CHAPTER 6

SOURCES, LEVELS AND MOVEMENTS
OF LEAD IN THE ENVIRONMENT

NATURAL OCCURRENCE

Lead occurs naturally in low concentrations in all rocks, soils and dusts, usually ranging from 2 to 200 parts per million. The total amount of lead in the earth’s crust is estimated to be $3.1 \times 10^{14}$ tonnes. Some soils have relatively high concentrations of lead, where the underlying parent rock has significant lead content. Lead contents of waters are generally low, but significant amounts of lead-rich dusts and vapours are carried in the air, from windblown material and volcanoes. However, these natural emissions are small in comparison with those resulting from human activity.

ANTHROPOGENIC SOURCES OF LEAD

Production of lead – Mining, smelting and refining of lead and other metals have in former times caused large emissions. Most of this is solid waste material, but sizeable emissions have also occurred to the atmosphere and to water. Modern techniques have minimized emissions to meet statutory requirements, including employment of best available technology.

Use of lead – Mobile sources (i.e. vehicles running on leaded petrol) continue to be a major contributor of lead to atmosphere in some countries, and this gives rise to elevated lead levels in soils, dusts and surface waters. Emissions are declining in many countries with the phasing out of leaded petrol, but lead deposited from petrol in the past remains in the environment. Residues from leaded paints, though now not used except for a few specialised outdoor applications, still continue to present a significant source of lead in house dusts and garden soils. Emissions from direct use of lead in other forms are small, resulting from abrasion and corrosion of lead or its compounds in some applications. Much of this material ends up in the sewage system, and contributes to levels of lead in discharged water and sewage sludge.

End-of-life of lead products – Most of the lead used at present is in products, such as batteries and lead sheet, which are largely recycled. Emissions can occur
from collecting and processing operations, but these are small in modern well-run installations; legislation in all EU countries limits permissible industrial emissions. Recycling is certainly the preferred end-of-life option. For items which are not recycled, releases to the environment are much greater at the end of their lives than during use. For example, lead shot from hunting and firing ranges can locally result in high levels of lead in the soil, and lost lead weights add to the burden of lead in aquatic systems. These applications together can be the prime sources of lead inputs to waters and soils, in countries where there are no significant emissions from industry or leaded petrol. However, in general these inputs are relatively small and local.

Lead in the waste stream: landfill, incineration and compost – Many lead-containing products (such as leaded solder, glass, PVC, and small lead items) are disposed of as waste. Lead in most forms is fairly inert, and if buried in a modern well-maintained landfill, any releases should be very small. However, in the long term, some small losses of lead and other metals can be expected in leachate.

Disposal by incineration can result in emissions. However, EU legislation requires that exhaust gases are thoroughly cleaned, and the lead-rich dusts and vapours are trapped and must be disposed of, usually to landfill. Several countries in Europe use incineration (sometimes with energy recovery) as a preferred disposal method for municipal solid waste; it is also the recommended route for the non-metallic fraction from end-of-life vehicles, even though this fraction contains up to about 0.5kg of lead per vehicle. Lead in incinerator ash is usually subject to final disposal in controlled landfills to prevent releases to the environment.

Some countries in Europe compost significant amounts of biodegradable waste. In a few cases, lead items in the waste stream can enter this fraction if not separated fully; if resulting composts have levels of lead or other metals above agreed standards, this cannot be used for agriculture or gardens.

OTHER SOURCES OF LEAD

Coal and oil combustion results in the emission of small amounts of lead, along with many other metals. Sewage sludge often contains lead and other metals, from various sources, though inputs to farmland are strictly controlled by EU legislation. Application of sludge to land continues to be a source of lead input at low levels to agricultural soils.

CHEMICAL SPECIES OF LEAD

The behaviour of lead in the environment depends upon the chemical form it is in. Natural weathering processes usually turn metallic lead and its compounds
into compounds which are relatively stable and insoluble. However, under acid conditions soluble compounds can also result in increasing mobility and potential bioavailability.

