4 Anthropogenic Sources

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4.1 Introduction

As outlined in Chap. 3, the geochemistry of environmental media is largely dependent on the chemistry of the natural sources from which they have been derived, or with which they have interacted. Thus soil and surficial sediment chemistry are strongly influenced by the composition of their parent materials. Similarly stream and river waters, derived initially from precipitation, depend on the rocks, sediments, and soils from which they come into contact and interact with for their chemical composition. However, with the evolution of humans in the relatively recent geological past there have been anthropogenic impacts on the environment, which have increased dramatically with increasing population, urbanization, and industrialization (Fyfe 1998). Thus humans have contaminated or polluted the once pristine environment, and this impact is manifested in the chemistry of environmental materials that reflect anthropogenic signals superimposed on the natural composition.

Many human activities have resulted in environmental contamination and these include:

1. Mineral extraction and processing
2. Smelting and refining of mineral ores and concentrates
3. Power generation—fossil fuel, nuclear, geothermal, and hydroelectric
4. Other industrial and manufacturing activities—metallurgical and chemical industries, brick and pipe manufacture, cement manufacture, the ceramics and glass industry, plastics and paint manufacture, and fertilizer manufacture
5. Waste disposal—household refuse, fly ash, sewage, nuclear, and the open burning of refuse
6. Agricultural practices—application of mineral-based fertilizers and manure together with sewage sludge, application of pesticides and herbicides, farmyard runoff including such materials as sheep dip, etc., and deforestation, which has contributed to problems of mercury contamination of Brazilian rivers

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7. Transportation,—motor vehicle derived contamination; this is particularly important in urban environments
8. Treatment and transport (through metal pipes and fittings) of potable water

Nowhere is the impact of environmental pollution more apparent than in the urban environment. Road dust and soils in the urban environment can be heavily contaminated, particularly by metals. Road dust and fine soil particles are the major sources of house dust and as such represent a potential pathway into the human body from inhalation and inadvertent ingestion from hands, etc., particularly for children.

There are many examples of anthropogenically derived substances having marked effects on human health; for example, in 1956 the mercury poisoning experienced in the Minimata region of Japan, known as "Minimata disease." This resulted from a factory situated on the coast releasing mercury, which was used as a catalyst in plastics manufacture, into Minimata Bay. From there it was passed through the marine food chain in a methylated form [CH_3Hg^+ or $(CH_3)_2Hg$], and into humans via consumption of fish. Mercury attacks the central nervous system and causes irreversible brain damage. The methyl form of mercury represents a particularly serious toxic threat, as it is able to cross membranes and accumulate in the central nervous system. It has been estimated that over 20,000 people were affected.

Although the main thrust of this book concerns the impact of the natural environment on human health, this chapter deals briefly with anthropogenic impacts on the composition of environmental media together with some brief considerations of health impacts. This is included for the sake of completeness and as such it is not a detailed account of the topic; indeed, such a detailed account would require a second book.

4.2 Impact of Mineral Extraction and Refining

4.2.1 Mining and Mineral Extraction

Mineral deposits represent concentrations of an element or elements to a level at which they can be profitably extractable. As such these deposits represent concentrations of several elements well above crustal abundance. Such naturally occurring high concentrations are reflected in the chemistry of the soils, waters, sediments, plants, etc., in the immediate vicinity of the deposit. Indeed, measurement of the concentrations of various metals and non-metals in media such as soils, sediments, and waters have been used to locate mineral deposits. This practice is described as geochemical exploration.

Although there are likely to be significant natural enrichments of several elements in the vicinity of mineral deposits, mining and extraction of the deposit will add greatly to these enrichments. The mining and subsequent beneficiation of minerals and the separation and refining of their various components is one of the most serious sources of contamination of soils, waters, and the biosphere.

Humans have extracted minerals, particularly the metalliferous ores, since ancient times, and the extraction and refining of metals have played a major role in human development. The mining and processing of minerals have increased through time, due to population growth and the greater utilization of raw materials for manufacture. Many areas of past mining activity, in both the Old and New Worlds, bear witness to these extractions in the form of abandoned workings and extensive waste tips. Modern mineral extraction technology is generally far more efficient than past practices, and in many countries such processes are heavily regulated to limit the degree of contamination from extractive industries. However, historical mineral extraction involved less efficient technologies, and in those times virtually no environmental regulations were in place. Long-abandoned mineral workings are currently the cause of serious environmental pollution in many countries.

A large number of different materials are extracted from the Earth ranging from fuels such as oil and coal, industrial minerals such as clays and silica, aggregates for building and roadstone, and minerals for fertilizers as well as sources of non-metals. However, the major cause of concern are the metalliferous ores that are used as sources of metals and metalloids. Some of the more important metalliferous ore minerals are listed in Table 4.1.

The extraction and subsequent processing of ores can be summarized as follows:

Mining	➔	crushing/grinding
	➔	concentration of ore mineral
	➔	smelting/refining

Ores are extracted from the Earth by either subsurface mining, open pit surface techniques, or in a few cases by solution mining, which carries with it risks of groundwater pollution. Both subsurface and surface extraction result in waste material, which is generally piled on the surface in the vicinity of the mine. However, while such waste piles, which frequently contain ore minerals, are sources of environmental contamination, it is the subsequent processing of the ores that results in the greatest environmental problems. The crushing and grinding (comminution) of mineral processing has the objective of separating the ore minerals

Table 4.1 Some of the important, mostly metalliferous minerals

Mineral	Composition	Comments
Arsenopyrite	FeAsS	Frequently occurs as a gangue mineral
Barite	$BaSO_4$	Major use in drilling muds
Bauxite	Mainly $Al(OH)_3$	Only ore of aluminum
Bornite	Cu_5FeS_4	Important ore of copper
Carrollite	$Cu(Co,Ni)_2S_4$	Important ore of cobalt
Cassiterite	SnO_2	Main ore of tin
Chalcocite	Cu_2S	Important ore of copper
Chalcopyrite	$CuFeS_2$	Major ore of copper
Chromite	$FeCr_2O_4$	Main ore of chromium
Cinnabar	HgS	Main ore of mercury
Galena	PbS	Main ore of lead
Gold (native)	Au	Main source of metallic gold
Haematite	Fe_2O_3	Major ore of iron
Ilmenite	$FeTiO_3$	Important ore of titanium
Magnetite	Fe_3O_4	Important ore of iron
Molybdenite	MoS_2	Main ore of molybdenum
Pentlandite	$(Fe,Ni)_9S_8$	Major ore of nickel
Platinum	Pt (with other metals)	Main source of platinum
Pyrite	FeS_2	Common gangue mineral
Pyrrhotite	$Fe_{(1-x)}S_2$	Common gangue mineral
Rutile	TiO_2	Important ore of titanium
Scheelite	$CaWO_4$	Important ore of tungsten
Sphalerite	ZnS	Major ore of zinc
Stibnite	Sb_2S	Main ore of antimony
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	Copper ore—often contains silver
Uraninite (Pitchblende)	UO_2	Main ore of uranium
Wolframite	$(Fe,Mn)WO_4$	Important ore of tungsten
Zircon	$ZrSiO_4$	Main ore of zirconium

from the waste, generally referred to as gangue. To effect separation, the mined ore is finely crushed to liberate individual ore mineral grains to enable concentration of the sought after ore minerals. The very fine waste material left after this concentration process is referred to as tailings, and this material can contain, along with the gangue minerals, residual amounts of the ore minerals and can be a serious source of pollution. The tailings are very fine and are subject to wind ablation and can easily be transported by surface runoff. At many long-abandoned mine sites tailings have been left open to the environment resulting in serious contamination of surrounding soils and waters. In more recent mining operations, tailings are stored wet in tailings ponds often behind artificial dams. However, leakage of metal ions into both surface and subsurface waters has, in some cases, resulted in serious contamination of these waters, some of which have been sources of potable water. In addition, after mine closure tailings ponds will dry out unless arrangements are made to keep them permanently wet, which renders the fine material susceptible to spreading across the neighboring area. In modern mining operations, upon closure, remedial action such as isolation of the tailings material by covering serves to limit subsequent environmental pollution.

