# Chemicals in the environment: implications for global sustainability

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The impact of chemicals on the environment and human health is a cause of increasing concern. Although many studies continue to be carried out on this subject, most address only individual chemicals or particular groups of chemicals, such as metals or radioactive substances. In this paper, we consider the availability of data and knowledge about potentially harmful chemicals from the national to international scale and suggest a strategy to help prevent chemical pollution or deficiencies damaging global sustainability into the 21st century. The main groups of chemicals considered are:

- (i) Potentially harmful inorganic elements such as As, Cd, Hg and Pb known to have adverse physiological effects at low levels, and elements and species such as Se, I and NO<sub>x</sub> that can be essential or harmful depending on their concentration, speciation and bioavailability. Chemical elements such as Ga, In and the PGEs that are increasingly used in the development of new materials, including nanotechnology applications, are also discussed briefly.
- (ii) Radioactive substances, including naturally occurring radioisotopes, such as <sup>238</sup>U and its decay products <sup>226</sup>Ra and <sup>222</sup>Rn, and processed materials, such as depleted uranium (DU), which affect the environment and human health because of their radiological and chemical toxicity. Data on isotopes from the nuclear industry, such as the relatively short-lived isotopes <sup>137</sup>Cs and <sup>90</sup>Sr, are also discussed, including from accidental releases such as Chernobyl in 1986. Isotopes with longer half-lives such as <sup>243</sup>Am and <sup>240</sup>Pu, which are important in the development of nuclear waste management strategies are also considered.
- (iii) Persistent organic pollutants (POPs) including many synthetic chemicals such as dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), flame retardants and their metabolites, which are characterised by their persistence, bioaccumulation (lipophilicity) and toxicity (PBT) properties. Other synthetic chemicals such as perfluorooctane sulphonate (PFOS), which have different bioaccumulation properties, are considered briefly.

#### **INTRODUCTION**

There is growing awareness, world-wide, of relationships between ecosystem and human health and the distribution of chemicals in the environment (RCEP, 2003). There is also an increasing realisation that (iv) Human and veterinary pharmaceuticals, of which there is increasing evidence of their presence in the environment. These substances are of particular concern because many are designed to target specific biological receptors and hence can have potentially deleterious effects at exceptionally low concentrations.

All these groups of chemicals include endocrine disrupting chemicals (EDCs), capable of disrupting animal and human hormone systems (including sex and thyroid).

Geochemical databases such as those prepared by the Forum of European Geological Surveys (FOREGS) and the British Geological Survey (BGS) provide systematic information on levels of inorganic chemicals in the environment. Similarly, airborne radiometric databases provide systematic information on the distribution of radioactive substances. Examples of such data are used to demonstrate how the distribution of chemicals in the environment can be mapped, and how modelling and monitoring systems derived from them are of strategic importance in understanding the impact of chemicals on ecosystems and human health from the national to global scale. There is concern, however, about the lack of such systematic data for organic chemicals. It is argued that such systematic data for all chemicals is crucial for sustaining the Earth's life-support systems into the 21st century.

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although geohazards such as volcanoes and earthquakes are dramatic and cause sudden and significant loss of life, the threat from chemicals, which is frequently insidious, can cause even greater loss of life and debility over the longer term (Skinner and Berger, 2003). The problem of chronic exposure to potentially toxic chemicals in the environment is also articulated by the European Environment Agency and the United Nations Environment Programme (EEA/UNEP, 1999). The increase in concern about chemicals in the environment is reflected by the growing number of European Union (EU) Directives and national and international conventions relating to chemicals.

In addition to damage to human health caused by toxicity conditions, damage can also be caused by deficiency conditions. The World Health Organization (WHO), for example, has calculated that 800 million people, world-wide, are at risk of serious diseases such as goitre and cretinism, the latter because of iodine deficiency in mothers during pregnancy (UNICEF-WHO Joint Committee on Health Policy, 1994).

In this paper, we first review data on problems associated with inorganic substances for which, in the case of many of the 92 naturally occurring chemical elements, there is now much systematic data on their distribution in soils, sediments and water at the national and, increasingly, international scale. These data can be used for understanding the distribution, behaviour and potential impact of such chemicals in complex and highly varied surface environments world-wide, ranging from glaciated to tropical terrains. Some of the latter contain deeply leached ancient landscapes, suggested in some cases to date from the Proterozoic (Butt, 1989; Daniels, 1975). We also discuss similar systematic information for radioactive substances.

In contrast to inorganic and radioactive substances, the situation for synthetic organic substances, including persistent organic pollutants, POPs, such as pesticide residues, phthalates and other plasticisers, surfactants and detergents and waste products from incineration such as dioxins, is characterised by a paucity of systematic data, information and knowledge. There is increasing awareness, as a result of recent monitoring and modelling studies (Sweetman and Jones, 2000; Halsall et al., 2001; Prevedouros et al., 2004), of damage to ecosystems and man caused by the long-range transport of these chemicals and their accumulation at high latitudes (EEA/UNEP, 1999). Moreover, it has been estimated that there are about 30 000 synthetic industrial chemicals on the market, of which relatively little is known, even about their hazardous (PBT) properties (EEA/UNEP 1999). Their distribution and behaviour in the environment is also poorly understood, making meaningful exposure and risk assessment almost impossible.

In the case of pharmaceuticals or their residues, there is currently no regulatory requirement on their use or disposal, even within the US or EU, despite their potentially high ecotoxicity/toxicity. Studies of sewage effluent and surface water in the UK and world-wide have shown many pharmaceuticals, including the female contraceptive pill,  $17\alpha$ -ethinyl oestrodial (EE2), for example, to occur at concentrations with the potential to cause harm (Sumpter, 2002; Pickering and Sumpter, 2003; Plant and Davis, 2003).

All of the groups of chemicals discussed, both

inorganic (*e.g.* Pb and Cd) and organic (*e.g.* PCBs, DDT) include substances that can disrupt the endocrine system of many species, including humans (UKEA, 2000). More than 70 EDCs are now listed on the UK Institute of Environment and Health's relational database of information on potential endocrine disrupters (IEH, REDIPED website).

Among OECD countries, Japan appears to be the only nation that uses environmental monitoring data to evaluate the risks of such chemicals in the environment (RCEP, 2003). Here, we show how systematic geochemical and radiometric data strongly support such an approach and can be used to inform government and the public of potential threats to the health of ecosystems and humans posed by deficiencies or excesses of chemicals in the environment.

## CHEMICALS OF CONCERN IN THE ENVIRONMENT

## Potentially harmful and essential inorganic chemical elements and species

Two main groups of inorganic chemical elements and species are of particular importance for health: potentially harmful chemical elements and species, and those that can be essential or harmful, depending on their concentration, speciation and bioavailability. The level of many of these chemicals can vary naturally as a result of geology or climatic history, although their natural background has frequently been altered by the activity of humans, including historical mineral working, industrialisation and urbanisation. New materials, including those used in nanotechnology, are increasingly introducing new applications for many chemical elements that have not previously been of environmental concern, *e.g.* Ga, In and the PGEs (Table 1).

#### Potentially harmful elements

Potentially harmful elements (PHEs) known to have adverse physiological significance at relatively low levels, for which there is little or no evidence of essentiality, include As, Ag, Be, Cd, Pb, Hg (Skinner and Berger, 2003) and possibly some of the rare earth elements (REEs; Smith *et al.*, 1998a). Arsenic, Pb and Hg are used here as examples.

Acute toxicity from As can cause severe gastrointestinal symptoms, fluid loss and circulatory collapse, psychotic symptoms, neurological changes, including demyelination of the peripheral nervous system, and/or severe heart disease. Chronic exposure is linked to increased risk of cancer, including of the skin, liver, lung and bladder (Tchounwou, 2000; Wong *et al.*, 1992). Significant adverse effects of Ascontaminated groundwater including from naturally arsenical aquifers have been reported from Argentina, Bangladesh, Chile, China, Ghana, Hungary, India, Mexico, Taiwan, the UK and the US (Naidu and Nadebaum, 2003). In Mongolia and parts of China, where arsenical groundwater is used for irrigation, it may also be ingested via crops or animals, or through

Commodity	New main uses	2002 production	Reserves	Comment
Arsenic trioxide	Electronics	35 000 t	875 ,000 t	Reserves are calculated as 25x annual production
Gallium	Electronics (solid state transistors)	61 t	150 000 t	Not all recoverable because of strong binding in bauxite and zinc ores
Germanium	Electronics (semi-conductors), gamma-ray detectors	68 t	NA	By-product of Pb and Zn processing
Indium	Alloyed with tin in full LCD and plasma TV screens	335 t	2500 t	Reserve base is 6000 t. By-product of Zn refining
PGEs – Pt	Autocatalysts, jewellery, fuel cells	171 000 kg	71 Mkg	80 Mkg reserve base. Reserves for total PGE
PGEs – Pd	Autocatalysts, jewellery	193 000 kg		
Rare earths	Glass polishing, ceramics, petroleum refining, autocatalysts and electronic	85 500 t s	88 Mt	
Rhenium	Petroleum refining catalysts, super alloys in aerospace industry, coatings for electronic contacts	23 100 kg	2·4 Mkg	
Tantalum	Electronics as Ta-capacitors, mobile phones	1530 t	39 000 t	110 000 t reserve base

#### Table 1Some new main uses of chemicals

British Geological Survey/United States Geological Survey.

dermal absorption during wetland farming. Chronic As poisoning as a result of burning arsenical coal, which affects at least 3000 people in Guizhou Province, China, has been described by Zheng *et al.* (1996) and Finkelman *et al.* (2002, 2003). Arsenic has also been used traditionally in biocides in agriculture and industry and, more recently, in the electronics industry. The transfer of As from the geosphere to the surface, where it adversely affects ecosystems and human health, is poorly understood. There is a general lack of knowledge about the distribution of As in the Earth's surficial materials because this element was rarely determined in geochemical surveys prior to about 1990 (Plant *et al.*, 2004).

Lead is a cumulative neurotoxin that poses the highest risk to children partly because of the development stage of their neurological system and partly because there is a greater likelihood of hand to mouth transmission. It has been associated with decreased learning ability and delinquent behaviour in later life (Needleman et al., 1996). Apart from natural emissions of Pb and problems associated with historical mineral working and refining, its distribution from ore deposits into the environment has been mainly from sources such as plumbing, commercial agrochemicals, Pb-based paints, sewage sludge, waste water and petroleum additives. Calculations by Mielke and Reagan (1998) suggest 5.9 Mt of Pb from the petroleum additives tetraethyl and tetramethyl lead (TEL/TML) have left 4-5 Mt of Pb in the environment, mainly in urban areas, in the US alone.

