

The role of geochemistry in environmental and epidemiological studies in developing countries: a review

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Abstract: Concern over the effects of chemicals in the environment on the health of man and animals is growing as rapid economic and population growth extends such problems as land degradation, pollution and urbanization from industrialized nations to the developing world.

In this paper we review the principal socio-economic and environmental pressures on developing countries before discussing the role of geochemistry in: (1) preparing high resolution baseline data to identify potential hazards; (2) understanding the pathways of chemical elements from rocks and soils to man and animals; and (3) developing amelioration strategies to reduce the impacts of inappropriate land use, power generation and mining. The particular geochemical problems of tropical terrains are discussed and some case histories from the international work of the British Geological Survey (BGS), funded by the Overseas Development Administration, are described.

It is recommended that developing nations prepare modern geochemical maps, ideally to the standards set out in International Geological Correlation Programme Project 360 World Geochemical Baseline, and that aid agencies should fund integrated environmental geochemical surveys as being of primary importance, especially for health studies and land use planning; particular attention should be paid to the environmental impact of urbanization. Further understanding of chemical and mineralogical speciation is required to improve the interpretation of geochemical data for environmental purposes.

Multidisciplinary studies, involving epidemiologists, biochemists and nutritional specialists, are essential if natural and anthropogenic impacts are to be properly assessed and practical amelioration measures implemented.

There is a growing awareness of the relationships between animal and human health and the distribution of chemical substances in the environment, first demonstrated by Webb (1964). In industrialized countries, concern continues to focus on anthropogenic accumulations of potentially harmful elements (PHEs) such as As, Cd, Hg and Pb, and on organic compounds such as DDT, PCBs and dioxins. Some of these chemicals may be classified as carcinogens, neurotoxins or irritants; others may cause reproductive failure or birth defects (WHO 1988). In the case of domestic livestock, conditions caused by deficiencies in one or more of the essential trace-elements Co, Cu, Zn, Se and I are also well documented (Mertz 1986). However, the extension of such links to humans in developed countries remains controversial, since diets are diverse and generally considered to provide adequate trace-element levels.

In recent years the availability of regional geochemical data for Britain, Canada, Scandinavia and many other developed countries has demonstrated that in addition to pollution related to man's activities, large areas have high concentrations of heavy or radioactive elements which occur naturally (BGS atlas series 1978-95;

Appleton 1992). Extensive regions have also been shown to have levels of essential trace elements well below those recommended for soils and pasture (Darnley *et al.* 1995). Excellent epidemiological data are available for some developed countries and certain associations between environmental geochemistry, diet and degenerative disease have been suggested (e.g. Martyn *et al.* 1989). Attempts to link the occurrence of degenerative diseases, such as cancer and heart disease to diet may, however, be jeopardized by lack of knowledge of the chemistry of dietary components as well as by the wide range of confounding factors. Variations in the trace element status of most crops reflect that of the soil in which they are grown, but in developed countries the effect on humans is masked by the use of food from different areas.

By contrast, people in many developing countries, particularly those living on subsistence agriculture, obtain much of their food from local sources and problems such as land degradation, pollution and increasing urbanization may be particularly intense. Equally, trace-element deficiencies or toxicities may be much more critical for human and animal health than

in developed countries. Studies of the relationship between environmental geochemistry and health are therefore likely to be of more immediate value in developing than developed countries, although the results could have worldwide significance. Unfortunately, modern geochemical data are rarely available for developing countries, or may be inadequate for environmental purposes, having been collected principally for mineral exploration.

In this paper we first briefly review the socio-economic threats to the environment of developing countries, with particular reference to the special problems of tropical terrains. The basic requirements for preparing baseline geochemical data are described with reference to International Geological Correlation Programme Project (IGCP) 259/360 guidelines (Darnley *et al.* 1995) and the geochemical factors affecting the pathways of chemical elements from soils and water to plants, animals and man are discussed. New methods of processing geochemical data to indicate speciation and hence bioavailability are also suggested, and some specific geochemical case studies carried out by the British Geological Survey (BGS) in developing countries are briefly outlined. Such research can help not only to identify potential environmental problems and develop amelioration strategies, but also to act as a basis for the development of appropriate policy and legislative frameworks. It also has the potential to cast new light on several types of degenerative disease which affect man, animals and crops.

Socio-economic pressures on the environment of developing countries

The annual increase in world population is approaching 100 million per year (UN 1992), approximately 90% of which is in the poorest countries where one-quarter of the population live in 'absolute poverty' (having an annual income below US\$ 450) as defined by the World Bank (1992). According to McMichael (1993) population pressure and poverty have adverse inter-related environmental impacts. For example, the effects of large-scale coal burning in industrializing developing countries, of increasing ricefield methane emission and of widespread deforestation throughout the third world, can be attributed to population pressure. Problems associated with the use of marginal farmlands, soil erosion from cash cropping, uncontrolled industrial and urban pollution and the accumulation of potentially harmful wastes are particularly intense in some developing countries

(McMichael 1993).

Each year around six million hectares of the world's agricultural land are lost through soil degradation (UN 1992), which is perhaps one of the most fundamental problems. Soil is a complex mixture of rock and mineral detritus, organic matter, microbes (bacteria, yeasts and fungi) and invertebrates. The removal of protective plant cover, overgrazing or overcropping leading to the depletion of essential nutrients, the addition of toxic chemicals, salination (in some cases as a result of irrigation) and acidification from power generation and industrialization, can cause all soil organisms to die and soil to turn to inert mineral dust (desertification).

Economic and population pressures on rural economies cause migration, especially to urban centres. In developing countries the growth of very large cities (with populations greater than five million) is of particular concern; on current trends the population of some eight to ten cities will reach 15–25 million by the end of the century (UN 1991; McMichael 1993). Urbanization in turn leads to further adverse environmental effects, such as contamination of surface water and aquifers through poor sanitation. Pollution of air, water and soil from vehicles, power plants and factories is at its most extreme in cities, and may result in increased incidence of childhood diseases associated with heavy metal poisoning (WHO 1988; US Geological Survey 1984). However, despite the growing need, geochemical studies of major cities in developing countries are currently lacking.