A further problem of tailings dams is the possibility of dam failure releasing large quantities of highly contaminated sediments and waters into the local environment. There have been several such dam failures in the last decade such as at the Omai gold mine in Guyana in 1995 and at the Mar copper mine on Marinduque Island, Philippines. A major failure of the Los Frailes tailings dam at Aznalcóllar, Spain, in 1998, spilled 6.8 million m^3 of water and pyrite-rich tailings that covered approximately 2,000–3,600 ha of agricultural land. In 2000 a gold mine tailings dam at Borsa in northwestern Romania released large quantities of cyanide and metals into local rivers, the Vaser and Tizla, which ultimately drain into the Danube River. This caused the death of many fish and birds that ate the fish.

In addition to the major metal components of the various ore minerals, many trace constituents are included and these frequently cause as much environmental concern as the major elements in the ores (see Table 4.2). Of the trace elements perhaps the most notorious is cadmium. It is ubiquitous in zinc ores with concentrations of up to 4.4% having been recorded in some ores. Weathering of the ore minerals within the abandoned mines and in waste and tailings tips results in the release of the trace constituents along with the major components of the ore. Soils and waters in the vicinity

Table 4.2 Some trace constituents of selected sulfide minerals (values in mg kg^{-1})

Element	Normal range	Maximum found
Galena (PbS)		
Ag	500–5,000	30,000
As	200–5,000	10,000
Bi	200–5,000	50,000
Cu	10–200	3,000
Sb	200–5,000	30,000
Tl	<10–50	1,000
Sphalerite (ZnS)		
As	200–500	10,000
Cd	1,000–5,000	44,000
Cu	1,000–5,000	50,000
Hg	10–50	10,000
Sn	100–200	10,000
Tl	10–50	5,000
Chalcopyrite ($CuFeS_2$)		
Ag	10–1,000	2,300
Co	10–50	2,000
Ni	10–50	2,000
Sn	10–200	770
Pyrite (FeS_2)		
As	500–1,000	50,000
Co	200–5,000	>25,000
Cu	10–10,000	60,000
Ni	10–500	25,000
Pb	200–500	5,000
Sb	100–200	700
Tl	50–100	100
Zn	1,000–5,000	45,000

From Levinson (1980)

of disused metal mines are frequently heavily contaminated. Figure 4.1 is a geochemical map for cadmium in stream plants in Sweden. The high cadmium concentrations in the central area of the country reflect metal mining in the area.

The most important ores of several base metals such as lead, zinc, and copper are sulfide minerals. The sulfide ore minerals represent the most serious threat of environmental contamination, because they are fairly easily oxidized in the presence of air to the considerably more soluble sulfates such as:-

$$ZnS + 2O_2 \rightarrow ZnSO_4$$

As a result surface and groundwaters in the vicinity of the weathering sulfide minerals can be seriously impacted.

A particular problem concerning weathering of sulfide minerals is that of pyrite and marcasite (both FeS_2). These iron sulfides oxidize to give various iron oxides and hydroxides together with some sulfates; these oxidation products are collectively called ocher. In addition to ocher,

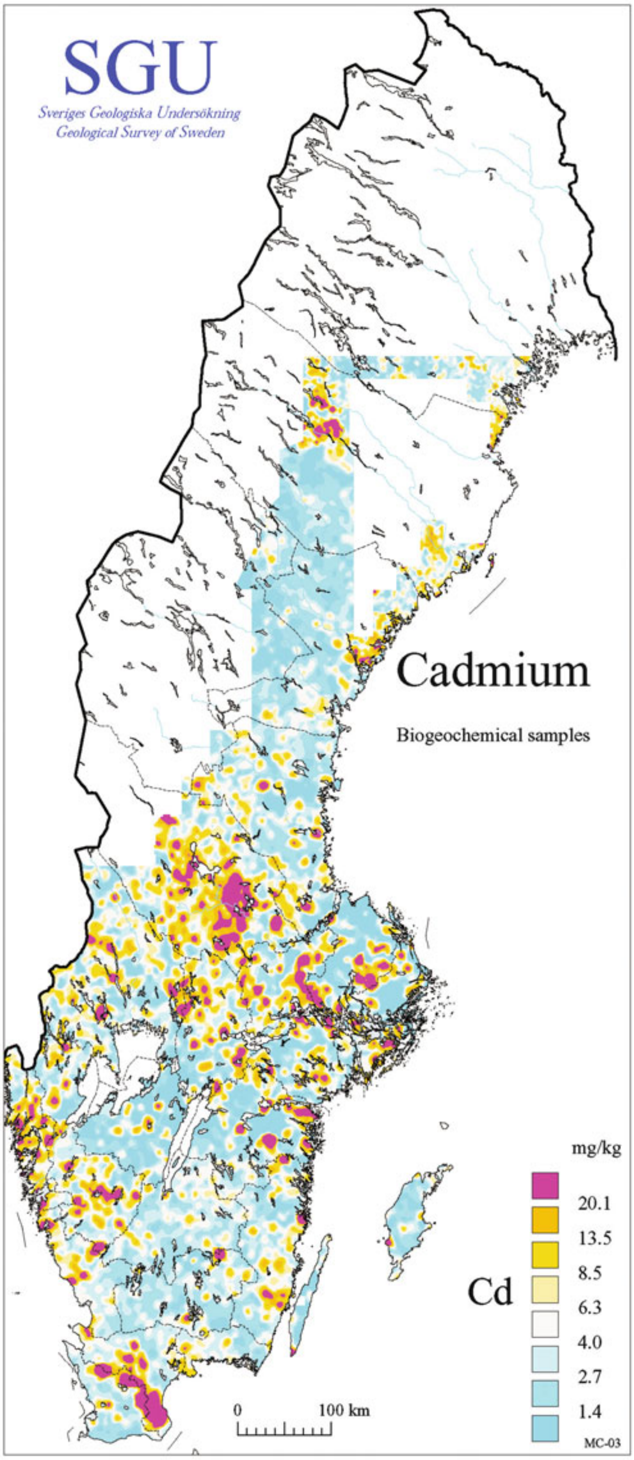

Fig. 4.1 Geochemical map for cadmium in stream plants in part of Sweden. (Reproduced with permission of the Swedish Geological Survey.) The high cadmium concentrations in south central Sweden are due to anthropogenic sources, those on the east coast are due to long range aerial deposition, those in the central area are derived from metal mining, and those in the central eastern area are derived from fertilizer. The high cadmium concentrations in the extreme south of the country are natural and are derived from cadmium-rich sediments

a by-product of the oxidation process is sulfuric acid; the resultant runoff from mines and waste piles is called acid mine drainage or acid rock drainage. Such acidic solutions can chemically attack other ore minerals and rocks to produce a cocktail of elements that can have a serious environmental impact on receiving rivers and streams. The reactions resulting in acid drainage can be summarized in the following equations:

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4$$

$$2FeSO_4 + H_2SO_4 + \frac{1}{2}O_2 \rightarrow Fe_2(SO_4)_3 + H_2O$$

$$FeS_2 + Fe_2(SO_4)_3 + 2H_2O + 3O_2 \rightarrow 3FeSO_4 + H_2SO_4$$

The ferrous iron produced is oxidized to ferric iron and hydrolysis of this results in ocher precipitation:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad \text{followed by}$$
$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

Recently, Kimball et al. (2010) demonstrated that chalcopyrite, the major ore mineral of copper, can produce very significant acidity when oxidized by ferric iron:

$$CuFeS_2 + 16Fe^{3+} + 8H_2O \rightarrow Cu^{2+} + 17Fe^{2+} + 2SO_4{}^{2-} + 16H^+$$

Most of the world's economic source of copper is that occurring in Porphyry copper deposits, where chalcopyrite is finely disseminated throughout a large volume of rock. Such deposits are mainly extracted using open pit mining operations, with huge volumes of rock being extracted, and result in very large waste piles. As a result of the acidity generated by chalcopyrite and associated pyrite, waste tips are serious potential sources of acid mine drainage and disused open pits frequently fill up with highly acidic waters. Rice and Herman (2012) have estimated that globally a minimum of 4×10^6 tonnes of H^+ are produced annually from the extraction of copper.

