the data. Methods to integrate monitoring networks should be investigated and there should be better communication and collaboration between all these international initiatives.
5. At the global scale, there is a need for international standardisation of data collection so that information from different countries can be compared directly. In the field of geochemistry, this process is already in progress via the IUGS/IAGC Working Group on Global Geochemical Baselines.
6. In order to study spatial links between environment and health, there is a need for greater georeferencing of data. This is particularly important for human health data, which is presently often reported as regional or district information. This makes the assessment of links between environmental factors and health difficult.
7. Many of the current regulatory guidelines dealing with contamination and toxicity fail to take account of the fact that several potentially harmful substances have highly variable natural abundances. Furthermore, most risk assessments are based on single substances whereas many populations are exposed to complex mixtures of substances. There is, therefore, a need for more research into dose-response relationships, the relative importance of different exposure pathways and the distribution of potentially harmful substances in the environment. This will determine whether or not current accepted toxicological thresholds such as those adopted by the US-EPA and WHO can be applied globally.

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#### *IUGS/IAGC Global Geochemical Baselines*

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