Mining has also caused contamination, including cyanide, mercury and arsenic releases from gold mining, and radioactive element pollution from tin mining. Although large international mining companies now generally work to high environmental standards, mineral working by uncontrolled and disorganized groups (especially for gold) continues to cause environmental problems in developing countries, as in the recent incidents of mercury pollution in Brazil (Stigliani & Salomons 1993).

The surface environment in developing countries

The socio-economic pressures on the environment in developing countries are frequently compounded by the nature of their surface environment, which can be particularly susceptible to degradation and pollution, especially in climatic regions classified as equatorial, tropical or sub-tropical (Köppen 1936). Climates have

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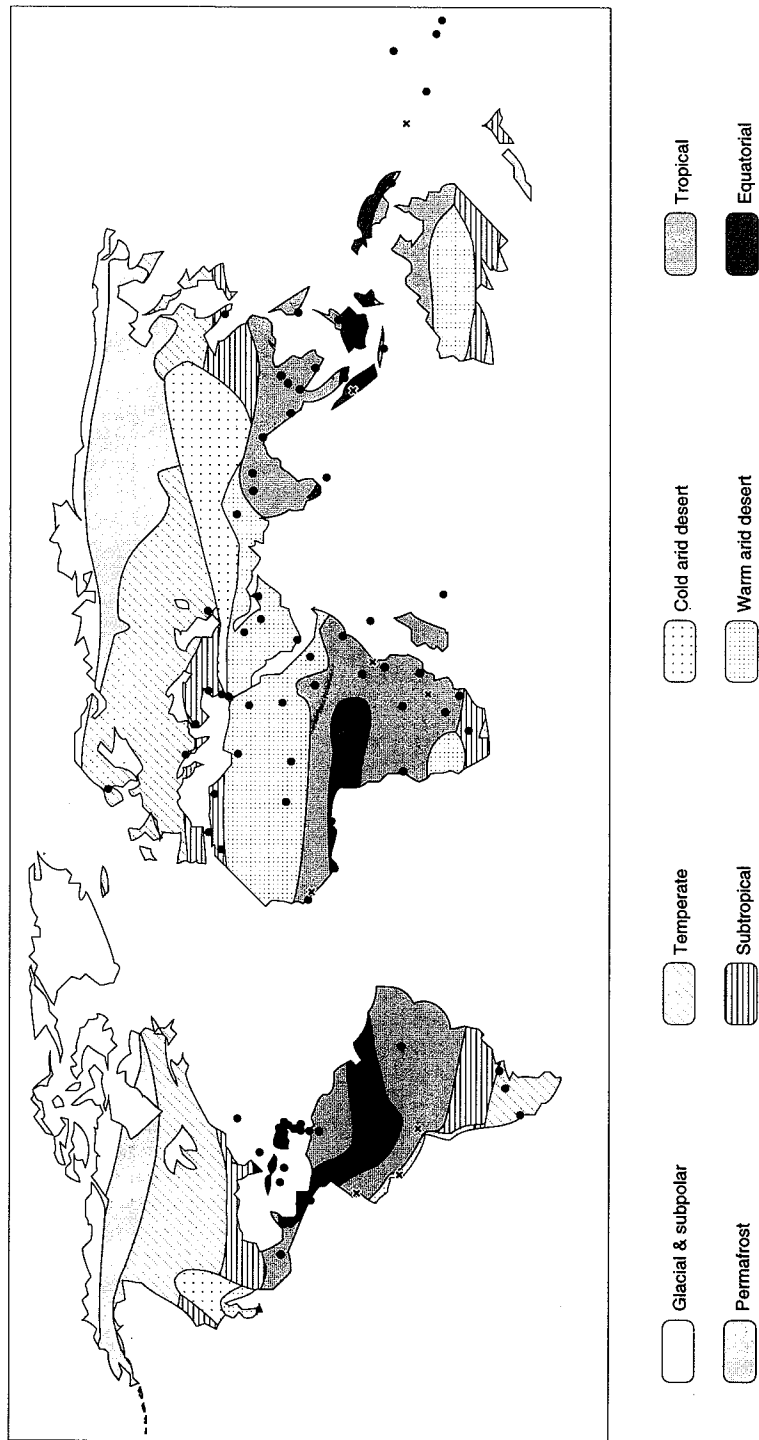


Fig. 1. Morphoclimatic zones of the world (after Budel 1982).

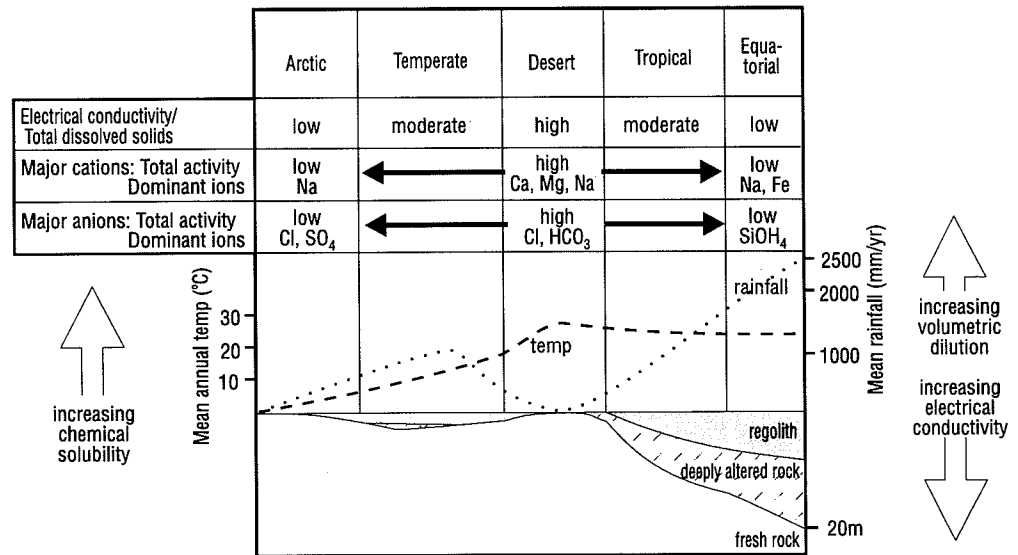


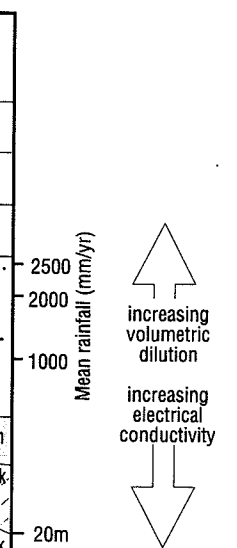
Fig. 2. Generalized relationships between regolith, thickness of the weathering zone, climatic factors and water chemistry (modified after Pedro 1985).