Acid mine drainage from metalliferous mines is generally strongly enriched in potentially harmful elements. In acid mine drainage impacted rivers, lakes, and estuaries the contaminants can cause extreme damage to the biosphere. This is exacerbated by the precipitation of ocher, which is enriched in metals such as cadmium, copper, zinc, and aluminum, and metalloids such as arsenic. The ocher is frequently fine enough to be ingested by fish. With decreasing acidity which results from dilution and neutralization of the acid by interaction with rocks, the concentration of contaminant metals in the ocher increases. This results in sediments in the impacted streams becoming heavily enriched in potentially harmful elements.

In addition to its occurrence in metalliferous ore deposits, pyrite is frequently associated with coal, with drainage from coal mines and associated waste piles being heavily ocherous, but generally not as strongly enriched in environmentally harmful elements.

As stated above, historical mineral extraction processes were much less efficient than current methods and were not subject to strict environmental regulation. In many orefields where mining occurred in river valleys, the plentiful supply of water was used to separate ore minerals by gravity. As a result of this inefficient process, considerable amounts of highly contaminated sediment and fine ore grains were released into rivers. Due to subsequent flooding, they were also released onto the floodplains of the river valleys concerned. Thus many floodplain soils in old mining areas are highly enriched with contaminant metals.

One problem concerning gold mining, which deserves a special mention, is that of associated mercury pollution. Mercury has long been used to extract gold from ores and gold-rich sediments due to its ability to amalgamate with gold. As a result of this process many areas where gold has been extracted, particularly from river sediments, have suffered serious mercury contamination.

4.2.2 Smelting and Refining

Following the mining and processing of the ores, the resultant concentrate is transported to a smelter. Pyrometallurgical smelting involves roasting of the ore concentrate at high temperatures with the consequent emission of large quantities of potentially harmful elements. The smelter emissions can be in the form of gases, such as sulfur dioxide, aerosols, and larger particulates. Modern smelter stacks are fitted with electrostatic precipitators and other dust recovery mechanisms, which results in the retention of most of the particulates, but some gaseous and aerosolic emissions are still released into the atmosphere. Although any larger particulates released are likely to be deposited close to the source, aerosols and gases can be transported long distances and as a result the smelting of ores has far wider aerial impact than the mining and processing of these ores.

As many of the ores are sulfides and the smelting process is designed to be oxidizing, the gases sulfur dioxide (SO_2) and sulfur trioxide (SO_3) are produced. These gases react with water vapor in the atmosphere to produce sulfuric acid (H_2SO_4), which results in acid rain with potentially serious consequences for the environment.

During the smelting of metalliferous ores many metals and metalloids are released to the environment. The elements released depend on the ore being smelted and include antimony, arsenic, bismuth, cadmium, chromium, cobalt, copper, lead, mercury, nickel, thallium, selenium, and zinc. Extremely high concentrations of some of these elements have been recorded in close proximity to the smelters. Rieuwerts and Farago (1996) showed that soils within 500 m of a lead smelter in the Czech Republic contained up to 3.73% lead and 2.76% zinc. It has also been shown that high concentrations of elements can be transported considerable distances from the smelter. Reimann et al. (1998) demonstrated that nickel from smelters in the Kola Peninsula of Russia was transported over 100 km in the direction of the prevailing wind. These same authors state that one of the smelters in the Kola Peninsula (Monchegorsk) emitted 1,619 tonnes of nickel during 1994.

While present day smelters emit potentially harmful elements, areas of past smelting operations also continue to be sites of environmental contamination. In the area of the lower Swansea Valley, South Wales, UK, a major smelting center for copper from 1717 until 1925, soils contain up to 200 mg kg^{-1} copper with the affected area extending 25 km north and 20 km east, the prevailing wind direction being from the southwest. The contamination is thought to have resulted from smelter fumes and wind ablation of smelter waste piles. More recently, in the same area, extreme selenium and tellurium contamination has been identified around a site of a nickel refinery with concentrations of selenium in soils ranging up to 200 mg kg^{-1} and tellurium up to 11 mg kg^{-1} (Perkins 2011).

Many specialist refining facilities have also been shown to cause environmental contamination. Perhaps the best documented is the release of fluorine during aluminum production. Aluminum is derived from alumina (aluminum oxide), which is recovered from bauxite ore by high temperature electrolysis with the alumina in a fluorine-rich electrolyte. The fluorine released during the process has been found to cause toxicity in plants in the vicinity of the refineries, and high fluorine occurs in the skeletons of animals in the same areas.

Smelter contaminants have been shown to have a detrimental effect on human and animal health. Copper toxicity was found to occur in cattle in the vicinity of a copper smelter in Mpumalanga (eastern Transvaal), South Africa (Gummow et al. 1991).

4.3 Power Generation

4.3.1 Fossil Fuel

Globally, fossil fuel (coal, oil, peat) combustion provides most of the power generated for industrial and domestic use. Burning of these fuels has achieved notoriety in recent years due to the large volumes of carbon dioxide (CO_2) produced, the consequent buildup of this gas in the atmosphere, and its possible contribution to the greenhouse effect on the Earth. In addition, combustion of high sulfur-containing fuels in some areas has resulted in production of sulfur dioxide and sulfur trioxide that, as in the case of smelter emissions (see Sect. 4.2.2 above), results in acid rain.

An additional environmental consequence of the use of fossil fuels for power generation derives from the many trace elements contained in the fuels. Although fossil fuels are predominantly made up of organic matter—the combustion of the carbon in these fuels being the source of energy—they also contain variable amounts of inorganic constituents retained in the ash left after the combustion process with some emitted in fine combustion products into the atmosphere. The ash residue, called fly ash, can contain many potentially harmful elements and therefore needs to be carefully disposed of (see Sect. 4.5). However, some of the inorganic components are emitted during combustion and can impact the soils, water, and biosphere in the vicinity of the power plant.

Many trace elements have been detected in fossil fuels. The actual concentrations of individual elements are variable and depend on the source of the fuel. However, it has been suggested that in Europe oil and coal combustion contribute significantly to atmospheric deposition of arsenic, cadmium, chromium, copper, nickel, and vanadium (Rühling 1994). Coal combustion is thought to have made a significant contribution to atmospheric lead deposition in the UK, with the coals containing up to 137 mg kg^{-1} (Farmer et al. 1999). It has also been suggested that coal combustion is the major anthropogenic source of selenium in the environment, and United States coals contain up to 75 mg kg^{-1} (Coleman et al. 1993). Enhanced concentrations of uranium in many coals have resulted in enrichments of this element around coal-fired power stations. Elevated concentrations of mercury occur in some oils with values up to 72 mg kg^{-1} recorded (Al-Atia 1972). Elements enriched in oils such as vanadium have also been found to be elevated in the environment in the vicinity of oil refineries (Rühling 1994).

The occurrence of fluorine in coal has been shown to impact the biosphere. Fluorine is highly phytotoxic and combustion of fluorine-rich coals has caused toxicity in vines downwind of a power station in New South Wales, Australia (Leece et al. 1986). Dental fluorosis occurring in cattle in the vicinity of large power stations in Yorkshire, England, was suggested by Burns and Allcroft (1964) to be due to the use of high-fluorine coals. Human fluorosis from burning fluorine-rich coals as a domestic fuel occurs in Guizhou Province, China (Zheng and Hong 1988).

Arsenic is enriched in coals from various parts of the world; however, in Guizhou Province, China, extreme enrichments have been found with up to 3.5% arsenic found in some samples (Ding et al. 2001). More than 3,000 cases of arsenic poisoning have occurred from the combustion of these coals for domestic heating (Ding et al. 2001). Abandoned coal gasification sites are another source of contamination related to fossil fuels. Such sites have residual waste piles that are sources of elements such as arsenic, cadmium and copper, and cyanide and organic compounds such as phenols and tars which may have leaked into the subsoil.

4.3.2 Nuclear

Nuclear power generation has been utilized since the mid-1950s and accidental leakages and permitted effluent releases have impacted the environment. The nuclear industry is now strictly regulated, but in the early years this was not so and authorized discharges of radioactivity were considerably larger. Radionuclides released during these early years still pose a problem. For example, radioactive elements such as americium and plutonium released from Sellafield nuclear power station in Cumbria, northwestern England, are still retained in nearby marshy areas.