Mercury is another powerful neurotoxin that can have health impacts (Table 2). It is a highly toxic trace metal that becomes especially concentrated in aquatic food webs, although one well-known example of Hg affecting human health was caused by the accidental consumption of Hg-treated grain in Iraq in 1971 (Bakir *et al.*, 1973). Adverse human health impacts caused by the highly neurotoxic organomercury species monomethyl mercury (MMHg) are most frequently related to consumption of contaminated fish (Fitzgerald and Clarkson, 1994; US National Research Council, 2000; Fitzgerald and Lamborg, 2004). Natural degassing of the Earth's crust, combined with emissions from burning fossil fuels, is estimated to contribute up to 150 000 t of Hg a year. High natural Hg concentrations occur in particular zones of the Earth's crust, such as the tectonically active area around the Pacific Ocean (Turekian and Wedepohl, 1961; Fitzgerald and Lamborg, 2004;

Table 2Symptoms of mercury (vapour) toxicity (after Lindh<br/>et al., 2003)

Acute (1 mg m <sup>-3</sup> )	Chest pains Shortness of breath Cough Coughing blood Impairment of pulmonary function
	Pneumonitis
Chronic	Violent muscular spasms
	Pricking or burning sensations
	Trembling handwriting
	Irritability
	Excitability
	Insomnia
	Hallucinations
	Shyness
	Nerve pain
	Drowsiness
	Delirium
	Fine tremor
	Loss of taste
	Loss of hearing
	Loss of memory
	Loss of smell
	Death

### Table 3 Some human health impacts of iodine and selenium deficiencies and excesses

#### IODINE

Deficiency

Iodine is an essential component of thyroid hormones. Inadequate supply of iodine leads to insufficient production of these hormones resulting in disease states collectively known as iodine deficiency disorders (IDD). The consequences are:

- (i) Mental retardation/reduced IQ (cretinism in infants)
- (ii) Defects in the development of the nervous system
- (iii) Goitre (enlarged thyroid)
- (iv) Physical sluggishness
- (v) Growth retardation
- (vi) Reproductive failure
- (vii) Increased child mortality (Venkatesh-Mannar and Dunn, 1995)

#### Excess

An excess of iodine has a negative impact on thyroid function:

- (i) Hashimoto's thyroiditis
- (ii) Iodine hyperthyroidism (jodbasedow)
- (iii) Iodide goitre
- (iv) Thyroid carcinoma
  - (Koutras et al., 1980)

#### SELENIUM

Deficiency

Keshan disease – an endemic degenerative heart disease Kaschin-Beck disease – an endemic osteoarthropathy which causes deformity of effected joints (Fordyce *et al.*, 2000b)

Excess

Selenosis – resulting in hair and nail loss and nervous system disorders (Fordyce *et al.*, 2000b)

Lindh *et al.*, 2003). Most modern metal mining, which in the past caused release of natural Hg from ore deposits, is now carried out to extremely high environmental standards minimising Hg pollution, but historical problems remain. For example, Hg was contained in the mine tailings in the Aznacollar incidence in Spain that caused serious environmental damage (Grimalt and MacPherson, 1999). The main problem of Hg contamination from mining now is related to artisanal gold mining (Porcella *et al.*, 1997). Dental amalgams also contribute to environmental mercury levels, through release of mercury vapour or incineration of dental waste, and also human cremation (Selinus *et al.*, 2005).

#### Essential chemical elements and species

The chemical elements and species identified as essential to animal and plant life include K, Na, Ca, P, Cl<sup>-</sup>, SO<sub>x</sub> and NO<sub>x</sub>, as well as the first row transition elements Fe, Mn, Ni, Cu, V, Zn, Co and Cr, and Mo, Sn, Se and I (Mertz, 1986; WHO, 1996).

Some of the disorders associated with deficiency or excess of these elements are given in WHO (1996). Recent reviews of the importance of geochemistry as a controlling factor in Se deficiencies and excesses to human health include those of Fordyce *et al.* (2000a), Plant *et al.* (2004) and, for I, Johnson *et al.* (2003) and

Fordyce *et al.* (2003). Table 3 illustrates the consequences of I and Se deficiencies and excesses.

Boron has not yet been shown to be necessary for animals, although it is essential for higher plants and has been suggested by some authors to be toxic to humans (WHO, 1996). All trace elements are toxic if ingested or inhaled at sufficiently high levels for long enough periods of time. Se, F and Mo are examples of elements that have a relatively narrow concentration range (of the order of a few micrograms per gram) between deficiency and excess (toxic) levels. In the case of F, for example, more than 10 million people in Guizhou Province, China, suffer from various forms of fluorosis as a result of the high F in domestic coal, combined in some cases with high F in water. The condition has also been reported from 13 other regions of China (Ando et al., 1998; 2001). Typical symptoms of fluorosis include mottling of teeth and skeletal deformation, including knock knees, bow legs and spinal curvature. In children, especially when combined with nutritional deficiencies, it can cause severe bone deformation.

The difficulties of diagnosing disease in animals and man, particularly sub-clinical conditions related to trace element deficiencies or excesses, are discussed by Mills (1996). Except in some specific cases such as As (Smedley et al., 2001; Plant et al., 2003a), Hg toxicity (Fitzgerald and Lamborg, 2004) or I deficiency disorders (IDD; Johnson et al., 2003; Fordyce et al., 2003), symptoms may be non-specific and diagnosis, based on tissue or blood sampling, is costly. The concentration of essential trace elements such as Se in crops (rice, corn, soybean) was shown by Levander (1986) to correlate closely with their concentration in the soil in which they are grown, although the relationship has been shown to be more complex (Appleton et al., 1998; Johnson et al., 1999). Presently, much effort is focused on groundwater as the principal pathway for many PHEs to humans. The situation is, however, more complicated, with soil, crops and animals, aerosols, dust and surface waters also being significant pathways for most elements (Plant et al., 2003a). Work by Williams et al. (1999) using physiologically based extraction tests (PBETs) and risk assessment has shown that, in non-industrialised countries, soil is likely to be an equally significant exposure pathway for As as groundwater. This is likely to be the case for most PHEs in developing countries where significant soil contamination can occur during harvesting and food preparation processes (Smith et al., 1998a), especially where geophagy is practised (Abrahams, 2002; 2004).

In higher animals, including humans, assimilation of essential and potentially harmful inorganic chemicals occurs by ingestion of nutrients and contaminants from food crops, animal tissues and drinking water, or the inadvertent ingestion of soil, by dermal absorption, and/or by respiration (WHO, 1996). Ideally, geochemical data on soil and dust, stream sediment and ground and surface water should be available to identify, assess and model sources and pathways of such chemicals likely to lead to toxicity or deficiency conditions with the potential to harm ecosystems and humans.

#### **Chemical speciation**

The speciation of chemical elements affects their distribution, mobility and toxicity. This has been known for a long time in the case of the common anions  $(\text{HCO}_3^-, \text{NO}_3^-, \text{SO}_4^{-2})$  and, more recently, for a wide range of chemical elements in the 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; Levander, 1986). Considerable developments have been made in the prediction of chemical speciation by modelling thermodynamic and kinetic equilibria (Bassett and 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 these were relatively poorly understood until recently (Ehrlich, 1990; Deighton and Goodman, 1995).

Some of the most important controls on trace element speciation and 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. The two most important factors directly controlling mobility and solubility are Eh and pH. 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 controlled by pH. 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 by-products are present, however, stable organo-metallic complexes (which can behave as anions) can form, 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 influence of humans.

Geochemical interaction between the geosphere, hydrosphere and 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 metal cations, such as Cu, Pb, Cd and Hg, are more soluble in the low pH conditions induced by natural organic acids and root exudates.

Speciation studies are of particular importance in areas affected by land degradation, deforestation or pollution caused by (mainly historical) mining, industrial activity, energy generation or urbanisation, and they can be used to optimise amelioration strategies and improve management practices. A knowledge of the factors controlling speciation in different environments can be used to predict the potential for absorption of PHEs.

Speciation and lability, both in the natural environment and in the gastro-intestinal tract, exert a major influence on the uptake and assimilation of trace nutrients and PHEs (WHO, 1984; WHO, 1994; Powell and Thompson, 1993). For example, Al, which is the commonest metal at the Earth's surface, occurs in both inert and bioavailable forms, and its potential toxicity depends on its chemical form or speciation. It can occur in a large number of dissolved aqueous species, especially in conditions of low or high pH. In certain species of animals, particularly fish, and plants, Al can have adverse physiological effects in trace amounts (Sposito, 1989) or be bound on colloidal organic carbon or silica, which limit its bioavailability and, therefore, its toxicity.

The toxicity of other elements also depends on their chemical form. Arsenic, for example, is most

Element and formal oxidation state	Major chemical forms
As(-III)	Arsine [H <sub>3</sub> As]
As(-I)	Arsenopyrite [FeAsS], loellingite [FeAs <sub>2</sub> ]
As(0)	Elemental arsenic [As]
As(III)	Arsenite $[H_2AsO_3, H_3AsO_3]$
As(V)	Arsenate $[AsO_4^{3-}, HAsO_4^{2-}, H_2AsO_4^{-}, H_3AsO_4]$
Organic As (V and III)	Dimethylarsinate [DMA, (CH,),AsO(OH)], monomethylarsonate [MMA(V), CH,AsO(OH),
	or MMA(III), CH <sub>3</sub> As(OH) <sub>2</sub> ], arsenobetaine [AsB, (CH <sub>3</sub> ) <sub>3</sub> As <sup>+</sup> CH <sub>2</sub> COO <sup>-</sup> ],
	arsenocholine [AsC, $(CH_3)_3As^+ CH_2CH_2OH$ ]
Se(-II)	Selenide [Se <sup>2-</sup> , HSe <sup>-</sup> , H <sub>2</sub> Se]
Se(0)	Elemental selenium [Se]
Se(IV)	Selenite [SeO <sub>3</sub> <sup>2-</sup> , HSeO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> SeO <sub>3</sub> ]
Se(VI)	Selenate $[SeO_4^{-2}, HSeO_4^{-}, H_2SeO_4]$
Organic Se	Dimethylselenide [DMSe, CH <sub>3</sub> SeCH <sub>3</sub> ]; dimethyldiselinide [DMDSe, CH <sub>3</sub> SeSeCH <sub>3</sub> ],
	selenomethionine [H <sub>3</sub> N <sup>+</sup> CHCOO <sup>-</sup> CH <sub>2</sub> CH <sub>2</sub> SeMe], selenocysteine [H <sub>2</sub> N <sup>+</sup> CHOO <sup>-</sup> CHSeH]

 Table 4
 Chemical forms of arsenic and selenium

After Plant et al., 2004.

toxic in the As<sup>3+</sup> gaseous state with decreasing toxicity in the sequence As<sup>3+</sup> > As<sup>5+</sup> > methyl-As (Abernathy, 1993; Chen *et al.*, 1994). Unlike Hg, which is most toxic when it is methylated, the toxicity of As is much lower in organic species such as arsenobetaine and arsenocholine in which it can occur at high concentrations in fish (Plant *et al.*, 2004). Arsenic and selenium interact with each other in various metabolic functions in animal models (Davis *et al.*, 2000). Human selenosis at the population level is rare and is generally related to excesses from food rather than drinking water. The principal species of As and Se are shown in Table 4.