**TRANSPORT OF LEAD IN THE ENVIRONMENT**

Small lead particles emitted to air can remain in the atmosphere for over three weeks and in that time they may travel many hundreds of kilometers, though larger particles, which may constitute up to 95% of the emission, settle out within very short distances of the source. Deposition from atmosphere is a major contributor to lead inputs to water and to land but this continues to fall as the use of leaded gasoline is phased out. Lead can be carried in water, either dissolved or as waterborne particles. However, few compounds of lead dissolve readily in water, though most of this lead is then precipitated as a solid and becomes incorporated in the sediments at the base of the watercourse or ocean. In most cases lead in soil is relatively insoluble and has a low mobility. Thus, soils contaminated with lead retain high lead contents for many hundreds, even thousands, of years. Lead compounds are more mobile under acidic conditions, which can occur in mine wastes or from landfill leachate.

**BIOAVAILABILITY OF LEAD**

Knowledge of the total lead content of a surface soil is not very helpful in assessing the potential risk to humans or other organisms, because the degree of exposure to lead depends very much on the chemical and mineral form in which the lead occurs. The majority of lead compounds are relatively insoluble, though the small amounts of lead passing into the soil solution are easily taken up by biota. Some very insoluble lead compounds have little or no effect on living organisms. However, there is no single test for bioavailability: a compound which is unavailable to plants because it does not dissolve in soil water, may dissolve in the acidic stomach of an animal which ingests it. The development of simple cost-effective tests for bioavailability remains an urgent research requirement.
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INTRODUCTION

Lead is ubiquitous in the environment, present usually in small amounts from natural geological sources in all rock, soil, dust, water and air. These may influence the composition of foodstuffs for human consumption, the composition of dusts, which may be inhaled or ingested, and the composition of water supplies. All of these sources can contribute to human exposure.

In addition, lead mineralisation, coupled with mining and smelting of lead ores, has over many centuries given rise to extensive contamination of the environment in many parts of the world, though this is often very localised. For example, in Britain alone, it has been estimated that in excess of 4,000 km² of land is affected as a result of mining activity commencing in Roman or earlier times (Davies, 1980; Thornton, 1980).

6.1 NATURAL OCCURRENCES AND CONCENTRATIONS OF LEAD

Natural sources

Natural sources of lead in the surface environment arise from the weathering of geological materials and emissions to the atmosphere from volcanoes, wind-blown dust, sea spray, biogenic material and forest fires. Rasmussen (1996) discusses the difficulties in estimating lead emissions from natural sources. For example estimates of lead flux from volcanoes range widely from 540 tonnes/year to 6,000 tonnes/year. This uncertainty has been attributed to the difficulty in obtaining representative data due to the episodic nature of volcanoes (Nriagu, 1989). Large uncertainties in estimating metal fluxes from wind-blown dust are due to order-of-magnitude variation in metal concentrations of unconsolidated surface materials (Darnley 1995).

6.1.1 LITHOSPHERE / GEOSPHERE

Lead, like all other metals, occurs naturally in small concentrations in all rocks and soils. Its average concentration in the Earth’s crust is estimated to be approximately 16mg/kg, (Thornton, 1995), though it is not evenly distributed.

The most abundant metals or semi-metals found in the earth’s crust are silicon, sodium, potassium, calcium and aluminium; however rocks also contain small amounts of other metals. These trace elements altogether make up less than 1% of the earth’s crust. (Alloway and Ayres, 1997). The various processes by which these rocks were formed, together with the atomic size and chemical behaviour
of the metals, determine which metals are most usually associated with what types of rocks.

Lead is found in significant concentrations in certain sedimentary rocks, in particular in black shales, which have very fine particles, are rich in organic matter, and often have a number of other metals associated with them. Other rocks containing significant amounts of lead are shales and clays, granites, and sandstones, at levels ranging from 1 to 150 ppm (the higher limit being in black shales). The concentrations of lead in these rocks on average have been found to be 12-30 ppm. However, some other rocks, namely limestones, basalts and igneous ultramafic rocks, only contain traces of lead, with mean concentrations being reported as 1 to 9 ppm (Canon et al., 1978, cited by Thornton, 1995). Concentrations of lead are much higher (>10 percent) in some ore bodies, that is, naturally occurring rocks which are very rich in metals. These are exploited in order to obtain lead metal. Lead does not occur in isolation in these deposits which may also be rich in other metals, in particular, zinc, cadmium and silver.

Lead in soils

Soils are formed from underlying rocks, and from materials transported by wind, water and glacial activity. Natural weathering processes, such as abrasion and attack by water and air, slowly break down the rock into grits, sand and eventually finer particles, and biological activity assists in the transformation of the resulting particles into soil.