Although much of the contamination released from nuclear power plants affects only the immediate environment of the nuclear installation in question, the catastrophic explosion at Chernobyl in April 1986 caused widespread contamination, which seriously affected the Ukraine and Belarus with radioactivity spreading over much of Europe and many other parts of the world. Some of the more important radioactive species released in the explosion are listed in Table 4.3. Radioactive cesium from the Chernobyl accident rained out over upland areas of the UK and high concentrations were found in sheep in the area. The accident at the Fukushima nuclear plant in Japan resulting from an earthquake and subsequent tsunami, in March 2011, resulted in major release of several radioactive species. Estimates suggest that the amount of ^{137}Cs released was about 42% of that released from Chernobyl, while the release of ^{133}Xe was the largest non-bomb release of radioactive noble gas in history (Stohl et al. 2011). About 4/5 of the radioactive cesium was deposited in the sea while about a fifth was deposited on Japan. However, radioactive iodine released from Fukushima Dai-Ichi was detected in the western USA within 4 weeks of the disaster.

Anthropogenic radioactivity in the environment poses a serious threat to human health. Of particular concern is radioactive iodine, mainly ^{131}I, which has been found to move through the food chain rapidly. As a result of exposure to radioactive iodine, humans are prone to increased incidences of thyroid cancer, as evidenced in the aftermath of Chernobyl (see Soils and Iodine Deficiency, Chap. 17, this volume).

Table 4.3 Some of the more important radioactive isotopes released by the chernobyl accident

Isotope	$T_{1/2}$
Relatively short half-life isotopes	
^{132}Te	78 h
^{133}Xe	5.27 days
^{131}I	8.07 days
^{95}Nb	35.2 days
^{89}Sr	52 days
Isotopes with longer half-lives	
^{134}Cs	2.05 years
^{85}Kr	10.76 years
^{90}Sr	28.1 years
^{137}Cs	30.23 years
Actinides (some of the more problematic)	
^{241}Pu	13.2 years
^{244}Pu	8×10^7 years
^{241}Am	458 years

4.3.3 Geothermal

Geothermal energy has often been assumed to be a "clean" form of power generation. However, many geothermal areas are associated with volcanic activity and many of the hot springs actively precipitate arsenic, antimony, mercury, and thallium, whereas some geothermal waters contain very high concentrations of boron. Thus spent waters from geothermal production in areas such as New Zealand contain very high concentrations of arsenic (see Arsenic in Groundwater and the Environment, Chap. 12 this volume), which pose serious environmental problems for the receiving rivers.

4.3.4 Hydroelectric

Hydroelectric power generation has led to problems resulting from flooding of areas for dams. In flooded areas where soils have been inundated it has been found that fish frequently contain elevated concentrations of mercury. The source of the mercury has been found to be the waterlogged soil where this element becomes converted to a methylated form which is bioavailable (see also Sect. 4.1 of this chapter).

4.4 Other Industrial Activities

There are a large number of other industrial activities that have the potential to cause environmental contamination. In this section only a small selection typifying such processes is discussed.

4.4.1 Metallurgical

Many metals and metalloids are used in the manufacture of alloys, with steel being the major product. The manufacture and recycling of steel results in the release of many elements into the atmosphere with subsequent deposition and contamination of the local environment. Figures obtained for atmospheric pollutants in the north of the former Soviet Union show that 79% of the chromium, 76% of the manganese, and 75% of the zinc together with significant quantities of antimony, arsenic, cadmium, lead, nickel, and vanadium were derived from the iron and steel industry (Pacyna 1995). More modern electric arc furnaces processing steel scrap give rise to a large amount of metal-rich flue dusts.

In the proximity of a steel plant in Mpumalanga (eastern Transvaal), South Africa, chronic vanadium toxicity occurs in cattle as a result of air pollution from the steelworks (Gummow et al. 1994). Another health problem related to steel production could possibly stem from the use of the mineral fluorite (calcium fluoride) as a flux in the process. An occurrence of fluorosis in cattle in northern England was suggested by Burns and Allcroft (1964) to be due to fluorine releases from local steel plants. In addition the waste, or slag, from steel plants can contain many metals that can have a detrimental effect on the environment, and this needs to be disposed of appropriately. Some slags have been used in fertilizers and Frank et al. (1996) reported vanadium poisoning in cattle after grazing on pasture land that had been amended with basic slag.

4.4.2 Brick and Pipe Manufacture

Bricks and pipes are very important in the construction industry. Both are produced from naturally occurring clays and clay-containing rocks. Manufacture of these materials involves shaping the clays and then roasting them at temperatures up to 1,200°C. As a result of this roasting, elements, which are contained in the clay minerals such as copper, lead, and zinc, are released to the environment (Fuge and Hennah 1989). However, a more significant health problem is the release of fluorine, which is frequently enriched in the minerals of the clays and rocks used during the manufacture. Very serious fluorosis in farm animals occurring in the East Anglia region of the UK in the 1950s was due to the extensive brick manufacture in this area (Burns and Allcroft 1964).

4.4.3 Cement Manufacture

Cement is also manufactured by a process involving the roasting of clay-rich rocks. A mixture of limestone and shale rocks is heated in a furnace at temperatures around 1,450°C. Shale is a clay-rich rock and can contain elevated concentrations of potentially harmful elements, and as in brick and pipe manufacture, these can be released at high temperatures.

4.4.4 Others

Many other industrial activities have been shown to result in environmental contamination. The production of enamel, ceramics, and glass releases appreciable concentrations of fluorine into the environment (Koritnig 1972). Another industry shown to release large quantities of fluorine into the environment is the manufacture of phosphate fertilizer from the fluorine-containing mineral apatite $[Ca(PO_4)_3(OH,F,Cl)]$ (Dabkowska et al. 1995).

Of the many other industrial processes that impact the environment, it is perhaps relevant to mention the serious impact of chromium in the environment from tanning plants (Davis et al. 1994). In addition, the chlor-alkali industry, which manufactures sodium hydroxide and chlorine from seawater by electrolysis with mercury electrodes has resulted in serious environmental contamination of the atmosphere and waterways with mercury. Spillages and leakage from the electrodes is also an environmental problem. Although the chlor-alkali process is being phased out, disused chlor-alkali works are a continuing source of contamination.

4.5 Waste Disposal

Large quantities of waste materials are produced on a daily basis from urban and industrial sources. Although there is a move to recycle and reuse waste products, the vast majority of waste has to be treated and subsequently disposed of. Many of the waste products created in modern society have a detrimental effect on the environment.

4.5.1 Refuse

Most household refuse together with waste materials from industrial sources is consigned to landfill sites. Such landfill sites produce leachate that contaminates soils, surface waters, and groundwaters in the vicinity. Landfill leachate chemistry is variable and depends on the components of the landfill plus varying conditions within the buried material, such as the differing redox conditions of various parts of the landfill and the percolation and flow of water into and through the site. Modern landfill sites are lined with low permeability materials such as high-density plastics to eliminate leachate leakage. However, old landfill sites made use of suitable depressions, such as disused quarries, and were not lined. These sites have become serious sources of contamination. Because landfills can contain a wide range of waste materials, many elements and organic compounds can be released, which include toxic metals such as cadmium and mercury and substances such as ammonia, nitrate, and sulfate. Due to the generally anaerobic nature of landfills, methane gas is generated and in modern facilities this is collected and used as fuel.

Incineration is the other commonly used method of refuse disposal. This process, which is utilized to provide a source of energy in some instances, results in the production of ash that contains many elements that are potentially harmful to the biosphere so necessitating disposal in a landfill. Additionally, incinerators can vent various elements and organic compounds such as dioxins into the atmosphere which impact local soils and waters. In this context it is perhaps relevant to note that uncontrolled burning of refuse, particularly in the developing world, and the consequent emissions into the atmosphere are of particular concern because they are likely to increase in the future.

4.5.2 Fly Ash

The residue from the combustion of coal is called fly ash and large quantities are created which result in disposal problems. This ash is composed of finely powdered glass-like particles and is highly reactive. It contains high concentrations of many potentially harmful elements, some of which could be readily mobilized in the environment. The composition of fly ash depends on the composition of the original coal, and it can contain relatively high concentrations of arsenic, barium, boron, cadmium, chromium, copper, fluorine, germanium, lead, molybdenum, nickel, selenium, and zinc together with high quantities of sulfur in the form of the sulfate anion.