Monomethylmercury (MMHg) is the most harmful form of Hg to organisms, demonstrating bioconcentration and biomagnification, and it has a long residence time in organisms. Most of the Hg in fish and their eggs is present as MMHg and this is the main source of mercury to humans (de Larcerda and Salomons, 1998; Campbell et al., 2003). Fish embryo methylmercury may exposure to occur via environmental interaction or by maternal transfer. Well-known examples of MMHg affecting human health include the occurrence of Minamata disease in Japan in 1953, which was caused by eating fish contaminated with waste-water discharge from a factory (Irukayama, 1977).

Geochemical techniques can be used to identify not only the total amount of each element in soil, dust or water, for example, but also the amount which is bioavailable. This is more important than the total amount but is less easy to establish. Several workers have developed and applied physiologically based extraction tests (PBETs) that attempt to predict the bioavailability (the total fraction of an element that is available for absorption during transit through the digestive tract) of a given trace element (Davis et al., 1992). Such tests have significant advantages over conventional sequential leach tests because they attempt to reproduce physiological factors, such as stomach emptying time and the ratio of solid to digestive fluids as well as the pH and Eh of upper gastro-intestinal tract solutions, in particular target groups, such as young children. In the case of As, the values for bioavailability in the upper intestine (neutral pH) are consistently significantly greater than those estimated from simple acid stomach solutions (Ruby *et al.*, 1996). Although such tests need further calibration and validation, they represent an important step forward in understanding exposure pathways for both potentially toxic trace and essential trace elements (Renner, 1998).

#### **Radioactive substances**

These comprise both naturally occurring and manmade radioactive substances, the toxicity and carcinogenicity of which depend on their chemical properties and the nature of their ionising radiation. Their adverse health impacts also depend on their biological and radioactive half-lives.

The principal chemical elements contributing to natural terrestrial radioactivity are those in the U and Th decay chains and K. In nature, U has two primary isotopes, <sup>238</sup>U and <sup>235</sup>U, which occur today in the ratio of 99·3% <sup>238</sup>U to 0·7% <sup>235</sup>U. These, together with <sup>232</sup>Th, have long and complex decay series (*e.g.* Kaye and Laby, 1986; Burns and Finch, 1999). The principal hazards posed by U are its chemical toxicity and the radiological properties of some of its decay products, especially those that are alpha emitters, such as <sup>226</sup>Ra and <sup>222</sup>Rn, which are of concern if they are inhaled or ingested because of their association with cancer, particularly lung cancer in the case of <sup>222</sup>Rn.

Radioactivity may also be introduced into the environment as a result of contamination from a wide range of anthropogenically produced radionuclides including the manufacture, testing and use of nuclear weapons, nuclear accidents and, to a lesser extent, nuclear power generation; some radionuclides are also now used for domestic, medical and industrial applications.

Since the development of nuclear power, radioactive isotopes including those of Am, C, Cs, H, I, Kr, Np, Pu, Sr, Te and Xe, have been released into the natural environment as water, soil and airborne contaminants (Shutov *et al.*, 2002). While much of this has been associated with known and licensed releases, some



1 Sources of radiation exposure contributing to average effective dose in the UK (NRPB data from Appleton, 2004)

 Table 5
 Average radio-element content in rocks and waters

	U	Κ	Th
Crustal abundance (mg kg <sup>-1</sup> )	2.7	17 500	10
Ultramafics (mg kg <sup>-1</sup> )	0.001		0.003
Basalt (mg kg <sup>-1</sup> )	0.6		2.2
Granodiorite (mg kg <sup>-1</sup> )	3		10
Andesite (mg kg <sup>-1</sup> )	2		
Granite (mg kg <sup>-1</sup> )	4.8		17
Shale (mg $kg^{-1}$ )	4		12
Sandstone (mg kg <sup>-1</sup> )	2.2		
Limestone (mg kg <sup>-1</sup> )	2		2
Soil (mg kg <sup>-1</sup> )	1		13
River water ( $\mu g k g^{-1}$ )	0.0004		0.0001
Sea water ( $\mu g k g^{-1}$ )	0.003		

Data for U and Th from Taylor (1964; 1966), except river water data (Th from Turekian (1969); U from Reeder *et al.* (1972)); data for average crustal abundance for K from Weaver and Tarney (1984).

significant releases have been associated with nuclear weapons' testing, for example at the Hanford site in the US (Siegel and Bryan 2004), and with nuclear accidents, such as those at Chelyabinsk, near Kyshtym, Russia, in 1957 (Medvedev, 1979), at Windscale in 1958 (Chamberlain and Dunster, 1958) and at Chernobyl, Ukraine, in 1986 (Abagyan *et al.*, 1986). The Goiania incident in Brazil in 1987, which involved the mishandling of a medical <sup>127</sup>Cs source previously used for radiotherapy, involved acute contamination at a much more local scale with serious human health impacts (IAEA, 1998).

Nevertheless, the average dose from these sources over most of the Earth's surface is generally small compared to natural radioactivity. For example, the average dose experienced by a UK citizen and its sources are shown in Figure 1. This indicates the very small doses from the nuclear industry compared to natural radioactivity or to medical diagnostics or food.

#### Naturally occurring radionuclides

<sup>226</sup>Radium and <sup>222</sup>Rn are decay products of the much more abundant U isotope <sup>238</sup>U, and are of particular importance due to their impact on human health and their role in the discovery of radioactivity in the early 20th century. While of little environmental significance, <sup>214</sup>Bi is an important decay product of <sup>238</sup>U because it is the isotope by which 'equivalent U' (eU) is determined quantitatively using gamma ray spectrometry and it is a decay product of <sup>226</sup>Ra and <sup>222</sup>Rn. The radio-elements within the U and Th decay chains have different chemical behaviour and can become separated in the surface environment from their parents (U and Th), leading to fractionation and secular disequilibrium. This is most common where there are recent surficial deposits of U decay products that result in eU analyses that do not reflect the total U concentration. Nevertheless, eU may closely reflect areas of high radon potential, for example over the Derbyshire Peak District of central England (see Plate 4; Jones *et al.*, 2002a).

Uranium and the other two important natural radioelements, Th and K, are strongly partitioned into the continental crust and are especially concentrated in certain types of granites and organic rich black shales and phosphatic sediments (Plant *et al.*, 1999). Some average radio-element contents are given in Table 5.

The natural radio-elements <sup>232</sup>Th and <sup>40</sup>K are associated with many U deposits. Thorium can be of environmental significance because it reaches high levels in certain types of mineral deposits such as heavy mineral sands (Gilbert and Park, 1986), and isotopes within its decay chain emit high energy (2.7)MeV) gamma rays. The average Th to U ratio in most unmineralised rocks is 3.5 to 1. High levels of potentially toxic elements, such as As, are also often closely associated with high levels of U, for example with the Variscan Cornubian Batholith in the historical mining district of south-west England (Appleton, 1995a; 1995b). Such associations increase the potential environmental and health problems of U concentrations and mineralisation and have been cited as co-factors with <sup>222</sup>Rn in links between mine dusts and lung cancer (The Royal Society, 2001; WHO, 2001). Other naturally occurring radionuclides that occur in small amounts include <sup>237</sup>Np, <sup>239</sup>Pu and <sup>99</sup>Tc (Siegel and Bryan, 2004).

The concentration factor of U from average crustal abundance  $(2.8 \text{ mg kg}^{-1})$  to ore grade, ranges from approximately 100 in the case of low-grade deposits, such as the Rössing deposit, Namibia (0.03% U) to about 65 000 in the case of high-grade deposits such as the McArthur River deposit in Canada (18.5% U). The surface expression of the deposits, however, is controlled by a variety of natural factors specific to each mining district. Frequently, deep-seated, high-grade deposits, such as McArthur River have little, or no, surface radiometric or geochemical expression, in

 Table 6
 The five most economically important types of U deposits

Type of deposit	Examples
Unconformity-related deposits	Athabasca Basin, including Cigar Lake, McArthur River, Key Lake, Cluff Lake (Canada), Nabarlek, Jabiluka, Ranger (Australia)
Sandstone deposits	Colorado Plateau (USA), Koenigstein (Germany)
Quartz-pebble conglomerate deposits	Witwatersrand Basin (RSA), Elliot Lake (Canada)
Vein deposits	Saint Sylvestre, Limousin (France); the polymetallic Jachymov orefield, Western Erzegebirge (Germany), Pribram District (Czech Republic)
Breccia complex deposits	Olympic Dam (Australia)

IAEA, 1996; OECD, 1998.



2 Back scattered electron microprobe image showing depleted uranium-rich particle from Kosovo (Milodowski, 2001)

contrast to low grade, near-surface deposits, such as that of Rössing. The five most economically important types of U ore deposits are shown in Table 6.

#### Anthropogenic sources of radioactivity

Prior to the advent of nuclear fission technology in 1942, U was used mainly for colouring glass, ceramic glazes (Plant *et al.*, 1999) and, to a much less extent, as a remedy for diabetes (WHO, 2001). Following the pioneering work of Marie Curie and others in the early 1900s, U ores were also used as a source of the decay product <sup>226</sup>Ra, in the treatment of cancer as well as for producing luminescent displays and paints until the mid-1960s. Contamination from the latter has required significant remediation of contaminated airfields and military sites where it was used until the mid-1960s.

In 1942, demonstration of the controlled nuclear fission of <sup>235</sup>U led to the development of its use in nuclear weaponry and energy and the production of 'enriched' uranium at an industrial scale. Since that time, the most important environmental impacts have been from nuclear weapons' testing (fission and fusion) and, to a lesser extent, nuclear power generation, including from nuclear fuel fabrication, nuclear reactors and reprocessing plants (Siegel and Bryan, 2004). The increase in the numbers of miners and workers exposed to U as a result of these applications appears to have had a relatively insignificant effect on their health overall (The Royal Society, 2001). Radioactive and associated heavy metal and As contamination can reach high levels in U tailings in areas of former U mining. In the US, for example, 230 Mt of tailings are now stored at 24 remediated sites (Siegel and Bryan, 2004). In the former Soviet Union (FSU), contamination from U mining is generally more serious, partly because of fewer environmental and health and safety controls in the past and partly because of the use there of strong mineral acids in solution mining operations (Siegel and Bryan, 2004).

Nuclear fuel is produced by the enrichment of natural  $^{235}$ U from about 0.7% to about 3.5%. The main residue, 'depleted' U (DU), which contains

about 0.2% <sup>235</sup>U and only small amounts of decay products, has been used for several applications because of its similar physicochemical properties to U and its significantly lower radioactivity. Applications include pigments, chemical catalysts, counter weights and shielding. Depleted U has also been used in fast-breeder nuclear reactors to produce fuel and weapons-grade Pu (predominantly <sup>239</sup>Pu typically with less than 7% <sup>240</sup>U) by neutron activation. Since the 1970s, when alloys with a high DU content were developed for armour-piercing artillery and anti-tank shells because of their high density, self-sharpening and pyrophoric properties, they have caused contamination following some military conflicts (Fig. 2).