changed frequently and in some cases profoundly in the geological past, so that some areas have been affected by a succession of different weathering and dispersion processes (Fig. 1). At lower latitudes and particularly in continental areas of low relief, the regolith may be an expression of the cumulative effects of subaerial weathering during many millions of years (Butt & Zeegers 1992). Some soils have been deeply leached under various climatic conditions, including long periods of high rainfall and temperature to which they have been repeatedly subjected from Tertiary times or even as far back as the late Proterozoic (Daniels 1975; Butt 1989). Tropical and semi-tropical soils, partly because of their age and the number of weathering cycles to which they have been subjected, tend to be poorer, thinner and more fragile than those in temperate regions (Murdoch 1980). This is particularly the case in shield areas of Africa and Latin America where soils have developed on crystalline basement and are generally older. In contrast, those of southeast Asia developed on alluvium or volcanic rocks are generally younger and more fertile (McMichael 1993).

In tropical countries laterites, which have been forming continuously for at least 100 million years (since the Jurassic) in parts of Africa, India, South America and Asia (King 1957; Michel 1973), are common. Weathering profiles

may extend to depths of over 150m, with weathering fronts at great depth (Trescases 1992), so that the fresh supply of chemical elements from rocks into the biosphere is limited. Laterites, which include Fe- and Al-rich tropical weathering products such as bauxites, ferricretes and Fe- and Al-duricrusts, have markedly homogeneous mineralogical and chemical compositions which usually bear little relationship to underlying bedrock (Nahon & Tardy 1992). They have well defined chemical profiles but, depending on the climatic and tectonic history, the land surface may be highly complex with the profiles truncated or buried by later detritus (Butt & Zeegers 1992).

In such conditions, intense oxidation, which generally extends to the weathering front, results in a lack of organic matter (which is stored in the biota rather than soils) and of other major elements such as phosphorus, nitrogen and potassium, and also in the formation of stable insoluble minerals such as clays (especially kaolinite) which markedly increase the Al/Si ratio. Generally, such soils are deficient in soluble cations (Na^+ and Ca^{2+}) and anions (Cl^- , PO_4^{3-} and NO_3^-), but have high levels of resistant oxides of Fe, Al, Ti and Mn. They are typically kaolinitic or ferralitic, with local calcrètes or silcrettes in areas of inland drainage affected by evaporation and a fluctuating water table. Hardening of aluminium and iron oxide to



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form cuirasses, which armour the otherwise friable surface, is common in tropical terrains. As natural vegetation is cleared from such environments, essential nutrients are further leached and the top soil may be completely eroded.

Evidence exists that some deserts were formerly subjected to extreme leaching under tropical conditions during the Cretaceous and Tertiary (Butt & Zeegers 1992). Most desert soils are typically lithosols, the important constituents of which are resistate detrital quartz and accessory minerals such as zircon and secondary clay minerals. Organic material in desert soils is minimal and surface waters are highly oxidizing, with variable pH (frequently with high pH values). They generally have higher salinity than those in other environments, with chloride rather than bicarbonate as the main anionic species. Some generalized relationships between different surface environments are shown in Fig. 2.

Chemical elements tend to undergo more pronounced separation in tropical environments than in temperate regions, although this depends on their chemical mobility and on the nature of the local environment (Trescases 1992). Hence areas with a potential for deficiency or toxicity conditions are likely to be much more common in tropical countries than in temperate regions. The most deeply leached environments retain only the most inert elements such as Fe, Mn, Zr, Hf and the rare earths, either as secondary or primary oxides. On the other hand the most mobile elements, such as the alkalis, alkaline earth elements, the halogens and elements mobile in conditions of high pH, including anions and oxyanions, such as those of B, Se, Mo, V and U accumulate in arid environments generally, inland drainage systems and near the base of weathering profiles. The variable oxidation states of the first row transition elements Co, Cr, Cu, and Zn also favour removal from solution by ion exchange, precipitation and surface sorption. The lack of organic matter as a result of intense oxidation can mean that total levels of such elements in the regolith may be high, but they may be bound on Fe-Mn oxides and thus their bioavailable levels may be exceptionally low, resulting in potential deficiency for plants and animals, especially in deeply oxidized surface environments. The controls on the speciation of As, Cd and Pb are broadly similar to those of the first row transition metals, although the oxidation states of these elements, with the exception of As, exhibit less control on mobility (Ure & Davidson 1995).

Essential and potentially harmful chemical elements

Two main groups of chemical elements are of particular importance for health. Those identified as essential to animal life (according to Mills 1996) include the first row transition elements Fe, Mn, Ni, Cu, V, Zn, Co and Cr, together with Mo, Sn, Se, I and F. The disorders associated with deficiency of these elements are given in Mills (1996). Boron has not yet been shown to be necessary for animals, although it is essential for higher plants. By contrast potentially harmful elements (PHEs), known to have adverse physiological significance at relatively low levels, include As, Cd, Pb, Hg and some of the daughter products of U. Aluminium can also have adverse physiological effects in trace amounts in animals and particularly in fish and plants (Sposito 1989). All trace elements are toxic if ingested or inhaled at sufficiently high levels for long enough periods of time. Selenium, F and Mo are examples of elements which show a relatively narrow concentration range (of the order of a few $\mu g g^{-1}$) between essential and toxic levels.

The difficulties of diagnosing disease, and particularly subclinical conditions, in animals and man related to trace element deficiencies or excesses are discussed by Mills (1996). Except in some specific cases, for example Iodine Deficiency Disorders (IDD), symptoms may be non-specific and diagnosis, based on tissue or blood sampling, costly. Geochemical maps, however, can indicate areas where there is the potential for trace element deficiency or toxicity, enabling expensive veterinary or medical investigations to be better targeted.