Generally, fly ash is disposed of as a water-based slurry into lagoons or as a dry powder in landfills. In the case of slurry disposal, water from the lagoon is drained to local rivers after treatment and dilution. The soluble components of the ash are then transferred to local drainage systems.

A modern approach to fly ash disposal is to reuse it economically. Thus fly ash has been used in the manufacture of blocks for use in building; it has also been added to agricultural soils to neutralize acidity and to add essential elements to the soils.

4.5.3 Sewage

Sewage effluent is transported to treatment plants where the solid material, sewage sludge, is separated and the remaining liquid portion is discharged into rivers and seas. The liquid effluent can greatly impact the aqueous environment. The effluent can be enriched in nitrate, which results in algal blooms and eutrophication in coastal waters (see Sect. 4.6 for discussion of problems of eutrophication). This problem has been exacerbated due to effluent enriched in phosphate due to the addition of detergents. These additions have since been limited or banned in many countries.

Although liquid effluent can cause serious environmental problems, it is the solid waste or sludge that is the larger problem. Sewage sludge is produced in very large quantities and its disposal can have serious environmental implications. The methods used for its disposal include application to agricultural land (see Sect. 4.6), burial in landfills, and incineration. Disposal at sea, which was once a common practice, has been banned in most countries since the late 1990s. While several methods of sludge disposal are used, it is its use on agricultural land that causes the greatest concern.

The composition of sewage sludge is variable because it is derived from many sources such as domestic effluent, surface runoff that includes soil and street dust, and from different industrial effluents. Thus sludge derived from a predominantly urban area will be very different compositionally from that derived from highly industrialized areas. The composition of sewage sludge is variable and it has been found to contain metals such as cadmium, chromium, copper, lead, mercury, molybdenum, nickel, and zinc along with elements such as arsenic and fluorine and several organic contaminants such as polyaromatic hydrocarbons (PAHs) and chlorophenols. Nicholson et al. (2003) noted that in the UK controls on discharges from industrial sources mean that domestic sources of metals have become relatively more important. Thus copper and zinc from water pipes (see Sect. 4.10) and elements such as zinc and selenium, which are contained in many shampoos, are mainly derived from urban sources.

The impact of sewage sludge application to agricultural land is discussed in Sect. 4.6.

4.5.4 Nuclear

The disposal of nuclear waste is a relatively modern issue that is and will continue to be a serious problem for mankind. This waste is classified as high-, medium-, and low-level waste depending on its radioactivity. The favored method for disposal of high- and medium-level waste is long-term storage in underground vaults, and the potential for leakage and transport from these is currently the subject of much research.

Medium- and high-level waste needs to be isolated in vaults, but low-level waste is frequently disposed of in surface locations. It is of note that drainage from one such site in northwestern England, which is the low-level waste disposal site for the nuclear installation at Sellafield, contains 61 μg L^{-1} uranium with associated stream sediments containing 48 mg kg^{-1} uranium, far higher concentrations than are found in surrounding streams (British Geological Survey 1992).

4.6 Agricultural Practices

The well-documented environmental contaminants from agricultural practices are the nitrate and phosphate derived from fertilizer and farmyard manure that are applied to soils. These soluble ions are washed into surface and groundwaters. Nitrate and phosphate are essential nutrients and in lakes and coastal marine waters they can cause algal blooms and ultimately eutrophication when massive algal growths cause all of the oxygen in the water to be depleted. This results in the death of the algae and other biota, which leads to masses of rotting organic matter. In addition, the leaching of nitrates into groundwater in some agricultural areas has caused problems when the groundwaters are sources of potable waters. Such nitrate-rich waters have been shown to have caused methemoglobinemia in young babies due to nitrate interfering with the iron in blood which results in defective transport of oxygen. This is the cause of so-called “blue blood,” and methemoglobinemia is sometimes referred to as “blue baby syndrome.” It has also been suggested that ingestion of nitrates can contribute to gastric cancer when some of the nitrates are converted to nitrosamines, which are thought to be carcinogens (Mirvish 1991).

In addition to the problems of nitrate and phosphate derived from fertilizers, many other contaminants are added to soil, surface, and groundwaters due to agricultural activities. Thus many substances applied to soil as fertilizers contain trace elements known to be detrimental to the biosphere and potentially toxic to humans. These substances can accumulate in soils and be leached into local waters (Table 4.4). Of the inorganic fertilizers used, phosphate fertilizers manufactured from apatite-rich rocks are of particular interest because they can contain elevated concentrations of several potentially harmful elements. High cadmium in some soils and surface waters in agricultural areas has been linked to the application of phosphate fertilizer, as shown in Fig. 4.1 by stream plant chemistry for an area of Sweden, where the high concentrations in the east central part of the country reflect fertilizer sources. Phosphate fertilizers have also been linked to high uranium concentrations in waters draining agricultural areas and have been found to be the source of elevated concentrations of the element in surface peats and waters in the Florida Everglades (Zielinski et al. 2000). It should be mentioned that modern phosphate fertilizers contain less contaminant metals than the earlier varieties such as superphosphate.

Table 4.4 Concentrations of some trace elements in fertilizers added to agricultural land (mg kg^{-1})

	Phosphate fertilizer	Nitrate fertilizer	Manure	Sewage sludge
As	1–1,200	2–120	3–25	2–30
Cd	0.1–190	0.05–8.5	0.1–0.8	<1–3,400
Cr	66–245	3.2–19	1.1–55	8–41,000
Cu	1–300	–	2–172	50–8,000
Hg	0.01–2	0.3–3	0.01–0.4	<1–55
Mo	0.1–60	1–7	0.05–3	1–40
Ni	7–38	7–34	2–30	6–5,300
Pb	4–1,000	2–27	11–27	30–3,600
Se	0.5–25	–	0.2–2.4	1–10
U	20–300	–	–	<2–5
V	2–1,600	–	–	–
Zn	50–1,450	1–42	15–570	90–50,000

Data from several sources but predominantly from Alloway (1995)

The application of sewage sludge has been shown to be a source of elemental and organic contamination of agricultural soils. As mentioned in Sect. 4.5.4, one of the methods of disposal of sewage sludge is its application to agricultural land as a fertilizer. The composition of sewage sludges is extremely variable depending on their geographical source, and their application to soils is generally controlled with limits that are a function of their elemental compositions. However, some sludge applied to agricultural land has, in the past, resulted in health effects in livestock; for example, Davis (1980) found that an outbreak of fluorosis in cattle on a farm in the UK was due to the application of sewage sludge containing 33,000 mg kg^{-1} of fluorine.

The composition of livestock manure is also variable with its elemental composition essentially derived from their food and water intake. However, in some cases feeds are supplemented with metals, as in pig and poultry diets where copper and zinc are added; thus, pig and poultry manure are particularly rich in these two metals. In the past arsenic was added to pig diets, but this has recently ceased. It is worth noting also that both sewage sludge and animal manure can add pathogens to soil and subsequently to surface and groundwaters.

From a study of metal inputs to agricultural soils in the UK, Nicholson et al. (2003) suggested that of the fertilizer sources, livestock manure represents the greatest source of zinc and copper. Sewage sludge was the most important source for lead and mercury, and inorganic fertilizers (mainly phosphate fertilizer) were the major source of cadmium. However, Nicholson et al. (2003) concluded that the major input of metals to agricultural soils in the UK was atmospheric deposition (see Sect. 4.8).

The application of pesticides—insecticides, herbicides, and fungicides—contributes to contamination of soils and surface and groundwaters. Many organic and inorganic compounds are utilized in pesticides. Some of the insecticides are chlorinated hydrocarbons (organochlorines) that include DDT and lindane, both of which were found to be toxic to humans. The use of these insecticides has been banned for some years, but they still persist in the environment as they decay slowly. Other insecticides such as organophosphates have replaced the organochlorines and, together with other organic compounds, are extensively used. There are a large number of organic herbicides and fungicides that show varying degrees of persistence in the environment ranging from a few weeks to many years. Many of these compounds have been found in groundwater, some of which is used as a source of drinking water. Several pesticides are based on inorganic compounds containing elements such as arsenic, lead, manganese, and zinc. Copper salts are used extensively as pesticides, for example, the fungicide Bordeaux mixture.