The use of these weapons in the First Gulf War in 1991 and subsequent wars in the Balkans and Iraq has been linked by some scientists to an increased incidence of cancers, birth defects and syndromes in those exposed (Fahey, 1998). Such concerns have demonstrated the need for better information on background levels and chemical speciation of naturally occurring radionuclides such as U to help assess the impact of exposure to humans (WHO, 2001; The Royal Society, 2001, 2002). Recent studies have also highlighted the need for improved understanding of the chemical toxicity of U, particularly in drinking water supplies, where animal and human models show a dose dependent toxicological response at extremely low levels (Kurttio *et al.*, 2002).

Whilst of little economic importance in the past, Th has been used in the manufacture of ceramics, carbon arc lamps and welding electrodes, although Zr, Y and some lanthanides are now commonly substituted for Th in Mg alloys used in aerospace applications to reduce levels of radioactivity (USGS, 2004).

#### Anthropogenic radionuclides

The principal sources of anthropogenic radionuclides are associated with the nuclear fuel cycle, especially nuclear weapons' production, testing and nuclear accidents and, to a lesser extent, nuclear power generation which produces small quantities of waste. The principal difference between the chemistry and impacts of anthropogenic and naturally occurring radioactive isotopes reflects their generation by the fission of the heavy nuclei of <sup>233</sup>U or <sup>239</sup>Pu.

Over 300 different intermediate weight fission product isotopes are formed as a result of splitting the heavy U or Pu nuclei (Fig. 3), with half-lives varying from fractions of a second to months or years. From current knowledge of the impacts of radiation on human health, the most important are generally considered to be  ${}^{90}$ Sr and  ${}^{137}$ Cs.

The residual radiation hazard from a nuclear explosion in the form of radioactive fallout and neutroninduced activity also includes unfissioned material, especially U and Pu, that are dispersed but are generally of relatively minor importance. Nuclear-induced activity, whereby elements such as Na, Mn, Al and Si in rock, soil, air or water near the nuclear explosion capture neutrons also occurs, although this process normally affects only a limited area. (NATO, 1996).



3 Yield of radioisotopes produced by nuclear fission (Crouch, 1958)

Following their release, all such radionuclides become part of a large number of geochemical cycles with the potential for exposure to ecosystems and humans. Indeed, anthropogenic radionuclides are now used as tracers in such cycles and processes at various scales. For example, releases of <sup>137</sup>Cs from Chernobyl in 1986 have been used to improve understanding of the migration and attenuation processes of radionuclei in soils and models of atmospheric dispersion (NEA, 2002).

#### Nuclear weapons' manufacture, testing and accidents

Atmospheric and subsequently underground nuclear weapons' testing were carried out by the FSU, France, the UK and the US throughout the cold war until the early 1990s. The health impact of nuclear weapons testing has been estimated to have resulted in 80 000 additional cases of cancer (25% fatality rate) amongst people who lived or were born in North America between 1951 and 2000 alone (CDC, 2001; IEER, 2002). Large-scale radioactive contamination is also associated with nuclear weapons' production (Siegel and Bryan 2004). One of the most extensive areas of radioactive contamination known is associated with the Chelyabinsk-65 complex for nuclear weapons production near Kyshtym, Russia. Between 1948 and 1992 over 5.5 x 1019 Bq of radioactive waste was produced from the Mayak facility there. More than  $4.6 \times 10^{18}$  Bq of long-lived radioactive isotopes were discharged into lakes and other surface storage sites, while between 1950 and 1951 other wastes were discharged directly into the Techa river. By 1993, > 4 Mm<sup>3</sup> of ground water had been contaminated by long-lived fission products from the lake. Several nuclear disasters have also been associated with the plant. In 1957, for example, the explosion of a storage flask for high level waste released  $7.4 \times 10^{17}$  Bq of radioactivity into the atmosphere (Medvedev, 1979).

The best-known nuclear accident was at Chernobyl in the Ukraine in 1986, when  $^{137}$ Cs (8·5 x 10<sup>16</sup> Bq),  $^{131}$ I (1·76 x 10<sup>18</sup> Bq) and  $^{133}$ Xe (6·5 x 10<sup>18</sup> Bq) were released into the environment; the total amount of Pu (isotopes 238, 239, 240 and 241) released was around 6 x 10<sup>15</sup> Bq (NEA, 2002). Emissions of  $^{137}$ Cs from the accident account for almost 10% of the total radioactivity emitted to the environment as a result of nuclear weapons' testing. The nuclides were emitted as gases, aerosols and fuel element particles. The mobile components adhered rapidly to atmospheric particles with a bimodal size distribution of around 1·5 and 10micron activity median aerodynamic diameter (AMAD) (NEA, 2002).

These releases were significantly greater than those associated with earlier nuclear accidents. They were, for example, about 1000-times greater than those emitted during the 1958 Windscale fires, and about a million times the levels released during the Three Mile Island incident in the US in 1979. They are, nevertheless, significantly less than 1% of the total amount of radioactivity released during the period of use and atmospheric testing of nuclear weapons between 1945 to the present day (NEA, 2002; UNSCEAR, 2000). After almost 20 years, the impacts of the Chernobyl incident and nuclear weapons testing are still measurable in the UK (see Plate 6), although levels of airborne <sup>137</sup>Cs and in rainwater are now below analytical detection limits (Defra, 2001).

The trans-boundary nature of contamination by anthropogenic radionuclides has led to significant improvements in standardising methods for their measurement in environmental samples and the establishment of international monitoring frameworks. For example, the European Union Radiological Data Exchange Platform (EURDEP), Radioactivity Environmental Monitoring (REM) project and the Urgent Radiological Information Exchange (ECURIE) have been established in Europe to ensure rapid early warning of nuclear accidents.

Following the events of 11 September, 2001, there is increasing concern about the potential use of 'dirty bombs' whereby radioactive material is released deliberately into a centre of population by terrorists. Monitoring the impact of such events will require high-resolution methods. The Goiania incident in Brazil (IAEA, 1998) provides an example of a situation where the decontamination of people and their properties required the establishment of detailed monitoring networks.

Increasingly, a wide variety of industrial, research and home products including medical diagnostic equipment, (<sup>60</sup>Co, <sup>137</sup>Cs and <sup>99m</sup>Tc), industrial thickness gauges (<sup>60</sup>Co), smoke alarms (<sup>241</sup>Am) and telephones (<sup>3</sup>H) use man-made radioactive isotopes. Monitoring the environmental fate of these and other anthropogenic radionuclides in the environment requires detailed, remotely sensed data and airborne radiometric monitoring coupled with integrated information management systems.

#### Nuclear waste

Inventories of nuclear reactor high-level waste (HLW) generally include spent fuel and the products of the reprocessing of such materials. Initially, the hazard from such material is mainly from short-lived radionuclides such as <sup>137</sup>Cs and <sup>90</sup>Sr, whereas between 10<sup>3</sup> and 10<sup>5</sup> years, most of the hazard is due to the decay of <sup>241</sup>Am, <sup>243</sup>Am, <sup>239</sup>Pu, <sup>240</sup>Pu and <sup>237</sup>Np. After 10<sup>5</sup> years the isotopes <sup>99</sup>Tc, <sup>210</sup>Pb and <sup>226</sup>Ra dominate the small amount of remaining radioactivity. The toxicity (hazard) of such spent fuel is about the same as ore containing 0.2% U, equivalent to naturally occurring relatively low-grade U-ore deposits (Siegel and Bryan 2004). It has been argued (Oxburgh, 2002) that the risk of an adverse health impact from ionising radiation from a properly constructed nuclear waste repository would be less than the increase involved in moving from Dorset, where the natural background radioactivity is low, to live in Cornwall, where it is exceptionally high as a result of mineralised granites and their historical working.

#### Persistent organic pollutants (POPs)

Persistent organic pollutants (POPs) include tens of thousands of chemicals such as polychlorinated biphenyls (PCBs) that have primarily industrial applications, others such as organochlorines and organophosphates used as biocides in agriculture (Ragnarsdottir 2000), and dioxins and furans which are the unintentional by-products of industrial operations or energy generation. Huge amounts of such synthetic chemicals have been introduced into the environment over the last hundred years. Many have not been tested for even the most basic indications of hazard to the environment or human health (Fig. 4), and current monitoring of their distribution and impact on the environment is quite inadequate (RCEP, 2003). Indeed, the present status of our knowledge of these chemicals was summed up by the Royal Commission as ignorance 'outweighing knowledge at every stage of assessing and evaluating synthetic chemicals'(RCEP, 2003).

Several organisations have developed criteria to identify the POPs of greatest concern. The UK's Chemicals Stakeholder Forum criteria for persistence, bioaccumulation and toxicity are shown in Table 7. The approximately 100 chemicals of concern identified by screening the IUCLID database using these criteria are now available on the Chemical Stakeholder Forum





website <<u>http://www.defra.gov.uk/environment/chemicals/</u> csf/concern/index.htm> hosted by Defra.

Some chemicals bio-accumulate by mechanisms not covered by these criteria. For example, PFOS binds to blood proteins rather than accumulating in body fat. This substance, which can be used to protect textiles and leather against water damage, in fire-fighting foams and to treat paper containers for fast foods, has been detected in human blood and breast milk (Kubwabo *et al.*, 2004; Olsen *et al.*, 2003; Olsen *et al.*, 2004). It is associated with cancer, especially of the bladder. The current regulatory approach to the management of synthetic organic chemicals is based almost entirely on a risk assessment approach as described in Table 8.

In practice, risk assessment for both the aquatic and terrestrial environment usually involves calculation of the predicted exposure concentration (PEC) and the predicted no-effect concentration (PNEC) and their ratio  $PEC_{soil}/PNEC_{soil}$  on the basis of toxicity data for aquatic or soil organisms or alternative equally simple calculations for higher animals, including humans. Few data are available on the hazards or distribution in the environment of most of the 30 000 synthetic industrial chemicals which include many persistent organic pollutants estimated to be on the market in Europe (Fig. 4). Moreover, regulatory monitoring is presently based mainly on water sampling, which is likely to under-

 Table 7
 The Stakeholder Forum first tier criteria for chemicals of greatest or high concern

Criterion	First tier thresholds
Persistence (P)	$t_{1/2}$ water > 2 months OR soil/sediment > 6 months
Bioaccumulation (B)	$\log K_{ow} > 5$ unless BCF < 5000 (greatest concern)
	$\log K_{\text{nv}} > 4$ unless BCF < 500 (high concern)
Toxicity (T)	$L(E)C_{50}^{-} < 1 \text{ mg } l^{-1} \text{ OR NOEC} < 0.1 l^{-1}$
vP and vB	(No T). Substance of concern but less so than PBTs
Safety net	Expert judgement from the ACHS on a case-by-case basis for substances of equivalent concern

 $t_{1/2}$  is the half-life of the chemical in water, soil or sediment.