Multi-media geochemical surveys (ideally incorporating soil, stream sediment and water data) can also be of considerable value in studies linking diet and health. Although many PHEs, such as Pb, are not phytotoxic, elevated concentrations in the regolith may be transmitted, through uptake by healthy plants, into the food chain and can thus lead to adverse health effects in animals and humans, the source of which can be difficult to diagnose (Mills 1996). The concentrations of certain essential trace elements (such as Se) in crops (rice, corn, soybean) has been shown to correlate with the concentrations in the soil in which they are grown (Levander 1986); and, regionally, levels in fine fraction stream sediments give a good indication of likely soil concentrations (Appleton 1992). Geochemical mapping can therefore be a cost-effective method of indirectly investigating the chemical composition of crops; and rural communities in

developing countries offer a particularly valuable opportunity for examining the relationship between geochemistry, diet and health.

The need for baseline geochemical data in developing countries

In many developed countries geochemical mapping is now an integral component of strategic systematic geoscience surveys (Plant *et al.* 1988; Darnley *et al.* 1995; Plant & Hale 1995), with applications for a wide range of economic and environmental purposes (Webb 1964; Thornton 1983; Thornton & Howarth 1986). It is clear from these studies that geochemistry, particularly the surface distribution and concentration of trace elements, can be difficult to predict from geological maps (Darnley *et al.* 1995). Areas underlain by different granites, for example, may have comparable major element concentrations but the levels of PHEs, such as U, Mo, Be and Pb, can vary by factors of an order of magnitude or more (Plant *et al.* 1983). Levels of environmentally important trace elements are even more difficult to predict in areas underlain by sedimentary and metamorphic rocks. Moreover, the geochemistry of some elements, for example Se, is not fully understood, so that any predictions based on geological maps can prove misleading. In tropical countries the problem is frequently compounded by deep weathering whereby levels of chemical elements in the surface regolith may show little or no relationship to bedrock composition. Indeed, many elements, including Al, Fe, Mn, Co, U, P, Cr, Ni, Cu and Au, may be concentrated to ore grade in the lateritic mantle; and high concentrations of PHEs such as As and Sb may also occur (Smith *et al.* 1987). In Jamaica, for example, the distribution of high concentrations of radioactive and other PHEs has been shown to follow closely that of bauxite (Simpson *et al.* 1991).

Geochemical mapping has long been used in conjunction with geological mapping as a mineral exploration tool in developing countries. Regional geochemical maps, such as those of Zambia and Sierra Leone, were first published some 30 years ago (Webb *et al.* 1964; Nichol *et al.* 1966); and atlases, such as that of Uganda, more than 20 years ago (Reedman 1973). Many of such surveys, however, covered only the regions considered most prospective for metalliferous mineral deposits and were designed specifically to cover large areas at low density and cost, for example in Peru (Baldock 1977).

More recent programmes, for example in Zimbabwe (Dunkley 1987, 1988) and Sumatra (Stephenson *et al.* 1982; Coulson *et al.* 1988)

have produced higher density multi-element data with some potential for application in environmental and animal and human health studies (Appleton & Ridgway 1993). Basic hydrogeochemical parameters and data for such environmentally significant elements as Se and I are generally lacking, however (Darnley *et al.* 1995).

There is now an urgent need in developing countries for high resolution geochemical data which are adequate for environmental and epidemiological studies, particularly in urban areas where conflicts between rapid development and environmental sustainability are severe and where surface water, groundwater and soils are increasingly becoming contaminated (WHO 1988).

The requirements and methodologies for preparing high resolution geochemical baseline data are discussed in detail in the final report of the IGCP Project 259 (Darnley *et al.* 1995) which includes internationally agreed standards for sampling, analysis and data processing in different terrains. Analytical methods aimed at providing comprehensive data for the most environmentally important elements, with limits of detection below estimated crustal abundance variance, are also recommended, together with a quality control system and recommendations for databasing and presenting data.

At present no international agency is responsible for mapping the distribution of chemical substances, other than radioactive elements for which the International Atomic Energy Agency continues to provide the scientific infrastructure. Hence geochemical mapping continues to be carried out using a range of different methods, often varying according to short-term goals and the practices established in the developed country or organization providing aid. Moreover, aid agencies continue to fund geochemical mapping only as a low cost adjunct to geological mapping for mineral exploration. This is unfortunate since geochemistry provides the most relevant geoscience data for environmental studies and land use planning and has a much lower cost per unit of area covered than other types of geoscience survey (Plant & Slater 1986).

The separate conduct of surveys of the chemistry of soils, water and stream sediments by different agencies – a legacy from the past when geochemistry developed as a component of geological, soil and hydrological survey organizations – also limits the effective application of geochemistry in addressing environmental problems. Ideally, comparable multi-element data for each sample medium should be collected as part of a single, holistic, multi-media geochemical campaign. This is particularly important since

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The national agency is responsible for the distribution of chemical and radioactive elements for the Atomic Energy Agency and the scientific infrastructure. The geochemical mapping continues to be carried out by a number of different methods, ranging from short-term goals and objectives to those included in the developed countries, providing aid. More attention is given to fund geochemical studies as an adjunct to geological exploration. This is particularly true in the industry provides the most accurate data for environmental monitoring and has a much larger area covered than other methods (Plant & Slater 1986). The results of surveys of the geochemistry of river and stream sediments are a legacy from the past and have been developed as a component of the geochemical survey organization. The effective application of geochemical data in solving environmental problems requires multi-element data for which could be collected as part of a multi-media geochemical survey. This is particularly important since

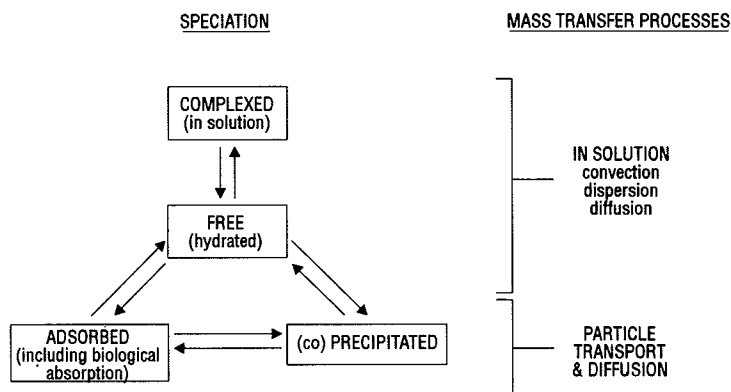


Fig. 3. Relationships between speciation of chemical elements and mass transfer processes (after Bourg 1988).

new data on speciation, combined with computer modelling and GIS, make possible the preparation of geochemical maps targeted at environmental problems.