Another agricultural practice that can impact soils is the addition of lime, which is used to reduce acidity. Lime derived from limestone can contain many trace elements that can influence the composition of the soils. However, the major influence of lime is in increasing soil pH, which in turn can reduce the uptake of some elements by plants. Lime is sometimes added to soils to limit uptake of potentially harmful elements; thus, in sewage sludge amended soils, where high concentrations of some metals occur in the sludge, liming of soils is used to limit the uptake of metals. In some cases liming of soils has a detrimental effect because it limits plant uptake of elements that are essential to grazing animals. Some animals have suffered copper deficiency when grazing on recently limed pasture. In addition, copper deficiency is exacerbated if there are high amounts of molybdenum in the diet, which can arise from liming soils. This increases alkalinity (pH) and enhances molybdenum uptake by plants. Molybdenum-induced copper deficiency (molybdenosis) has been suggested to be the cause of unexplained moose deaths in Sweden, which have occurred since the mid-1980s in an area that had previously been heavily limed (Frank 1998) (see also Chap. 21, this volume).

Many other agricultural processes impact soils locally, for example, the application of steelworks slag (see Sect. 4.4.1) and fly ash (see Sect. 4.5.2). The use of wood preservative, both in agricultural and urban areas, can add elements such as copper, chromium, and arsenic to soils and runoff. In addition, metal fences and gates are frequently coated with zinc (galvanized) and can act as a source of this metal in the environment. In arid areas the practice of irrigation can sometimes lead to problems. High selenium in waters in the San Joaquin Valley, California, which has lead to toxicity in birds in the area, was found to be due to leaching of natural selenium from soils by irrigation waters (Kharaka et al. 1996). Kharaka et al. (1996) also suggested that several other western states in the United States have similar leaching problems with selenium-rich irrigation waters.

A particularly interesting problem resulting from an agricultural practice has been manifested in Brazil. Elevated mercury concentrations occurring in tributaries of the Amazon were originally ascribed to artisanal gold mining in river sediments, which result from the use of mercury to amalgamate gold (see Sect. 4.2.1). However, it has subsequently been shown that the mercury in the rivers is derived from soil as a result of deforestation.

4.7 Transportation-Derived Contamination

It has been suggested that motor vehicles represent the greatest single source of atmospheric contamination. Motor vehicles are powered by gasoline or diesel, and their combustion in vehicle engines results in the production of exhaust gases in which there are large quantities of carbon dioxide. However, due to incomplete combustion, carbon monoxide, hydrocarbons, and nitrogen oxides are also evolved. These gases pollute the urban atmosphere and are thought to contribute, along with emitted particulates, to respiratory diseases. In addition the nitrogen oxide gases destroy ozone in the stratosphere, which aids in thinning of the ozone layer.

Vehicle exhaust gases can also contain metallic elements such as lead, manganese, nickel, and vanadium. Nickel and vanadium are derived from diesel fuel and these metals can be very rich in diesel exhaust fumes, which represent a major component of atmospheric nickel and vanadium loads. Roadside soils have been found to be markedly enriched in nickel, and diesel locomotives can emit significant quantities of nickel and vanadium.

Lead has been added to gasoline since the early 1920s as tetraethyl and tetramethyl lead to make its combustion more efficient. However, research showed that the lead emitted through the exhaust system had a detrimental effect on the environment with estimates that over 75% of environmental lead was derived from this source. As a result the use of lead-containing fuel has been phased out in many countries. This is not true of all countries and gasoline with lead additives is still used in many developing countries. Because of the phasing out and subsequent ban on the use of leaded gasoline in the UK, lead concentrations in the atmosphere

Table 4.5 Vehicular sources of metals

Metal	Source
Lead	Gasoline
Manganese	Gasoline
Nickel	Diesel + alloys
Vanadium	Diesel + alloys
Zinc	Tires + galvanized items
Cadmium	Tires + lubricating oils (minor amounts)
Chromium	Chrome plating, brake linings, etc.
Copper	Electrical wiring, thrust bearings, etc.
Platinum groupmetals	Catalytic converters

have decreased markedly. Although lead concentrations in roadside soils have also decreased, these soils together with road dusts still contain high concentrations that continue to be pathways into the biosphere. In some countries where lead additives have been banned methylcyclopentadienyl manganese tricarbonyl (MMT) is used as an alternative which causes emissions of manganese, a suspected neurotoxin, in exhaust emissions.

Many other pollutant metals in roadside soils are derived from motor vehicles (see Table 4.5). Zinc is added to the rubber used for tires and some steel components of cars are coated with zinc (galvanized) to minimize rusting. Cadmium, a component of zinc ores (see Sect. 4.2.1), finds its way into tires and is also used as an antioxidant in lubricating oils. Chromium is used in steel alloys and in chrome plating, and nickel is also used in some steel alloys, which provides a second potential source of nickel. Motor vehicles are also thought to be a source of copper pollution, it being released from copper wiring, thrust bearings, and brakes. Similarly, metals such as tungsten used in high-temperature alloys in turbojet components and airplanes may be found in the vicinity of airfields.

A fairly modern group of pollutant metals derived from motor vehicles are the platinum group elements mainly platinum, palladium, and rhodium, which have been used in catalytic converters. These converters were first introduced in the 1970s in Japan and the United States and subsequently in other countries to clean up motor vehicle exhaust. The catalytic converter essentially converts carbon monoxide to carbon dioxide, nitrogen oxides to nitrogen, and hydrocarbons to carbon dioxide and water vapor. These converters were originally assumed to be fairly indestructible, but a study by Hodge and Stallard (1986) showed that roadside dust in San Diego, California, was enriched in platinum and palladium. Subsequently there have been strong enrichments of the platinum group elements in roadside dust, urban river sediments, roadside drain sediments, sewage sludges, etc. The concentration of these elements in some of these sediments is similar to that found in platinum group metal ores.

4.8 Atmospheric Deposition of Contaminants

Many contaminants are released into the atmosphere and carried as gases, aerosols, and particles, and they are subsequently deposited on the surface where they are incorporated into soils and waters, absorbed by plants, or inhaled by animals and humans. Contaminant sources augment the many natural sources of elements and compounds contributing to the atmospheric load, such as volcanic and hot spring activity, forest and grassland fires, and wind-ablated soil particles. The sources of the atmospheric pollutants are listed in the proceeding sections of this chapter (Sects. 4.2, 4.3, 4.4, 4.5 and 4.7) but include mining, smelting and refining, power generation, various industrial processes, waste incineration, and transportation related activities. In addition, fine soil particles carried into the atmosphere can have contaminants adsorbed on their surfaces.

The degree of atmospheric contamination is geographically variable and depends markedly on meteorological conditions and potential sources. The degree of transport of contaminants varies depending on the form in which they are held. Many contaminants from vehicles are carried as fairly large particles and are not carried very far from their source, which accounts for much of the contamination of road dusts (see Sects. 4.7 and 4.9). However, gaseous and aerosol transport can carry contaminants very great distances, and such forms of atmospheric transport are the major causes of contamination of the Arctic regions where metals such as lead have been found to be enriched in ice cores.

Deposition of atmospheric metals and arsenic in Europe has been estimated using moss analysis (Rühling 1994). This has demonstrated the importance of various industries and power generation on the distribution of the elements, with coal and oil combustion and mining and smelting accounting for the majority of the deposition of arsenic, cadmium, and copper and much of the nickel and zinc. Almost all of the vanadium is derived from coal and oil combustion and oil refining, whereas the steel industry accounted for most of the chromium and iron and some of the nickel. Lead was also derived from industrial and power generation sources, but vehicular contamination was found to be a major source. Pacyna (1995) estimated that in the heavily industrialized northern part of the former Soviet Union, fossil fuel combustion accounted for 75% of the lead in the atmosphere, 87% of the vanadium, and 34% of the selenium with 79% of the chromium and 75% of the zinc derived from the steel industry. Eighty-five percent of the arsenic, 53% of the cadmium, and 51% of the antimony came from the mining and smelting industries.