 $\log K_{ow}$  is the partition coefficient between octanol and water that relates to the solubility in fats.

The bioconcentration factor (BCF) is the accumulation of a chemical in the tissue of an organism.

 $L(E)C_{50}$  is the concentration that is lethal for 50% of the population exposed.

NOEC, no observable effect concentration, is the highest concentration of the chemical at which no effects are identified. ACHS, 2003.

Hazard identification	The identification of the inherent capacity of a chemical to cause adverse effects, without regard to the likelihood or severity of such effects
Hazard characterisation	Following exposure to a chemical, the quantitative evaluation of the nature of adverse effects, including assessment of toxic potency (the relative toxicity of a chemical) and, where possible, a dose-response assessment
Exposure assessment	The quantitative evaluation of the likely exposure of the environment and, via the environment, humans to a chemical
Risk characterisation	The quantitative estimation of the probability that an adverse effect will occur, and of its severity and duration in a given population under defined exposure conditions, based on the three previous elements

Table 8 The four elements of current risk assessment

The first two elements comprise the hazard assessment. RCEP 2003.

estimate seriously levels of these substances in the environment. Some POPs are likely to partition to the solid phase while others are dispersed via the air. Because of the cycling of these compounds between environmental compartments, it can be difficult to distinguish between their sources and sinks (Vallack *et al.*, 1998).

Current regulatory approaches based on risk assessment have failed to anticipate some of the deleterious effects of chemicals. For example, the impact of organochlorine pesticides on birds (Carson, 1962; Hickey and Anderson, 1968; Edwards, 1973; Ratcliffe, 1980; Newton and Haas, 1984) and mammal populations (Chanin and Jeffries, 1978); human sickness and deaths from the use of organophosphate pesticides (Stine and Brown, 1996, Ragnarsdottir, 2000); the adverse effects of PCBs on the health of humans and ecosystems (Stringer and Johnston, 2001; Harrington and Macdonald, 2002); the uptake and bio-accumulation of polybrominated diphenyl ethers (PBDEs) used as flame retardants; and the endocrine disrupting effects of the biocide tributyltin (TBT) and many other POPs, were not predicted.

Serious chemical accidents involving POPs have also occurred. For example, in 1986 a fire in a chemical warehouse caused 11 pesticides to enter the Rhine in large quantities near Basel at the border of Switzerland, Germany, and France (UNEP, 2002). The organophosphate (OP) ester pesticides included disulfoton, thiometon, propetamphos, ethylparathion, etrimfos and fenitrothion. Measurements of dissolved OPs allowed the plume to be followed over 700 km to the North Sea. The accident demonstrated that large quantities of OPs can be transported by a major river with limited degradation by photolysis, hydrolysis or biodegradation. This hampers accurate modelling of the fate of the other OPs which enter the Rhine (Ragnarsdottir, 2000). Other serious chemical accidents have included a leak of poisonous methylisocyanate gas from a pesticide plant in Bhopal, India in 1984 and explosions at chemical plants at Seveso, Italy, in 1976 and Flixborough, UK, in 1974.

#### Endocrine-disrupting POPs

Many POPs have endocrine-disrupting properties and are known to have carcinogenic, reprotoxic or neurotoxic effects on living organisms. They include such compounds as alkylphenols (APs), alkylphenol polyethoxylates (APEOs), polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalates, bisphenol-A (BPA), polybrominated flame retardants (PBDEs), dioxins, furans, many pesticides and steroid hormones such as synthetic oestrogens used in the female contraceptive pill and hormone replacement therapy (Arcand-Hoy *et al.*, 1998). Natural oestrogens and Pb and Cd have also been found to have endocrine-disrupting properties (Birkett and Lester, 2002; EEA/UNEP, 1999; Plant and Davis, 2003). As our knowledge of endocrine disruption increases, so does the list of chemicals shown to have such properties.

Many EDCs have been found to be ubiquitous in the environment (Birkett and Lester, 2002). Sources include discharges from sewage treatment works, farm effluents, landfill leachates, drainage from agricultural land, urban sources and rainfall. Some of the most important pathways of EDCs to humans are via food and drink, including from chemicals used in plastic packaging and can linings. Some of the most important groups of such chemicals of concern are considered briefly below.

#### Natural and synthetic steroids

A report by the Food and Agricultural Organization-World Health Organization Joint Expert Committee on Food Additives (JECFA, 1988) found that levels of oestradiol, oestrone, progesterone and testosterone in animal tissue were all significantly increased (at least 2fold) in steroid-treated cattle compared with untreated herds. In Europe, the use of such steroids in meat production has been banned since 1989. Intensive farming practises also produce appreciable concentrations of oestrogens, and significant concentrations steroid hormones (e.g. oestradiol, oestrone, of progesterone, testosterone) have also been found in untreated fish, poultry, eggs, pork, cheese, milk and milk products (Hartmann et al., 1998). These authors found that milk products supply 60-80% of ingested female sex steroids, the remaining 20% being derived from other animal products such as meat, fish and eggs. The concentration of oestradiol in run-off and in the soil from land fertilised with chicken litter has been measured and demonstrates sizeable 'edge of field' losses (Finlay-Moore et al., 2000). A study of effluent concentrations (Shore et al., 1993) detected high concentrations of oestrogens from agricultural settlements. These are low compared to levels assumed to be produced by the body. For example, human steroid production has been suggested to far exceed the uptake from

food with levels of progesterone 20 times higher than intake in some children with oestradiol and testosterone production levels 1000 times higher (Hartmann *et al.*, 1998). The extent to which this reflects bio-accumulation from steroids in food has not been determined, however.

Natural and synthetic steroid oestrogens are present in sewage effluent and receiving waters at far lower concentrations than industrial chemicals (Garcia-Reyero et al., 2001). However, their potency is generally three orders of magnitude higher than most other EDCs (Christiansen and Korsgaard, 1998; Miyamoto and Klein, 1998). For example, effluent from a Swedish sewage treatment works of predomindomestic sources identified ately  $17\alpha$ -ethinyloestradiol (EE2) from the female contraceptive pill and hormone replacement therapy (HRT) at levels 45 times higher than that shown to be oestrogenic to fish (Larsson et al., 1999). EE2 has been shown to induce vitellogin production in male rainbow trout at levels as low as  $0.1 \text{ ng } l^{-1}$  (Purdom *et al.*, 1994). The growth and development of testes in maturing male trout has been shown to be retarded by 50% due to a single dose of EE2 at 2 ng l-1 (Jobling et al., 1996) resulting in sex reversal in fish more generally (Martin-Robichaud et al., 1994).

#### Bisphenol-A (BPA)

Industrial chemicals with endocrine-disrupting properties include bisphenol-A (BPA), which is manufactured in large quantities for the plastics industry and for flame retardants (Fromme et al., 2002). It is used widely in households and industry, and is present in raw sewage, waste-water effluents and in sewage sludge (Furhacker et al., 2000). Under the U.S. Toxic Substances Control Act (TSCA), the environmental concentrations in treated effluent must not exceed 0.1 mg l<sup>-1</sup> (Dorn et al., 1987). Reproductive effects, including inhibition of spermatogenesis, have been observed on fathead minnow (Pimephales promelas) (Sohoni et al., 2001). Although levels of BPA in surface water are usually one to several orders of magnitude lower than those causing effects in test organisms (Staples et al., 1998), and the potential for bio-accumulation in aquatic organisms is low (Gülden et al., 1998), the risk associated with sediment, soil and food is likely to be much greater.

#### Phthalates

Phthalates have been used for more than 40 years in the manufacture of PVC and other resins, as plasticisers and in insect repellents (Fromme *et al.*, 2002). Di-(2-ethylhexyl)-phthalate (DEHP), which is of greatest concern, has been detected in surface waters, sewage effluents, sewage sludge and sediments (Watanabe *et al.*, 1987). The toxicity to aquatic organisms increases with increasing alkyl chain length because of a corresponding increase in log  $K_{ow}$  and decreasing solubility (Call *et al.*, 2001). Calculated PNECs for some of these substances suggest they are of concern for aquatic organisms and benthic species (Staples *et al.*, 2000). New evidence indicates that levels of phthalate metabolites in human maternal blood correlate with indices of feminisation in their human male babies (Swan *et al.*, in press).

#### Dioxins

Dioxins, polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), are no longer produced commercially but are by-products of various industrial and combustion processes, including the incineration of wastes and fossil and biomass hydrocarbon fuels (Vallack *et al.*, 1998). Dioxin exposure to humans is mainly from food, especially animal fats from dairy products, beef, poultry, pork and fish (especially farmed fish), although average daily intakes for Europeans and Americans appear to be within the WHO recommended values of 1–4 pg of International Toxicity Equivalents (I-TEQ) kg<sup>-1</sup> of body weight (Huwe, 2002).

#### Tributyltin (TBT)

Tributyltin (TBT) enters the environment mainly from its use as an anti-fouling biocide. Evidence of the damaging effect of tri-organotins on the reproduction and growth of various marine organisms has led many countries to regulate or ban their use leading to a considerable decrease in concentrations in coastal and fresh water (Voulvoulis et al., 1999). Several studies indicate, however, that contamination of sediments by organotin compounds is still wide-spread with ecotoxicological consequences (Chau et al., 1997). Tributyltin is one of the best examples of severe effects on wildlife at the population level (Van der Kraak, 1998). Both lethal and sub-lethal effects have been observed in biota, including severely retarded larval development, masculinisation of female (imposex), behavioural changes and shell deformation in oysters (Oehlmann et al., 1995). In some areas, TBT exposure has resulted in sterility leading to species extinction (Minchin et al., 1996). Imposex has been determined at levels of 3 ng l<sup>-1</sup> TBT, and a no-effect concentration (NOEC) has yet to be identified (Burton and Scott, 1992).

#### Surfactants

Surfactants are predominantly used in detergents. Those of most concern are the alkylphenols (AP) and their ethoxylates (APEO), particularly nonylphenol (NP)-containing compounds. Direct sources of human exposure include residues of NP and NPEOs in food as a result of the use of pesticides, vegetable and fruit waxes, detergents and disinfectants in food manufacturing and packaging (Environment Canada, 2000). A recent study has detected 4-nonylphenol in a range of foodstuffs, including human breast milk (Guenther et al., 2002). Cosmetic products can also be direct sources of exposure for humans. Also nonoxynol-9 (NP9EO) is used as a spermicide in contraceptive products (Environment Canada, 2000). Surfactants are more toxic to aquatic organisms than mammals (Fent, 1995). A recent survey of wild roach in UK rivers found a high percentage of males with eggs in their testes and female egg yolk in their blood attributed to exposure to such surfactants (Jobling et al., 1998).

#### Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are formed from both natural and anthropogenic sources, largely by the incomplete combustion of organic matter. Natural sources of PAHs include forest fires, volcanic activity and the release of petroleum hydrocarbons by marine seeps. The principal sources of anthropogenic PAHs are the combustion of fossil and biomass fuels, stubble burning, aluminium smelting, refuse burning, coke ovens, petroleum processing and vehicle emissions (Baek et al., 1991). Other sources include sewage, sewage sludge, cigarette smoke, gas leakage and fuel spills and leakage (Bedding et al., 1995). PAHs in sediment are available to both benthic and demersal aquatic organisms (Landrum et al., 1991; Munkittrick et al., 1995), with the direct intake of particulates contributing a significant proportion of uptake (Woodhead et al., 1999).

#### Polychlorinated biphenyls (PCBs)

In the past, polychlorinated biphenyls (PCBs) have been used in a wide variety of industrial applications because of their high stability and electrical resistance (Stangroom et al., 1998). Although PCB production has been banned in most countries since the 1980s, it is estimated that over 1 Mt of PCBs have been manufactured (Stangroom et al., 1998), with about one-third of this quantity already in the environment (Jones et al., 1991; Vallack et al., 1998). PCBs have accumulated in food chains, including in aquatic and marine species, because of their high biostability and lipophilicity, (Brouwer et al., 1998). Thus, sources of human exposure to PCBs are generally from food, particularly animal fats, especially meat and dairy products, fish and fish products. In water, highly chlorinated PCBs are dominant (Tyler and Millward, 1996). PCBs exhibit a high affinity for total organic carbon (TOC) which also influences their bioavailability (Ferraro et al., 1990). Biomagnification has been demonstrated in the marine food chain, with increasing total PCB concentrations correlating with increasing trophic level (Borga et al., 2001).

#### Polybrominated diphenyl ethers (PBDEs)

Flame retardants, especially brominated compounds (PBDEs) have been used in plastics, textiles, electronic circuitry and other materials (de Wit, 2000). These substances are persistent, lipophilic, have been shown to bio-accumulate (de Wit, 2002), and are used worldwide in vast quantities (Darnerud *et al.*, 2001). Sewage sludge concentrations of PBDEs reflect household, industrial, traffic and other non-point sources (Sellstrom, 1999). All the brominated flame retardants (including PBDE, HBCD, TBBPA) have been reported in sewage sludge samples (Sellstrom, 1999). Directive 2003/11/EC of the European Parliament increases the restrictions on the marketing and use of several potentially hazardous substances including PBDEs and octabromodiphenylether (OBDE).

#### Pesticides

Several very persistent pesticides, including organochlorines, synthetic pyrethroids, organophosphates,

carbonates, chlorophenoxy herbicides and triazines, are also known to exhibit endocrine disrupting properties (Bulger et al., 1978; Ireland et al., 1980; Bedding et al., 1982; Bulger and Kupfer, 1983). An estimated 2.4 Mt of pesticides per annum are used world-wide (US EPA, 2004) and are absorbed by plants (Vallack et al., 1998) before bio-accumulating in meat and dairy products. Pesticide residues, especially in animal fat, are an important source of exposure to humans, and organochlorine pesticide residues have been found in human fat and breast-milk (Harris et al., 2001). There is much evidence linking organochlorine insecticide exposure to endocrine disrupting effects on wild-life, including thinning of eggshells, damage to the male reproductive system, and behavioural changes such as same sex nesting (Colburn, 1995; LeBlanc, 1995). Resistant lipophilic pesticides that do not bind to the soil enter watercourses and can accumulate in the aquatic food chain.

#### Pharmaceuticals

Pharmaceuticals, including, human, veterinary, and recreational drugs are a highly variable group of organic compounds with the potential to cause harm to ecosystems and humans. They receive considerable pharmacological and clinical testing during development but knowledge of their ecotoxicity is generally poor. Thousands of tons of pharmacologically active substances are used annually but surprisingly little is known about their fate in the environment. A large proportion of an administered dose (up to 90%) may be excreted unchanged, while metabolites can be converted back to the active compound by bacterial action (Jones et al., 2001). In addition, many unused medicines are disposed of into the sewage system so that much urban sewage is contaminated with pharmaceuticals. Recent studies have demonstrated that there is incomplete elimination of many pharmaceuticals during sewage treatment and concentrations in the high nanogram to low microgram per litre range have been found in surface water, groundwater and marine systems (Ayscough et al., 2000). Drugs can accumulate in landfills, posing a threat to surface and groundwater (Ahel et al., 1998). Moreover, the continual introduction of drugs through sewage effluents may have significant impacts on exposed aquatic organisms (Daughton and Ternes, 1999). One of the problems is that conventional sewage treatment technologies vary greatly in their ability to remove drug residues (Heberer et al., 2002; Reinhard et al., 2003; Snyder et al., 2003) and, in some instances, have even been shown to increase the bioactivity of the pharmaceutical residues (Jones et al., 2003). Activated carbon filtration, which is used by some states in the US, continues to be one of the most effective known methods of removing drug and other contaminant residues from drinking water (Ternes et al., 2002; Boyd et al., 2003; Petrovic et al., 2003).

Drugs are used to affect biochemical processes in humans or veterinary animals, and exposure of other species to them may have adverse or even fatal effects (Rand, 1995). Moreover, the use of pharmaceuticals is expected to increase following the completion of the

human genome project and because of the increasing age of the population. One major concern is that antibiotics found in sewage effluent may cause increased resistance amongst natural bacterial populations and the increase in the number of bacterial strains resistant to multiple antibiotics has been attributed by several authors to the increase in discharges of antibiotics to waste-water (Willis, 2000). Guidelines for testing environmental impacts of new pharmaceuticals have been introduced in the US and a draft environmental risk assessment for new pharmaceuticals has been prepared for the EU. The issue is complicated by the fact that mixtures of only a few compounds have been shown to affect ecosystems in laboratory-scale studies. The tolerance of organisms will depend, however, on the duration of exposure to chemical (and non-chemical) stresses, which could behave synergistically. Hence risk assessments should take account of the possible cumulative effects of pharmaceuticals, or they are likely to lead to a significant underestimation of risks (Jones et al., 2002b).

#### GEOCHEMICAL AND RADIOMETRIC SURVEYS TO SUSTAIN THE EARTH'S LIFE-SUPPORT SYSTEMS

#### **Geochemical surveys**

As concern about the environment has increased, emphasis has been placed by national governments, international agencies and development banks on studies concerned with such issues as the quality of water resources, waste and pollution related to historical mining, industrialisation or urbanisation, and soil degradation. Such studies make an important contribution to applied environmental research by improving understanding of the chemical processes operating at the Earth's surface. The limitation of these types of studies is that they tend to investigate only one specific medium; groundwater studies in particular tend to be carried out in isolation from those of surface water, stream sediment or soil. There is also a tendency to study one or two chemical elements in detail rather than an extensive range of

 
 Table 9
 Geochemical Baseline Survey of the Environment (G-BASE) in Britain

Geochemical mapping for economic and environmental applications					
High resolution	1 sample site per 1–2 km <sup>2</sup>				
Multi-media	Stream sediments and concentrates Surface stream waters soils (2 or more horizons)				
Multi-element	35 elements by XRFs (sediments and soils) 14 elements by ICP-AES (now 24 elements by ICP-MS) Water + pH, HCO <sub>3</sub> , conductivity, DOC and a range of anions				
Fully quality controlled					

British Geological Survey.

elements, species or compounds. Moreover, there are few systematic studies of the approximately 30 000 synthetic industrial organic chemicals estimated to be on the market or of pharmaceuticals. Hence, such studies fail to provide a complete picture of the potential cocktail of chemicals to which ecosystems and humans are exposed or information on interactions between chemical species in different environmental compartments. Methods of sampling, analysis and data interpretation also vary greatly (Plant et al., 1996, 1997). Moreover, such studies are generally published in the journals of learned societies and are communicated mainly to other experts in the same field with relatively little impact on society as a whole. A quite different approach is needed if any substantial impact is to be made on global environment problems related to chemicals; these need to be at the strategic level, rather than in the usual present, post hoc 'fire-fighting' mode.

In most industrialised Western countries, geological survey organisations now provide strategic information on the chemistry of the Earth's land surface. Initially, geochemical surveys based on rapid, low-cost analysis of easily collected surface samples (Hawkes and Webb, 1962; Rose et al., 1979) were carried out to explore for metalliferrous mineral deposits (Plant and Hale, 1995). Relatively little emphasis was placed on standardising methods, which were often based on orientation studies to optimise exploration for particular types of target ore in different terrains (Darnley et al., 1995; Plant and Hale, 1995; Plant et al., 1996, 1997). More recently, geochemical survey methods have been greatly extended and refined, especially for environmental applications (Plant et al., 2000). An increased range of sample media is being studied including stream sediments, soil and surface and shallow groundwater samples. Sampling is increasingly carried out to rigorous internationally agreed standards (Darnley et al., 1995; Salminen et al., 1998), with analysis based on state of the art, sensitive, high-precision methods (Sandström et al., 2003). Sophisticated methods of data processing and interpretation are used, including thermodynamic models and speciation codes and strict quality control and quality assurance procedures are maintained throughout all survey operations. In this paper, the British Geological Survey's Geochemical Baseline Survey of the Environment Programme (G-Base) and the extension of such work over Europe as part of the FOREGS Geochemical Baseline Programme are used as examples of this new approach to studying chemicals in the environment. The principal features of the G-Base programme in Britain are given in Table 9. Examples of the maps of Cu in stream sediments over the area of Britain covered to date by the programme (and the location of the Humber Trent region) are shown in Plate 1. Maps for the Humber-Trent region showing the distribution of Se and Sb in surface soils are shown in Plates 2 and 3.

Such data provide excellent information on pH, conductivity and the total concentrations of more than 60 determinands and can be used to provide

fundamental process information. For example, the data on major ions can be shown as a percentage of total negative or positive charge ionic dominance as described in Hem (1985). They can also be represented as three colour component images based on the diagrams developed by Piper (1944) to show variations in the relative proportions of cations (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>); and anions (HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>) and Cl<sup>-</sup>), respectively. In the UK, such maps clearly associate high NO3- concentrations with areas of intensive agriculture; areas of high acid precipitation with low buffering capacity (low Ca2+ and low Mg2+ with high  $SO_4^{2-}$ ) and areas of acid mine drainage with high SO<sup>2-</sup> and Cl<sup>-</sup> in areas of former coal working (BGS, 1999). Critical load maps can be prepared using models and displayed in a similar way, as can maps showing the degree of calcite or gypsum solubility based on their solubility diagrams. Moreover, since the surface waters studied have low ionic strength (interquartile range of ionic strength from 0.001 to 0.1007 M, with a maximum of 0.146 M), geochemical speciation codes such as PHREEQ and WATEQ can be applied, for example in modelling the bioavailability of PHEs such as Pb (Smith et al., 1998b).