Understanding the pathways of chemical elements from rocks and soils to man and animals

The total concentration of chemical elements indicated on geochemical maps can be of direct value in studies of relationships between disease and the levels of trace elements (e.g. Thornton & Plant, 1980; Plant & Stevenson 1985; Plant & Thornton 1986; Appleton 1992). However, the amount of each element which is bioavailable is more important for these studies than the total amount. For example Al, which is the commonest metal in the earth's surface layer, occurs in both inert and bioavailable forms, and its potential toxicity thus depends on its chemical form or speciation. It can occur in a large number of dissolved species, especially in conditions of low or high pH, or in colloids with organic carbon or silica which limit its toxicity. The toxicity of As and Sb also depends on their chemical form. They are most toxic in the M^{-3} gaseous state with decreasing toxicity in the sequence $M^{3+} > M^{5+} >$ methyl As/Sb (Abernathy 1993; Chen *et al.* 1994).

The speciation of chemical elements affects their distribution, mobility and toxicity (Fig. 3). This has been known for a long time in the case of the common anions (HCO_3^- , NO_3^- , SO_4^{2-}) and more recently for a wide range of chemical elements in the geosphere (Goldberg 1954) and surface environment (Stumm and Morgan 1981;

Buffle 1988).

The importance of chemical speciation in relating geochemical data to health was first established by agricultural scientists (Underwood 1979; Lander 1986). Recently considerable developments have been made in the prediction of chemical speciation by modelling thermodynamic and kinetic equilibria (Basset & Melchior 1990; Stumm 1991) and by experimental determinations (Buffle 1988; Marabini *et al.* 1992). Biochemical processes, induced by microbial, plant and animal activity, are also important controls on both speciation and mobility, but were relatively poorly understood until recently (Ehrlich 1990; Deighton & Goodman 1995).

Some of the most important controls, particularly on trace element speciation and the mobility, include hydrogen ion activity (pH), redox potential (Eh), temperature, surface properties of solids, the abundance and speciation of potential ligands, major cations and anions, the presence or absence of dissolved and/or particulate organic matter, and biological activity. Two of the most important factors directly controlling mobility and solubility are Eh and pH (Fig. 4). The solution chemistry of an element is affected profoundly by changes in oxidation state, while dissolution reactions, including hydrolysis, inorganic complexation, complexation with smaller organic anions (such as oxalate) and sorption/desorption, are all pH controlled. Under conditions of high pH, anions and oxyanions (such as those of Te, Se, Mo, U, As, P and B) are more mobile and most cations (such as those of Cu, Pb, Hg and Cd) are less mobile, while at low pH the reverse is generally true. Where humic substances or biological byproducts are present, however, stable organo-

RELATIVE MOBILITIES	ENVIRONMENTAL CONDITIONS			
	oxidizing	acid.	neutral-alkaline	reducing
VERY HIGH	I	I	I Mo U Se	I
HIGH	Mo U Se F Ra Zn	Mo U Se F Ra Zn Cu Co Ni Hg	F Ra	F Ra
MEDIUM	Cu Co Ni Hg As Cd	As Cd	As Cd	
LOW	Pb Be Bi Sb Tl	Pb Be Bi Sb Tl Fe Mn	Pb Be Bi Sb Tl Fe Mn	Fe Mn
VERY LOW TO IMMOBILE	Fe Mn Al Cr	Al Cr	Al Cr Zn Cu Co Ni Hg	Al Cr Mo U Se Zn Co Cu Ni Hg As Cd Pb Be Bi Sb Tl

Fig. 4. General relationships between Eh, pH and the mobility of some essential and potentially toxic elements (modified after Andrews-Jones 1968). Essential elements are shown in normal type and potentially hazardous elements in italics.

metallic complexes (which may behave as anions) are formed, increasing trace-element mobility. The kinetics of inter-species interactions also act as important controls on speciation, particularly where natural systems are disturbed by the influences of man.

Geochemical interaction between the geosphere/hydrosphere and the biosphere depends partly on sorption processes and partly on chemical speciation. Some elements, for example Al, Ti and Cr, are relatively poorly assimilated by plants, although others such as Cd, Se, Mo and Co, can readily cross the soil-plant barrier and enter the food cycle (Loehr 1987). In soils, sorption of elements by clay minerals and organic material is the predominant fixing mechanism, with soil pH controlling sorption processes and metal solubility/bioavailability. Many metals are more soluble in the low pH conditions induced by natural organic acids and root exudates (Fig. 5).

In higher animals, including man, assimilation occurs by ingestion of nutrients and contaminants, by absorption through the skin, and by respiration (WHO 1984). Speciation both in the natural environment and in the gastro-intestinal tract, exerts a major influence on the uptake and assimilation of trace nutrients and PHEs (WHO 1984, 1994).

Speciation studies are of particular importance in areas affected by land degradation, deforestation or pollution caused by mining, industrial activity or urbanization, where they can be used to optimize amelioration strategies and improve management practices. A knowledge of the factors controlling speciation in

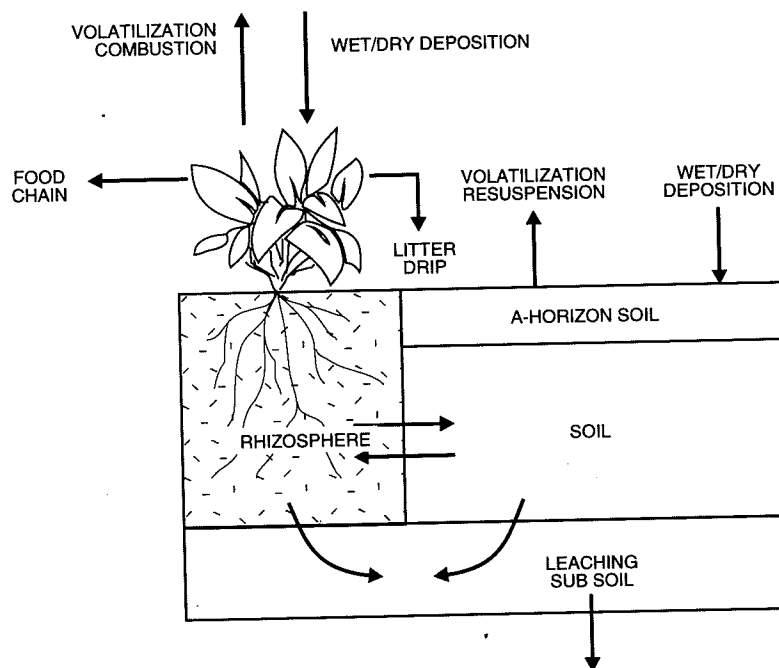


Fig. 5. Exchange processes at the plant/soil interfaces (modified after Cohen 1987).