Deposition from the atmosphere is a major source of elements for the surface environments. Nicholson et al.

(2003) showed that for UK agricultural soils atmospheric deposition was the major source of several metals and accounted for 85% of the total mercury input, 53% of the cadmium, 55–77% of the arsenic, nickel, and lead, and 38–48% of the zinc.

In Fig. 4.1 the high cadmium on the west coast of Sweden reflects long-range atmospheric transport.

4.9 Contamination of Urban Environments

Contamination of the urban environment is of major importance because over half of the world's population live in this environment. Urban contamination is derived from many sources and motor vehicles are a major present-day source (see Sect. 4.7); however, many urban areas also house industrial activities with consequent contamination. Even in modernized cities in many countries, even though industries have moved out of the urban area, historical industrial activities have left large areas of contaminated land. Additionally, in many urban areas fossil fuels are still burned as sources of household heating. Contamination can also arise from fertilizers applied in parks and gardens, pesticide use, and garden fires and bonfires adding to atmospheric and soil pollution. A further source of urban contamination is the disposal of waste and refuse in gardens and open areas, and uncontrolled burning in the latter.

Many contaminants have derived from urban sources with many elements noted as enriched in urban soils relative to their rural counterparts (Table 4.6). Thus arsenic, antimony, boron, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, tin, vanadium, and zinc, among others, have been listed as serious contaminants of the urban environment. The soils and street dusts of the urban environment are enriched in many potentially harmful metals (Table 4.6) and are the major sources of household dust. They represent a major pathway into the human body via inhalation and inadvertent ingestion from hands, which is a particular problem for young children. Although many of these elements are potentially harmful to humans, it is lead that has attracted the most attention because it has been shown to cause serious health problems in children from urban environments.

Lead in inner city areas is derived from a variety of sources. The use of leaded fuel in vehicles (see Sect. 4.2) either has been or is being phased out in most developed countries; however, it is still used in many less developed countries. Even in countries where leaded fuel is banned, much of the urban dust and soil lead is a legacy of its former usage (Table 4.6). Even though the major source of urban lead is likely to be the past or present use of leaded fuel, Mielke (1994) in a study of New Orleans, Louisiana, found that a major source of lead in soils of inner city areas was lead-containing paint. Although such paints are no longer used, the exteriors of older houses have layers of lead-based paint which have been painted over. Weathering of the paint or renovation of the houses where the old paintwork is scraped off results in the addition of lead to the soils. Old lead paintwork has also been shown to be a source of lead in children who ingest paint flakes that have been either picked off the paintwork or scraped off during renovation.

Table 4.6 Metals in the urban environment—Birmingham, England

Urban area—street dust	Range (mg kg^{-1})
Cadmium	0.4–25
Chromium	9–228
Copper	36–3,160
Lead	32–4,820
Nickel	11–683
Tin	3–332
Zinc	79–5,210
Urban area—soil	
Cadmium	0.7–1.6
Copper	38–715
Lead	75–350
Zinc	53–450
Rural area—soil	
Cadmium	0.2–0.5
Copper	5–57
Lead	14–74
Zinc	10–180

Data for street dust are from Brothwood (2001) and data for soils are from Davies and Houghton (1984)

Note: Data for dust was obtained with a strong acid attack and represents a virtually total extraction of metals. Soil data is for a weak acid attack and represents metals which are easily extractable

Lead is an extremely toxic element and attacks the central nervous system. Young children are particularly vulnerable. In extreme cases of lead toxicity, although now very rare, the brain swells (encephalopathy) and death can result. The obvious symptoms of lead toxicity are rare, but the subclinical effects are a cause for concern as they have been shown to impair learning and cognitive response. Surveys of children residing in inner cities have shown that relatively low intelligence quotients (IQ) correlate with high body burdens of lead. These levels are sometimes estimated from the lead content of the milk teeth of young children and monitored by blood lead levels. Studies have shown that exposure to Pb at an early age has a detrimental effect on educational achievement. It is also suggested that elevated lead in children's blood can increase the incidence of attention deficit hyperactivity disorder, while high blood lead in children/teenagers has been linked with antisocial and violent behaviour. Finally research has indicted that exposure to lead at an early age speeds the ageing process.

In addition to the elemental contaminants mentioned above, it is worth pointing out that many organic contaminants, such as dioxins and PAHs, are added to the urban environment from industry, fossil fuel combustion, and refuse burning.

4.10 Treatment and Transport of Potable Waters

Drinking water for humans comes from surface and groundwater sources and, hence, its initial chemistry is governed mainly by the chemistry of the surface sediments and rocks with which it interacts. The initial water is generally subjected to various treatments to ensure that it is fit for human consumption and this process modifies its composition. Subsequently, the water is distributed through a network of pipes that are frequently metallic; this transport can also modify the water composition.

Surface water frequently carries solid matter that needs to be removed. Although coarse material can be removed easily by filtering, finer material poses more of a problem and a coagulant is added to cause the flocculation and precipitation of this material. As a result of the coagulation process traces of the coagulant remain in the water. Several chemicals are used as coagulants and one of the most important is aluminum salts. However, concern has been expressed concerning elevated aluminum in drinking water, because some studies suggest that it is a contributory factor in Alzheimer's disease (premature senility). Iron compounds have also been used as coagulants, but their use can lead to subsequent strong leaching of metals from pipe surfaces.

Following removal of solid material the water is disinfected to remove any potentially harmful organisms. The most common disinfectant is chlorine. However, it has been shown that chlorine can react with organic matter in the water to produce chlorine-containing organic compounds (chlorophenols) that have been shown to be carcinogenic.

Following treatment the water is distributed through pipes, which are frequently metallic, and as a result traces of the pipe metal are transferred to the water. For example, where copper pipes are used copper and zinc are found in the water. The concentrations of these metals are generally low and Fuge and Perkins (1991) recorded $<65\ \mu g\ L^{-1}$ copper and $<40\ \mu g\ L^{-1}$ zinc for most samples analyzed in the main drinking water in north Ceredigion, Wales. However, in low-calcium containing (soft) waters from springs and wells where the drinking waters were untreated, much higher copper and zinc levels were present, with up to $500\ \mu g\ L^{-1}$ of copper and $125\ \mu g\ L^{-1}$ of zinc recorded.

Lead pipes have been extensively used in the past for transporting water, but in view of the known serious health effects of lead (see Sect. 4.9), this metal is no longer used and in many cases older lead piping has been replaced. However, due to its historical use some lead pipes are still in place and Fuge and Perkins (1991) record $29\ \mu g\ L^{-1}$ lead in a supply with lead pipes. Lead in drinking water is highly bioavailable, and it has been suggested that this is a major pathway into the human body in some areas where lead piping is still in use. To this end the World Health Organization (WHO) suggests that drinking water contain no more than $10\ \mu g\ L^{-1}$ of lead.

4.11 Summary

The geochemistry of environmental media is strongly dependent on the chemistry of the natural sources from which they have been derived or with which they have interacted. However, the chemistry of environmental materials demonstrates a superimposed anthropogenic signal. It has been suggested that no environment on Earth is free of contamination and even the polar ice caps have elevated lead concentrations. Anthropogenic impacts on the environment result from many human activities that range from the extraction of raw materials from the Earth and manufacturing the many products needed by society that provide the food and generate the power for the world's population and subsequent disposing of the resultant waste materials. With much of the world's population living in major conurbations, nowhere is the impact of anthropogenic activities more evident and much of this is derived from the use of motor vehicles.

The anthropogenic influence on the environment has resulted in many elements and inorganic and organic compounds impacting soils, waters, and the atmosphere. As humans and animals are dependent on these media for food, drinking water, and air, any contaminants can enter the biosphere and can potentially have a serious impact with resultant health problems. A summary of the major sources of elements that can have serious effects on the biosphere is given in Table 4.7.