The variety of media sampled, the wide range of elements and species analysed, and the high sample density used provide a better means of assessing overall environmental quality than data normally collected by regulatory agencies for monitoring purposes. Work by Appleton (1995b) and Breward (2003), for example, has shown the value of soil and sediment data in identifying areas of Cu, Pb, Zn, As, Cd and Sn contamination which would otherwise have gone unidentified, especially by the use of methods based on records of historical land use. Such data can also be used to calculate the relative contribution to the surface environment of natural and man-made sources of these chemical elements.

Recently, statistical methods have been used to optimise soil field sampling patterns and to estimate uncertainty due to sampling and chemical analysis and to assist in assessing the risk of soil contamination (Fergusson and Stewart, 1992; Ramsey and Argyraki, 1997; Goovaerts, 1997).

Distinguishing contamination from the natural background of chemicals has become increasingly important. Previously, this has been done, for example, by collecting different horizons in soil profiles and statistical analysis (Selinus and Esbensen, 1995). These methods are based on relating a proportion of a pollutant measured in soil with that of the same contaminant in the parent material and attributing the difference to anthropogenic sources. This approach fails, however, to identify specific sources of pollutants and allows only a qualitative interpretation of the results; moreover, the results cannot be applied where no baseline data are available. Recently, methodologies combining traditional statistics and geostatistics with modern spatial data analysis techniques and geographic information systems (GIS) have been used to distinguish between anthropogenic emissions and natural levels of chemical elements for sites with complex geological backgrounds and poorly recorded mining histories (Korre, 1999a,b) and to quantify and map different soil contamination sources and to distinguish them from natural sources (Korre and Durucan, 1999).

#### **Radiometric surveys**

High-resolution airborne radiometric surveys, such as the Hi-Res survey recently carried out by the BGS over northern England (Lahti and Jones, 2003; Peart *et al.*, 2003), provide detailed comprehensive data on the distribution of the naturally occurring radioelements eU, Th and K and other radioactive substances. The data on eU is particularly valuable for identifying radon-affected areas requiring special building regulations or the modification of existing buildings (Plate 4).

The distribution of <sup>137</sup>Cs from the Chernobyl accident in 1986 can also be mapped (Plate 6), as well as other areas of radioactive contamination from different sources. As in the case of geochemical data, radiometric data can be plotted in various ways to identify particular environment problems (Plate 5). The airborne platform can also be used to collect other data such as electrical conductivity, which provides an excellent non-invasive method of obtaining information on the distribution of pollution plumes from land-fill sites (Beamish, 2003); some of the sites identified have been proved by drilling (Klinck *et al.*, 2004).

High-quality, modern, regional geochemical and airborne radiometric data, especially when used in combination, provide a highly effective method of mapping and modelling a wide range of environmental problems in real time. Where such data for inorganic and radioactive chemicals are available, they can be used to predict, avoid and mitigate a whole range of problems caused by such chemicals in the environment. Moreover, outputs can be represented, analysed, modelled and visualised in clear, attractive graphical displays using GIS to assist policy makers, regulators and the general public to understand problems in context and to agree appropriate action.

#### Persistent organic pollutants (POPs)

Although issues of environmental pollution by POPs have been attracting increasing attention world-wide, there are few systematic data available on their distribution for modelling or monitoring. Problems of the long-range transport and accumulation in the environment and the impact of these chemicals on human health are being studied within the framework of many international programs such as those of OSPAR (Oslo and Paris Convention), WHO and UNEP. These fail, however, to address the need to map and monitor levels of these pollutants systematically. Once introduced into the environment, perhaps intentionally as an agrochemical or unintentionally as a by-product of combustion, many such chemicals or their metabolites remain in the environment for years, sometimes decades. Because of their slow degradation and their low solubility in water, this leads to their high bioaccumulation in soils, sediments and subsequently the fatty tissues of land animals and fish.



5 Surveys of PAH concentrations in UK soils (Smith *et al.*, 2002). National surveys are available only for Wales, with limited local studies of urban areas.

Dioxins and related compounds have recently been the subject of a consultation paper from the Department for the Environment and Rural Affairs (Defra) in the UK. They have also been the focus of an EU study aimed at compiling relevant data from member states (DETR, 1999) which highlighted the problems arising from the lack of standardised data over Europe. Other European studies also focus mainly on dioxins and PCBs (Federal Ministry for the Environment, 2000; European Commission, 2004). The disparity between the availability of data on even persistent synthetic organic chemicals such as PAHs and inorganic chemicals is highlighted using the UK as an example in Figures 5 and 6. The (UNEP) Stockholm Convention on POPs will initially monitor and reduce levels of 12 chemicals: DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, dioxins and furans, that are persistent, widespread and toxic (Ritter *et al.*, 1995), although DDT, properly used, is of value in controlling malaria. The convention, ratified by 50 countries, also has a mandate to reduce the levels of other such compounds in the environment as research becomes available. This information will be generated by the Global Monitoring Programme (GMP) and the Regional Based Assessment of Persistent Toxic Substances (RBAPTS). These surveys aim to co-ordinate the various regional and national monitoring studies in order to produce more



6 Surveys of inorganic substances in UK sediments (Smith *et al.*, 2002). Extensive national coverage is available for inorganic substances for England and Wales and Northern Ireland in the Wolfson Atlas, regionally for much of Britain and Northern Ireland as a result of the BGS G-BASE programme and locally as a result of the BGS Mineral Reconnaissance Programme.

Tuble To Triam phases of the Global Geochemical Dasennes Task Glob	Table	10	Main	phases	of the	Global	Geochemical	<b>Baselines</b>	Task	Grou
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Phase I (1988–1992): IGCP 259 International Geochemical Mapping
Assessment of requirements and methods for global geochemical mapping involving international working group of experts
Recommendations published in A global geochemical database for environmental and resource management (Darnley et al. 1995)
Recommendations published in A global geochemical database for environmental and resource management (Darnley et al. 1995)

Phase II (1992–1997): IGCP 360 Global Geochemical Baselines Establishment of world-wide network of professional geochemists Development of a set of methods for GRN sampling Publication of detailed Field Sampling Manual (Salminen *et al.* 1998)

Phase III: IUGS/IAGC Working Group on Global Geochemical Baselines Completion of collection of the GRN samples Increased standardisation of all geochemical survey methods world-wide

Plant et al., 2000.

accurate and representative data but, to date, no attempt has been made to use available sample archives. The treaty also encourages member nations to reduce or prohibit the production of these compounds in addition to carefully controlling their use and the disposal of any stockpiles.

#### Pharmaceuticals

The occurrence of pharmaceuticals in the environment and the extent to which they pose a risk to the environment and humankind has been investigated only since the early 1990s and there are still few systematic data available.

An initial risk assessment for the UK of more than 60 compounds thought to account for more than half of the known tonnage of pharmaceutical consumption (Ayscough *et al.*, 2000), suggested that the substances of most concern were paracetamol/acetaminophen, aspirin and dextropropoxyphene (pain killers), fluoxetine (antidepressant), oxytetracycline (antibiotic), propranolol (for heart disease and migraine), aminotriptyline (for neuralgia) and thioridazine (for adult schizophrenia).

Recently, the United States Geological Survey carried out the first nation-wide reconnaissance of the occurrence of pharmaceuticals, hormones and other organic contaminants in water (Kolpin *et al.*, 2002). The most frequently detected compounds were coprostanol (faecal steroid), cholesterol (plant and animal steroid), *N*,*N*diethyltoluamide (insect repellent), caffeine (stimulant), triclosan (disinfectant), tri(2-chloroethyl) phosphate (fire retardant) and 4-nonylphenol (detergent breakdown product). Samples commonly contained more than one contaminant and there were as many as 38 substances in some samples. Little is known about the potential interactive effects that occur from such complex mixtures and their breakdown products and their overall effect on human health and the environment (Halling-Sorensen *et al.*, 1998; Webb, 2001).

Other monitoring programmes in Europe, such as the European Union Poseidon Project and others of a smaller scale (Boxall *et al.*, 2002; Hilton *et al.*, 2003), and similar studies in the Americas (Brownawell and Iden; and Roberts and Bouwer, both in progress) have detected pain-killers, cholesterol regulators, antiseptics, chemotherapy agents, antibiotics and hormones in water.

#### **GLOBAL GEOCHEMICAL BASELINES**

Extending modern systematic geochemical surveys, such as those conducted by the BGS and other national geological surveys, over the Earth's land surface would clearly provide one of the most effective methods of addressing environmental concerns caused by chemicals world-wide. Standardised sampling and analytical procedures are required for such an exercise. The concept of internationally standardised geochemical mapping procedures originated in the 1970s under the auspices of the International Atomic Energy Agency, specifically for U (IAEA, 1973, 1976). In 1988, formal support was obtained from the IUGS/UNESCO International Geological Correlation Programme (IGCP) to determine the status of geochemical mapping throughout the world and to develop recommendations for providing data showing the geochemical diversity of the Earth's land surface. This effort has evolved into the present Task Group on Global Geochemical Baselines under the auspices of the IUGS and the IAGC (Darnley et al., 1995; Plant et al., 2000). Table 10 shows the three

Table 11 Present organisational structure of the Task Group on Global Geochemical Baselines

Steering committee	
Honorary President	A. G. Darnley, Canada
Co-leaders	J. A. Plant, British Geological Survey (BGS)
	D. Smith, United States Geological Survey
Scientific Secretary	Shaun Reeder, BGS
Treasurer	A. Demetriades, IGME, Greece
Leaders of Project Committees	
Analytical	G. Hall, Geological Survey of Canada
Sampling and Regional Co-ordination	R. Salminen, GTK, Finland
Public Relations and Finance	A. Demetriades, IGME, Greece

Website <http://www.bgs.ac.uk/bgs/w3/argg/iugs/iugshome/htm> Plant et al., 2000.

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Plate 1 Geochemical image of Cu in stream sediments prepared by the BGS G-BASE programme. The distribution of copper in stream sediments over Scotland, Wales, Northern Ireland and Central England; the highest levels, shown in red, reflect particular types of bedrock such as basalt, mineralisation or contamination. Low levels occur mainly over crystalline metamorphic rocks of northern Scotland

Table 12 Summary of requirements for a global geochemical database

- Commonly available representative sample media, collected in a standardised manner
- Continuity of data across different types of landscape
- Adequate quantities of the designed sample media for future reference and research requirements
- Analytical data for all elements of environmental or economic significance
- Lowest possible detection limits for all elements
- Determination of the total amount of each element present
- Tight quality control at every stage of the process

Plant et al., 2000.