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different environments can be used to predict the potential for absorption of PHEs and as a guide to the need for trace element supplementation for crops and animals, particularly where baseline geochemical data are available. Ideally, environmental geochemical surveys, particularly in tropical terrains affected by intense chemical weathering, should be based on chemical speciation. Extraction techniques can be used to provide an indication of speciation (e.g. Tessier & Campbell 1988), but sensitivity to changes prior to analysis limits the applicability of such determinations where large numbers of samples are involved.

Prediction of speciation using a range of thermodynamic models such as WATEQ4F (Ball & Nordstrom 1991), PHREEQV (Crawford 1996) and EQ3/6 (Wolery 1992) has greater potential, provided that suitable thermodynamic and/or kinetic data are available (Bassett & Melchior 1990) and the effects of biochemical processes are quantified. An iterative approach using detailed experimental studies of selected elements to validate model predictions is thought to offer considerable potential for developing speciation maps from geochemical baseline data for large-scale environmental and epidemiological studies. Studies of Al and As speciation, for example, are being used to develop methods of processing regional geochemical data to indicate speciation (Simpson *et al.* 1996; Smith *et al.* 1996).

Selected case studies

The role of geochemistry in identifying, and in helping to ameliorate, environmental and health problems resulting from trace element imbalances or contamination in developing countries is illustrated by selected case studies.

Natural trace element imbalances and animal health

Although undernutrition is the major limiting factor to grazing livestock production in tropical areas, trace element deficiencies or imbalances in soils and forages are also responsible for low production and reproduction problems. For grazing livestock, deficiencies of Co, Cu, I, Fe, Mn, Se and Zn, together with excesses of Cu, F, Mn and Mo, may particularly lead to adverse effects; As, Pb, Cd, Hg and Al also cause toxicity (Appleton 1992).

The diagnosis and mapping of affected areas have generally been carried out using forage, animal tissue or fluid compositions, all of which

are expensive and time consuming (Appleton 1992). Veterinary scientists and agronomists are generally familiar with the use of soil geochemistry, but the value of regional geochemical maps based on drainage samples is largely unknown, especially in developing countries (Appleton & Grealley 1992). Studies in Bolivia and Zimbabwe have been undertaken in order to assess whether such data, either collected specially or previously (e.g. for exploration), can be used to predict problems of animal health, and whether low levels of trace elements in drainage sediments correlate with reported deficiencies in grazing livestock.

In northeastern Zimbabwe stream sediments, soils and forage all exhibit significant correlation and the same regional patterns for Zn (Fordyce *et al.* 1996). The lack of a significant correlation between Zn levels in those media and the levels in cattle blood serum is ascribed in part to a range of dietary and physiological factors. It is suggested that high concentrations of Fe and Mn in soil and forage inhibit the availability and therefore the uptake of trace elements, such as Cu or Zn. Consequently Zn levels in blood serum from cattle foraging in areas with moderate to high Zn levels may be equally low as those from cattle feeding in low Zn areas (Fig. 6). Likewise the availability of P to plants and animals may be significantly reduced by high Fe oxide levels in soils. Nevertheless stream sediment geochemical data are shown to be of value in helping to target areas for specific veterinary investigations, because they provide regional information indicating both where Zn and Cu are likely to be deficient and where high Fe and Mn may induce low Zn or Cu status in cattle, despite moderate to high levels of these trace elements in sediments, soils and forage.

This case study (Fordyce *et al.* 1996) therefore supports the review by McDowell *et al.* (1993) which identified a lack of direct correlation between trace element levels in soil and forage and those in animal blood serum. The findings do not fully corroborate the conclusions of other reviews (Thornton 1983; Aggett *et al.* 1988; Appleton 1992) which suggest that stream sediment geochemical maps can be used directly to indicate areas where ruminants may be subject to trace element deficiencies. However, the conclusion that high concentrations of Fe and Mn oxides in soil may inhibit the availability of P to plants and of Cu and Zn to cattle could have wide implications in developing countries because of the preponderance of ferralitic soils in tropical regions. It also underlines the need to understand speciation or phase partitioning in order to relate 'total' geochemical

WET/DRY
DEPOSITION



Loehr 1987).

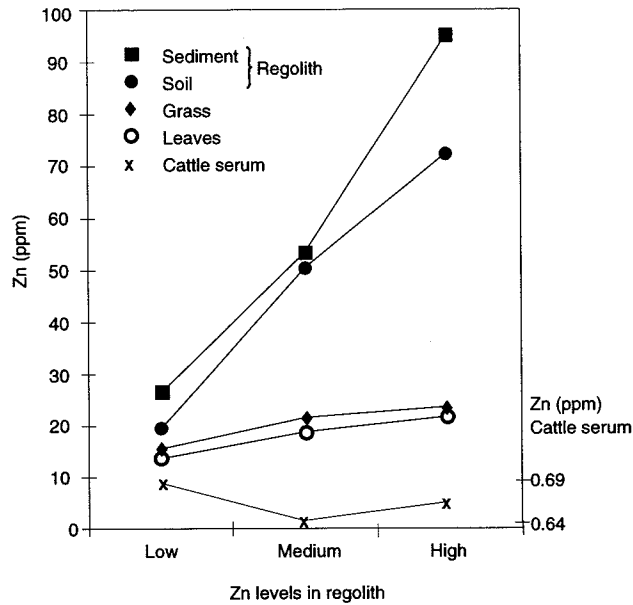


Fig. 6. Zinc concentrations in stream sediment, soil, grass leaves and cattle serum from northeast Zimbabwe (after Fordyce *et al.* 1996).

data to plant or animal health criteria.