See Also the Following Chapters. Chapter 3 (Natural Distribution and Abundance of Elements) • Chapter 12 (Arsenic in Groundwater and the Environment) • Chapter 21 (Animals and Medical Geology)

Table 4.7 Important anthropogenic sources of some elements known to have detrimental effects on the biosphere

Element	Sources
Antimony	Mining, smelting, fossil fuel combustion
Arsenic	Mining, smelting, steel making, fossil fuel combustion, geothermal energy production, phosphate fertilizer, pesticides
Cadmium	Mining, smelting, fossil fuel combustion, incineration, phosphate fertilizer, sewage sludge, motor vehicles
Chromium	Smelting, steel making, fossil fuel combustion, phosphate fertilizer, sewage sludge
Cobalt	Mining, smelting, fossil fuel combustion
Copper	Mining, smelting, fossil fuel combustion, manure, sewage sludge, pesticides
Fluorine	Mining, aluminum refining, steel making, fossil fuel combustion, brick making, glass and ceramic manufacture, phosphate fertilizer
Lead	Mining, smelting, fossil fuel combustion, sewage sludge, pesticides, motor vehicles
Mercury	Smelting, fossil fuel combustion, incineration, sewage sludge
Nickel	Mining, smelting, steel making, fossil fuel combustion, oil refining, sewage sludge, motor vehicles
Selenium	Smelting, fossil fuel combustion
Thallium	Smelting, fossil fuel combustion
Uranium	Fossil fuel combustion, phosphate fertilizer
Vanadium	Steel making, fossil fuel combustion, oil refining
Zinc	Mining, smelting, steel making, fossil fuel combustion, phosphate fertilizer, manure, sewage sludge, pesticides, motor vehicles, galvanized metal

References

Al-Atia MJ (1972) Trace elements in Iraqi oils and their geological significance. In: Mineral exploitation and economic geology. University of Wales, Aberystwyth

Alloway BJ (ed) (1995) Heavy metals in soils, 2nd edn. Blackie Academic & Professional, London

British Geological Survey (1992) Regional geochemistry of the Lake District and adjacent areas. British Geological Survey, Keyworth

Brothwood S (2001) Vehicle related emissions of platinum group elements and other heavy metals in the urban environment, PhD thesis, University of Wales, Aberystwyth

Burns KN, Allcroft R (1964) Fluorosis in cattle: occurrence and effects in industrial areas of England and Wales 1954–57, industrial disease surveys, reports 2, part 1. Ministry of Agriculture Fisheries and Food, London

Coleman L, Bragg LJ, Finkelman RB (1993) Distribution and mode of occurrence of selenium in US coals. Environ Geochem Health 15:215–227

Dabkowska E, Machoy-Mokrzynska A, Straszko J, Machoy Z, Samujlo D (1995) Temporal changes in the fluoride levels of jaws of European deer in industrial regions of Western Pomerania, Poland. Environ Geochem Health 17:155–158

Davies BE, Houghton NJ (1984) Distance-decline patterns in heavy metal contamination of soils and plants in Birmingham, England. Urban Ecol 8:285–294

Davis RD (1980) The uptake of fluoride by ryegrass grown on soil treated with sewage sludge. Environ Pollut B 1:277–284

Davis A, Kempton JH, Nicholson A, Yare B (1994) Groundwater transport of arsenic and chromium at a historical tannery, Woburn, Massachusetts, USA. Appl Geochem 9:569–582

Ding Z, Zheng B, Long J, Belkin HE, Finkelman RB, Chen C, Zhou D, Zhou Y (2001) Geological and geochemical characteristics of high arsenic coals from endemic arsenosis areas in Southwestern Guizhou province, China. Appl Geochem 16:1353–1360

Farmer JG, Eades LJ, Graham MC (1999) The lead content and isotopic-composition of British coals and their implications for past and present releases of lead to the UK environment. Environ Geochem Health 21:257–272

Frank A (1998) "Mysterious" moose disease in Sweden. Similarities to copper deficiency and/or molybdenosis in cattle and sheep. Biochemical background of clinical signs and organ lesions. Sci Total Environ 209:17–26

Frank A, Madej A, Galgan V, Petersson LR (1996) Vanadium poisoning of cattle with basic slag. Concentrations in tissues from poisoned animals and from a reference, slaughter house material. Sci Total Environ 181:73–92

Fuge R, Hennah TJ (1989) Fluorine and heavy metals in the vicinity of brickworks. Trace Subst Environ Health 23:183–197

Fuge R, Perkins WT (1991) Aluminum and heavy metals in potable waters of the North Ceredigion area, Mid-Wales. Environ Geochem Health 13:56–65

Fyfe WS (1998) Towards 2050; the past is not the Key to the future; challenges for science and chemistry. Environ Geol Health 33:92–95

Gummow B, Botha CJ, Basson AT, Bastianello SS (1991) Copper toxicity in ruminants: air pollution as a possible cause. Onderstepoort J Vet Res 58:33–39

Gummow B, Bastianello SS, Botha CJ, Smith HJC, Basson AT, Wells B (1994) Vanadium air pollution: a cause of malabsorption and immunosuppression in cattle. Onderstepoort J Vet Res 61:303–316

Hodge VF, Stallard MO (1986) Platinum and palladium in roadside dust. Environ Sci Technol 20:1058–1060

Kharaka YK, Ambats G, Presser TS, Davis RA (1996) Removal of selenium from contaminated agricultural drainage water by nanofiltration membranes. Appl Geochem 11:797–802

Kimball BE, Rimstidt JD, Brantley SL (2010) Chalcopyrite dissolution rate laws. Appl Geochem 25:972–983

Koritnig S (1972) Fluorine. In: Wedepohl KH (ed) Handbook of geochemistry. Springer, Berlin, chap. 9

Leece DR, Scheltema JH, Anttonen T, Weir RG (1986) Fluoride accumulation and toxicity in grapevines *Vitus vinifera* L. in New South Wales. Environ Pollut A 40:145–172

Levinson AA (1980) Introduction to exploration geochemistry, 2nd edn. Applied Publishing, Wilmette

Mielke HW (1994) Lead in New Orleans soils: New images of an urban environment. Environ Geochem Health 16:123–128

Mirvish SS (1991) The significance for human health of nitrate, nitrite and N-nitroso compounds. In: Bogárdi I, Kuzelka RD, Ennenga

WG (eds) Nitrate contamination exposure, consequences and control. Springer, New York, pp 253–266

Nicholson FA, Smith SR, Alloway BJ, Carlton-Smith C, Chambers B (2003) An inventory of heavy metals inputs to agricultural soils in England and Wales. Sci Total Environ 311:205–219

Pacyna JM (1995) The origin of Arctic air pollutants: lessons learned and future research. Sci Total Environ 160/161:39–53

Perkins WT (2011) Extreme selenium and tellurium contamination of soils – an eighty year-old industrial legacy surrounding a Nickel refinery in the Swansea Valley. Sci Total Environ 412/413:162–169

Reimann C, Äyräs M, Chekushin VA, Bogatyrev IV, Boyd R, de Caritat P, Dutter R, Finne TE, Halleraker JH, Jæger Ø, Kashulina G, Lehto O, Niskavaara H, Pavlov VA, Räisänen ML, Strand T, Volden T (1998) Environmental geochemical atlas of the central Barents region. Geological Survey of Norway, Trondheim

Rice KC, Herman JS (2012) Acidification of earth: an assessment across mechanisms and scales. Appl Geochem 27:1–14

Rieuwerts JS, Farago ME (1996) Heavy metal pollution in the vicinity of a secondary lead smelter in the Czech republic. Appl Geochem 11:17–23

Rühling Å (ed) (1994) Atmospheric heavy metal deposition in Europe—estimations based on moss analysis. Nordic Council of Ministers, Copenhagen

Stohl A, Seibert P, Wotawa G, Arnold D, Burkhart JF, Eckhardt S, Tapia C, Vargas A, Yasunari TJ (2011) Xenon-133 and caesium-137 releases into the atmosphere from the Fukushima Dai-Ichi nuclear power plant: determination of the source term, atmospheric dispersion, and deposition. Atmos Chem Phys Discuss 11:28319–28394

Zheng B, Hong Y (1988) Geochemical environment related to human endemic fluorosis in China. In: Thornton I (ed) Geochemistry and health. Science Reviews Limited, Northwood, pp 93–96

Zielinski RA, Simmons KR, Orem WH (2000) Use of ^{234}U and ^{238}U isotopes to identify fertilizer-derived uranium in the Florida everglades. Appl Geochem 15:369–383