Plate 2 Geochemical image of Se in surface soils prepared by the BGS G-BASE programme. The highest Se levels occur over the base metal mineralisation of the Derbyshire Peak, the industrial areas of the Yorkshire coalfield and around the edges of the Fens. Geological boundaries from the BGS 1:250 000 scale map series are shown in black



Plate 3 Geochemical image of Sb in surface soils prepared by the BGS G-BASE programme. The highest Sb levels are over the Carboniferous shales of East Staffordshire and West Derbyshire and contamination to the north of the Humber Estuary. Geological boundaries from the BGS 1:250 000 scale map series are shown in black

phases in the evolution of the Task Group and Table 11 outlines the current organisational structure.

The goal of the Task Group is to implement the recommendations from the IGCP 259 project as detailed in Darnley *et al.*, 1995. The primary recommendation from this project was to establish a network of geochemical reference samples for the land surface of the Earth based on a Global Reference Network (GRN) of approximately 5000 sample cells (available at <<u>http://www.bgs.ac.uk/iugs/></u>). The media sampled at sites within each cell would include stream or lake sediment, soil, floodplain sediment, humus (if present), and surface water (if present). The resulting database must meet the requirements as summarised in Table 12 and will serve multiple purposes:

- (i) Document the composition of a variety of surficial materials at sites evenly spaced over the land surface of the Earth.
- (ii) Provide locally relevant standard reference materials for use in the region collected.
- (iii) Provide reference points for levelling or normalising national geochemical data sets.
- (iv) Allow the preparation of a global geochemical atlas, including in digital form available over the internet.
- (v) Provide an archive of samples on which additional work may be done.
- (vi) Provide sites for recurrent monitoring in the future to facilitate the recognition and quantification of changes from either natural or human-induced processes.



Plate 4 Equivalent uranium data from the BGS Hi-Res programme. The distribution of high equivalent uranium levels (pink) indicates the high radon potential of the Derbyshire Peak District which is underlain by Carboniferous limestone. The area covered by the survey is shown in the small inset map

Over 120 countries have participated in the programme to date. The recommended sampling, analytical and data processing methods are described in a detailed sampling manual prepared by Salminen *et al.* (1998) and an analytical manual by Sandström *et al.* (2003).

A considerable amount of work on developing geochemical baselines using the GRN methodology is being carried out in Southern Africa, Colombia, Brazil, India, Korea and other CCOP countries. GRN-based sampling has been completed for China, parts of Russia, and in 26 European countries (Plant *et al.*, 1997; Salminen *et al.*, 1998). Unfortunately, to date, no funding has been obtained to determine even a limited range of synthetic organic chemicals or pharmaceuticals in this programme.

#### The FOREGS Geochemical Baseline Mapping Programme

The FOREGS Geochemical Baseline Mapping Programme is described briefly as an example of stage 2 of the IUGS/IAGC Global Geochemical Baseline Programme (Table 10). The FOREGS programme, led by Professor Reijo Salminen of the Geological Survey of Finland, was initiated following the preparation of an inventory of systematic geochemical datasets across Europe, which showed considerable variation in sampling and analytical methods used nationally (Plant et al., 1996; 1997). The new programme has conducted multi-media sampling at approximately 850 sites selected on the basis of the GRN in 26 European countries. An integrated GIS-based system of all



Plate 5 The distribution of natural radioactivity over the East Midlands, from the BGS Hi-Res programme. High levels of equivalent uranium (blue) indicating high radon potential occur over the Carboniferous limestones of the Derbyshire Peak District, the tributaries of the Trent that drain from it as well as over the Jurassic phosphatic limestones of Northamptonshire. High levels of potassium (red) occur over the Permian Sherwood Sandstone.



Plate 6 Contamination from <sup>137</sup>Cs from the BGS Hi-Res programme. High levels of <sup>137</sup>Cs reflect deposition following the Chernobyl accident in 1986 and pollution from the Sellafield nuclear reprocessing plant

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Plate 7 Geochemical image showing the distribution of As in water prepared by the FOREGS Geochemistry Programme (Salminem *et al.*, 1998). Note the high levels of As over the volcanic regions of Italy, the Iberian Pyrite Belt and Variscan Crystalline Massifs such as the Spanish Meseta and the Massif Central in France. High levels over South East England and North West Europe may reflect pollution. Low levels occur over the crystalline rocks of the Fennoscandian Shield and Caledonian belt and over Alpine rocks including those of Greece

environmental samples collected during the programme as a tool for decision makers is now available at <<u>http://www.gsf.fi/publ/foregsatlas/map\_compare.html</u>. The resulting database also provides a baseline against which all national datasets can be levelled (Salminen *et al.*, 1998). All of the samples have been archived in the Geological Survey of the Slovak Republic and are available for further study as the need arises. They could also be used to determine some of the more persistent organic chemicals, if a source of funding could be found.

The study area includes 26 European countries, including the Canary Islands, and covers a total land area of approximately 4.45 Mkm<sup>2</sup>. Sampling was carried out by the FOREGS Geological Surveys and associated organisations between 1998 and November 2001. Analyses were carried out between 1999 and 2003 in nine Geological Survey laboratories with one



Plate 8 Geochemical image showing the distribution of Se in water prepared by the FOREGS Geochemistry Programme (Salminem *et al.*, 1998). The highest levels of selenium occur mainly over sedimentary basins of Ireland, South East England, Southern Spain and Portugal, North West France, Holland, Germany, Denmark and Poland. Levels are also high over the volcanic regions of Italy and over Southern Greece. The lowest levels occur over the crystalline rocks of the Fennoscandian Shield and the Caledonides of Scotland, Alpine rocks of Central Europe and Variscan Crystalline massifs including the Massif Central of France

Waters		Humus		Top and sub-soils		Floodplain and stream sediments	
Survey	Method	Survey	Method	Survey	Method	Survey	Method
BGR BGS BGS NGU	ICP-MS/ICP-AES IC DOC Hg	GSSR NITG MAFI	Sample preparation ICP-MS Hg	GSSR NITG BGR GTK PGI MAFI	Sample preparation Granulometry/TOC XRF ICP-MS AR/ICP-AES Hg	GSSR GSSR BGS BRGM GTK/PGI MAFI	Sample preparation TOC XRF ICP-MS AR/ICP-AES Hg

#### Table 13 FOREGS samples analysis



Plate 9 Geochemical image showing the distribution of Ni in topsoil prepared by the FOREGS Geochemistry Programme (Salminem *et al.*, 1998). One of the main regional changes in the levels of nickel occurs approximately along the Trans European Suture Zone (TESZ) that trends WNW-ESE across North West Europe from Holland to Southern Poland. The TESZ separates the rocks of the Fennoscandian Shield and East European Craton and their sedimentary cover from younger Variscan rocks to the South and West. The highest Ni values occur over Greece reflecting the presence of large ophiolite slabs in the Alpine rock sequence there, and to a lesser extent over volcanic areas of Italy and the Canary Islands laboratory performing particular determinations for all samples of a specific type (Table 13).

The distribution of chemical elements in all media is presented on the world wide web as geochemical maps showing both interpolated baseline values using a colour scale and the element concentrations of individual sampling points as superimposed circles or dots. The exponential dot size function increases from the minimum value (or the detection limit) to the 98th percentile of observed values. Values higher than the 98th percentile are represented by large shaded dots.

The maps of the baseline concentration levels of trace elements are first interpolated and smoothed onto a regular  $64 \times 64 \text{ km}^2$  grid, with values calculated using a moving weighted median based on a circular window with a radius of 300 km, using a method described by Gustavsson *et al.* (1997). The estimated concentration of each cell is the weighted median of sample values and is shown by a graded colour scale, selected to represent the background distribution of chemical elements, based on percentiles.

Examples of maps for the distribution of Se and Sb in water are shown in Plates 7 and 8 and of Ni in topsoil in Plate 9.

Maps showing the distribution of U, together with a preliminary interpretation, are described in Plant *et al.* (2003b). These data used together with plots for normalised petrogenetic elements (spider diagrams) and chondrite normalised REEs clearly show that all the areas of highest U concentration in soil and sediment across Europe are related to granites emplaced during crustal extension. No areas of high concentration related to contamination from the nuclear industry have been identified to date.

It is clear from the preliminary interpretation of the FOREGS geochemical data that the data and their representation in map form, although of relatively low resolution, provide invaluable insight on the distribution of chemicals at the European scale. Also, much information can be determined by using various combinations or ratios of chemical elements, and by studying their concentrations in different media. The influence of bedrock geology, glaciation and superficial deposits is the major control on the distribution of many elements, for example the REEs, U, K and Th in soils and stream sediments. On the other hand, the distribution of other substances such as levels of  $NO_3^{-}$  in water appear to reflect anthropogenic contamination and high NO<sub>2</sub><sup>-</sup> levels closely follow the distribution of areas of intensive agriculture.

Much more detailed analysis and modelling of the data are required, ideally using higher-resolution national data sets levelled using the new FOREGS baseline data for chemicals in all of the different media. Kriging and multivariate statistical analysis methods including principal component and factor analysis tools are being used in combination with GIS analysis. Anthropogenic contamination will be distinguished from geogenic variation using other methods of statistical analysis, including canonical correlation (Korre and Durucan 1999). Further interpretation and thermodynamic modelling of the data for all chemical elements using data for other determinands such as pH, electrical conductivity and total organic content is also required and should prove to be of considerable economic, environmental and fundamental scientific significance for the area of Europe covered by the FOREGS geochemical baseline survey. This type of analysis is already being carried out for a selected number of base metals for risk analysis purposes.

#### CONCLUSIONS AND RECOMMENDATIONS

Persistent organic pollutants, such as certain organochlorine pesticides and polychlorinated biphenyls, and potentially harmful inorganic elements, such as As, Cd, and Hg, enter and accumulate in different compartments in the environment (*e.g.* water, soil, sediment). Each of these compartments may provide a pathway whereby the substances could pose a risk to human, animal and ecosystem health.

Systematic information on levels of inorganic chemicals in the environment has been generated for a few countries by national geological surveys. The value of merging these national-scale geochemical data sets to develop international-scale data and maps is frequently limited by a narrow focus on one sample medium, a tendency to study only one or two elements rather than an extensive range of elements, and by different sampling and analytical protocols. Systematic data on the abundance and distribution of synthetic organic compounds in the environment at international scales are almost non-existent.

Standardised geochemical baseline data for all inorganic, radioactive and organic chemicals of concern should be prepared to cover the land surface of the Earth. Much more work is required on persistent organic pollutants, many of which have been emitted into the environment only over the last 60 years. The methods used and the proposed data should be made available to all countries via the world wide web. Such a database would be of strategic importance in identifying areas of high potential risk to human, animal, and ecosystem health and would provide a basis for mitigating any problems related to chemicals in the environment prior to the development of serious effects, for example by optimising land use planning. Such a database would empower all nations to participate in actively reducing the use and impact of chemicals which presently threaten the Earth's life support system and its sustainability into the 21st century.

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