Environmental impact of coal-fired power stations

Many developing countries depend heavily on coal-burning power stations for energy generation and in some cases low grade or 'dirty' coal feedstocks are used, resulting in serious environmental degradation. Accordingly the fates and environmental impact of potentially harmful trace element emissions (PHEs) from coal-fired power stations have been studied, particularly in China.

The multi-element geochemistry of the coal feedstock has been compared with that of waste products and emissions at a power station in northeast China. Normalization of the output (slag, fly-ash) chemistry, to coal, characterizes element partitioning within the combustion products, which are generally enriched by up to an order of magnitude (Simpson *et al.* 1995), the slag containing particularly high levels of Be, As, Mo, Cd and W and the fly-ash high Li, As, Cd, U and Th. For example, the results of mass balance calculations (Fig. 7) show that of the 36 tonnes per annum of As consumed (6 ppm As in six million tonnes of coal feed) some 24 tonnes are output in solid wastes (slag 12 ppm, and fly-

ash 15 ppm), but that almost 12 tonnes per annum of As are emitted from the stack. By contrast, most U and all Mo is shown to partition into the solid wastes. The high levels of certain trace elements from stack emissions may have a considerable impact on the geochemistry of surface soils in the surrounding area, particularly from pollution plumes in the prevailing wind directions. Such emissions could therefore have adverse effects on the surface environment and on plant, animal or human health, partly because the emitted, potentially toxic elements may well occur as readily available and ingestible chemical species; however, more studies are needed to confirm this conclusion.

A further environmental hazard may result from leaching of PHEs from (often unlined) lagoons, in which slag and fly-ash slurries are dumped. A study of lagoon leachates (Simpson *et al.* 1995), normalized to cooling-water chemistry, shows that there is strong enrichment in some elements that can pose environmental threats, such as Al, Mo, V and particularly F, which exceeds 25 mg/l (Fig. 7). Experimental sequential leaching again suggests that high levels of bioavailable and therefore easily ingested species of certain trace elements are present.

The surface environment around the power

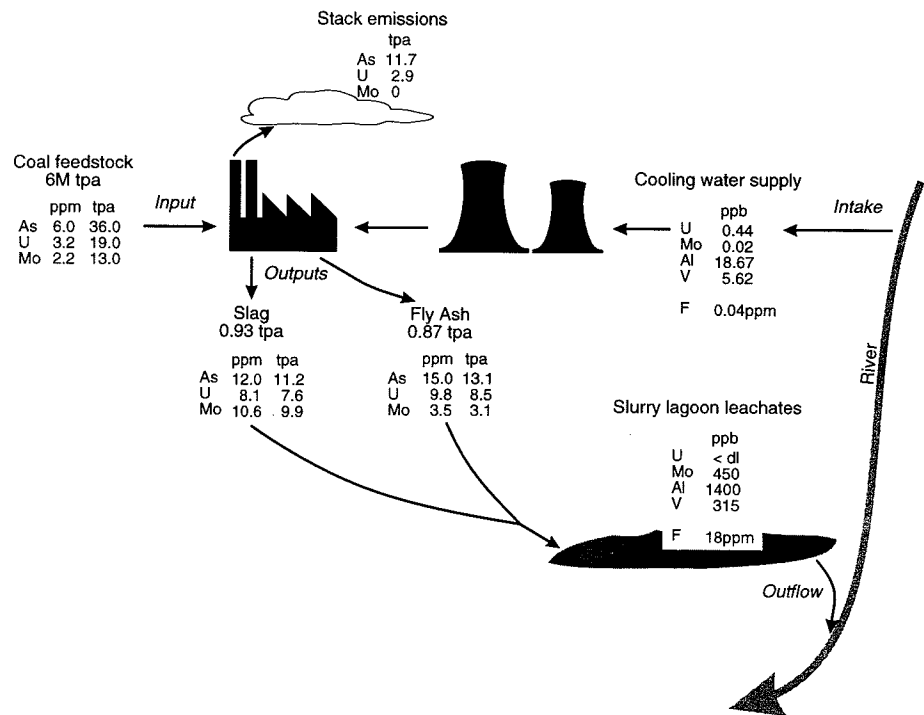


Fig. 7. Mass balance calculations for some PHEs in a power station in northeast China (after Simpson *et al.* 1995).

station has been geochemically characterized and compared with uncontaminated baseline regions of similar geology. The effects of emissions of such elements as As, F, Be, of gases such as SO₂, and of leachates from the slurry lagoon carrying elevated levels of available PHEs, are being assessed in terms of a critical loads analysis. Preliminary results confirm the importance of factors such as carbonate-rich rocks and well buffered soils in reducing both the potential for acidification and the mobility of PHEs (Simpson *et al.* 1992; Flight 1994).

Impact of mining

In many developing countries, the exploitation of mineral resources is of considerable importance for economic growth, employment and infrastructural development. It can also cause serious environmental problems, particularly in tropical regions characterized by high rates of weathering and biogeochemical cycling, because outputs of major constituents and impurities in the ore, or of chemicals used in processing, can accumulate to levels that may be harmful to plant, fish, animal and human health.

Studies of the environmental and health impacts of mining, undertaken at numerous representative mines in southeast Asia and southern Africa, have highlighted systematic relationships between mineral deposit geochemistry, mining methods and drainage quality (Williams 1993). The most important controls are water-rock interactions, sulphide oxidation rate at the fluid-rock interface and *in situ* buffering which is strongly influenced by gangue lithology/mineralogy and the weathering rate.

Mobilization of most heavy metals is controlled by local pH/Eh conditions and occurs principally at low pH under conditions of acid mine drainage (AMD). By contrast As and Sb are mobile across a much wider pH/Eh range (Fig. 4), a characteristic with important implications for remediation schemes, because conventional buffering, such as liming, may be ineffective for As contaminated mine-waters.