The mineral content of a soil often reflects that of its parent bedrock. Thus, soils which have formed from lead-rich rocks tend to have high concentrations of lead, entirely as a result of natural processes. It is difficult to obtain reliable information on typical lead concentrations in uncontaminated soils. Certainly in many parts of the world, there is widespread low level contamination reflecting long histories of urbanisation and industrialisation. A statistical study of soil lead for England and Wales has shown that in surface soils (0-15cm) lead ranges between 50 and 106mg/kg with a geometric mean of 42mg/kg (Davies, 1983). The distribution of lead in 5000 agricultural soils in England and Wales is shown by Archer and Hodgson (1987, Figure 2). It is of interest that lead values for over 3,000 surface soils from cropland in the US were lower than those in Britain, with a median concentration of only 11mg/kg (Holmgren et al, 1983). The reasons for this are uncertain but may reflect (a) differences in bedrock composition, (b) widespread anthropogenic emissions from UK lead mining and smelting over several hundred years to the early 20th century and (c) less dense urban development over the large agricultural areas of North America.

The result of long term contamination from atmospheric and other inputs has resulted in the accumulation of lead in surface soil horizons compared with lower depths. In normal agricultural soils an enhancement factor in the surface ranging
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from 1.2 to 2.0 is common, while in locations affected by historical mining and smelting, values have been found to range between 4 and 20 (Colbourne and Thornton, 1978).

The behaviour and pathways of lead, and its availability to living organisms, are discussed in the later sections (6.3, 6.4, 6.5) of this chapter.

6.1.2 HYDROSPHERE

Lead is a natural, usually very minor, constituent of surface and ground waters. In general, lead decreases in concentration from rainwater (generally acidic; about 20µg/l lead) to freshwater (generally neutral; about 5µg/l lead) to sea water (alkaline; below 1µg/l lead). In the course of this decreasing concentration gradient, lead is removed to bottom sediments, which provide a long-term sink in which the metal is stored in a relatively unavailable form.

Natural waters can dissolve minerals from soils and rocks. Concentrations of lead in river waters are dependent on local inputs as residence times are short. However, unlike some other elements, such as cadmium and arsenic, most lead compounds have low solubilities in water, and high concentrations of lead in water are rare. However, they can occur in acidic drainage from mine wastes (Alloway and Ayres, 1997); in areas of lead mineralisation, rivers can contain as much as ten times more lead than in unmineralised areas, in which background levels of lead tend to be well below 10µg/l (the WHO recommended limit for drinking water).

6.1.3 ATMOSPHERE

Dusts and vapours of metals can enter the air from natural as well as man made processes. It has been estimated that global natural emissions of lead to the atmosphere are in the range of 18.6 to 29.5 million kg per year. Out of this, 60-85% is believed to be windblown material, 5-10% from vegetation, and the remainder from volcanoes, sea spray and meteorites (Nriagu, 1978; Salamons, 1986, cited in Thornton, 1995). These amounts are small compared to the historical anthropogenic flux of lead in the atmosphere, but are increasing proportionately as the use of leaded petrol is discontinued.

Sensitive modern instruments allow detection of trace levels of lead in air. Levels at the South Pole, where anthropogenic influence is very small, are quoted as 0.63ng/m³ air (1ng is one billionth of a gram). For comparison, measurements of lead in air in Europe range from 55-340ng/m³. Near volcanoes, levels of 28-1200ng/m³ are quoted (Bowen, 1979, cited in Alloway and Ayres, 1997). Historical evidence in the northern hemisphere is provided by studies of lead in the profile of Greenland ice-sheet, showing maximum lead deposition in the 1960s, followed by a sharp fall in the 1980s and 1990s.
This fall reflects the large decrease over this period of atmospheric lead loads (Boulton, 1998).

6.2 **ANTHROPOGENIC SOURCES OF LEAD:** from mining, metal processing, manufacture, use and disposal of lead-containing products, and sources of lead not connected with the metals industry

6.2.1 **PRODUCTION OF LEAD**

6.2.1.1 **Mining operations**
Mining involves extracting minerals from the ground, breaking or grinding them down to a suitable size for further processing, and separating the mineral of interest from other material. (Separation may involve treatment with other substances which have their own impacts.)