Studies have shown that the precipitation of Fe oxyhydroxides is, however, a very effective practical process for scavenging and immobilizing As. Significant As contamination in surface drainage, soil pore water and groundwater over considerable areas may particularly occur in conditions of low ambient Fe concentrations

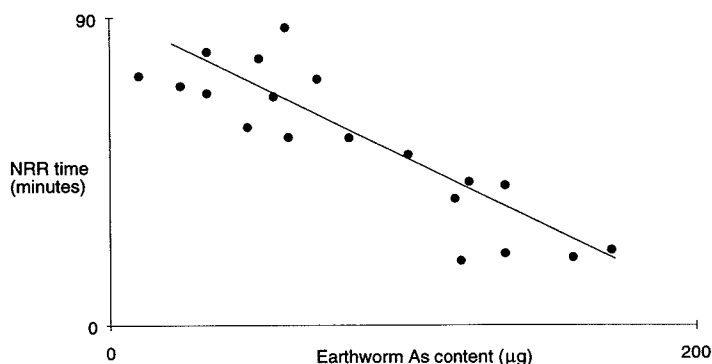


Fig. 8. Results of neutral red retention (NRR) pilot test: Wanderer Mine, Zimbabwe (after Williams & Breward 1995).

(e.g. Globe and Phoenix Mine, Zimbabwe). Some soils with low (< 5%) Fe content actually carry over 100 ppm water soluble As, resulting in marked uptake by crops (up to 10 ppm As in maize), whereas this is not observed in vegetation over sites with similarly high total As, but which also contain normal or high levels of Fe and in which the As is held as immobile ferric hydroxide/arsenate complexes (Williams 1994). The problem can be exacerbated by low soil P, as crops may assimilate As as a P substitute, due to the close chemical similarity of the phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) anions (Williams & Breward 1995). In another example at Ron Phibun, southern Thailand (National Epidemiological Board of Thailand 1993), shallow groundwater exceeds 5 mg/l^{-1} As (compared with the WHO drinking water guideline of only $10 \mu\text{g/l}^{-1}$) in areas where soils contain < 2% Fe. Where soil Fe increases to > 5%, As drops to < $100 \mu\text{g/l}^{-1}$ (Fordyce & Williams 1994). Modelling of Fe oxide sorption properties suggests that precipitation of dissolved Fe as hydrous oxide would, in most instances, scavenge As particularly effectively, and consequently may provide a practical remediation strategy for As-rich mine waters, as the As would be immobilized in inert solid materials.

Mining or beneficiation technology may also be critical for metal mobility. In the presence of cyanide complexing agents, the mobility of As and heavy metals is maintained at neutral and even high pH. Drainage waters of pH 8, for example at Globe and Phoenix, can hold $> 30 \text{ mg/l}^{-1}$ Cu, $> 10 \text{ mg/l}^{-1}$ As and $> 15 \text{ mg/l}^{-1}$ Sb in the presence of cyanides, even at low ($< 10 \text{ mg/l}^{-1}$) concentrations (Williams 1994).

The effective assessment of the ecotoxicological impacts of mining contamination may be

difficult and costly in developing countries. A practical pioneering method for assessing the toxicological impacts of exposures to As (and other PHEs) has recently been developed and tested successfully at Wanderer Mine, Zimbabwe, by the BGS working in collaboration with the Institute of Terrestrial Ecology (Williams & Breward 1995). Individual invertebrate cells are collected and spiked with neutral-red dye. Healthy cells retain the dye for lengthy periods (longer than one hour) but with increasing exposure to toxic conditions (As or heavy metals) the cells become stressed and release the dye increasingly rapidly (Fig. 8).

This study into the impacts of As or heavy metal contamination from mining again underlines the importance of understanding speciation/phase partitioning in characterizing the principal controls that determine sorption/precipitation or a high degree of mobility/availability, thus determining whether or not enhanced metal levels are likely to affect the health of plants, animals or humans. The study has also identified some potential methods for controlling As levels, as well as for assessing their ecotoxicological impact in practical, cost effective ways.

Conclusion and recommendations

Increases in our understanding of the chemistry of natural systems, coupled with improved computing power, analytical methods and information technology, now offer an opportunity for considerable advances in environmental geochemistry. For example, critical load analysis can be performed and regional geochemical data processed to provide an indication of speciation and hence bioavailability. Such new and sophis-

ticated geochemical tools can be used as a basis for targeting resources into areas worst affected by environmental degradation, predicting potential hazards and identifying factors limiting agricultural productivity or those likely to cause health problems in man. In order to benefit from these new approaches, more multi-element, multi-parameter baseline geochemical data are needed, as well as specific research into the speciation of PHEs and essential nutrients in different geological and climatic terrains.

Many studies have tended to concentrate on potentially toxic heavy metals. More work is needed on those trace elements that are essential to human health but have harmful effects unless a critical, narrow range is maintained, especially Se and I. The deficiency of Se has been linked to endemic osteo-arthropathic and cardiovascular disorders in parts of China (Jianan 1990), and to heart disease in Ohio (Schlamberger 1980), while Iodine Deficiency Disorders (IDD) including goitre and cretinism, are estimated as likely to affect up to 800 million people in developing countries (WHO 1994). Inter-element effects also require more study. Until recently, high quality geochemical data on elements such as Se and I have rarely been available because of the difficulty or high cost of determining these elements at levels at and below the average abundances in natural materials. Analytical methods for Se and for several other environmentally important chemical elements are now being developed by the BGS and other organizations to enable their distribution to be mapped cost effectively. Methods for studying Al and As speciation in the environment have also been developed. Studies of links between the distribution and speciation of environmentally important elements and their epidemiological significance should now be pursued, ideally in countries with good epidemiological data such as China (China Map Press 1979).

Despite the fact that urbanization is a major factor in the degradation of the natural environment, there has been little or no systematic work on the sustainability of the geosphere and hydrosphere, or on their ability to absorb the effects of land degradation and pollution, in the very large cities developing in the third world. Geochemical studies of the urban environment (including soil, water, dust and air) are urgently needed if the environmental damage caused by the rapid urbanization of the developing world is to be contained, including the threats to the marine environment from major coastal cities.

Environmental geochemistry, particularly the preparation of high quality baseline data (Darnley *et al.* 1995), has a crucial role to play in

aiding the understanding of land use problems and designing sustainable solutions appropriate for the economies of the developed and developing world.

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Impacts of As or heavy metals from mining again understood in understanding speciation in characterizing the degree of sorption/pre-ferential mobility/availability of whether or not are likely to affect the or humans. The study potential methods for as well as for assessing impact in practical, cost

Recommendations

Understanding of the chemistry coupled with improved analytical methods and in-situ now offer an opportunity to assess environmental quality, critical load analysis of regional geochemical data as an indication of speciation. Such new and sophis-

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