*Emissions of lead to air* - generated from windblown dusts, loaded with ore particles from handling and storage. These particles are large and are deposited in the near vicinity of the operation site. Modern after-operation care includes overlaying tailing dumps with uncontaminated soils to prevent windblown dust generation.

*Emissions of lead to land* - from ore tailings, i.e. the material discarded, but which will still contain a small proportion of ore. Some tailings from old mines had very high concentrations of lead, and have been suitable for profitable extraction by more efficient modern methods (Alloway and Ayres, 1997). These tailings are one major source of lead disposal to land, but present a highly localised source of contamination. Total global inputs in this category were estimated in 1983 at 130,000-390,000t per year, out of total global emissions to soils of 808,000 - 1,893,000t per year (Nriagu and Pacyna, 1988).

*Emissions of lead to water* - discharge of waste water from ore recovery and treatment, releases from tailings, where the sulphides oxidise and the acidic drainage waters dissolve lead. Thus old mine workings continue to be an important source of lead contamination in the environment today.

Estimates of global lead emissions to air, land and water, are given in Tables 6.1 - 6.4 but represent data for the year 1983, are based on a number of assumptions and are difficult to validate. Huge reductions have occurred in the intervening years due to improved environmental controls and changing patterns of use (eg lead in gasoline has been phased out in many countries). For example, more recent data for Europe estimate that the airborne emission levels of lead would drop from 40,000t in 1990 to an estimated 15,000t in 2010 after the
implementation of the UNECE Heavy Metals Protocol (TNO Report, January 1998).

6.2.1.2 Smelting operations
Details of smelting operations have been described in Chapter 4. Old smelting wastes can include slags (non-metallic solid material) with high metal contents. Historical smelting in uncontrolled conditions has resulted in considerable quantities of lead being lost as vapour, which would have condensed onto dust particles to be deposited on to soil and water. This has caused local contamination of land around historical smelting operations (Maskall et al 1995, 1996). Windblown dust can also be transported considerable distances as described later (in section 6.4.1).

While vehicles using leaded petrol continued to be the major source of lead to the atmosphere in the 1980s (Table 6.2), production of lead, copper-nickel, and zinc-cadmium also comprise significant emission sources. Nriagu and Pacyna (1988) estimated that total global emissions to atmosphere from smelting and refining of these metals in 1983 totalled between 28,270t and 64,800t (Table 6.1). The total emissions to atmosphere from non-mobile sources were estimated at 40,670t and 127,970t. More recent estimates of lead emissions to the atmosphere from primary and secondary lead smelters in the EU indicate a reduction from 7278 tonnes in 1975 to 4058 tonnes in 1985 with projections of 2186 tonnes in 2000 and 1640 tonnes in 2010 (Pacyna, 1996).

As a result of improved practice and legislation, emissions from smelters in the Western World are now much reduced. This development is still ongoing. BAT-technologies for smelting of primary lead achieve emission levels to air from 40g/t of lead and for secondary materials from <10g/t of lead produced (Behrendt and Steil 1997). Taking into account such emission status for the worldwide production of lead, emissions from this source could be limited to 200 t/year.

However, even smelters using BAT-technologies may be significant sources of atmospheric lead in the immediate vicinity of the plant caused mainly by contamination from older processing methods. This subject is covered in more detail in Chapter 8.

6.2.1.3 Refining and other processing
Any process which involves heating lead to above 500°C will potentially release lead fume, though this temperature is rarely exceeded in lead processing. The installation of fume and dust collection systems has markedly reduced this source of emission to the atmosphere.

6.2.1.4 Manufacture of lead and lead-containing products
There is the potential for emissions from any production processes involving lead or its compounds. However responsible action by the industry has attempted
to minimize such releases. The leaded glass industry may be taken as an example. Lead oxide is relatively volatile at the high temperatures required to melt the glass, and some small emissions can occur. However, the use of air filtration equipment reduces emissions to minimal levels.

6.2.2 USES OF LEAD

Some uses of lead and its compounds can result in some contamination of the environment, though the degree of this will depend upon the nature of the use. However, in many applications, lead products remain intact during use, and losses are minimal. Inputs to the environment from disposal of lead containing wastes are much more significant, and are discussed in the following section. Estimated emissions resulting from use and disposal of lead containing items are given in Table 6.2.

6.2.2.1 Lead metal

Batteries
The lead component of vehicle batteries is enclosed within a plastic container and potential for contamination of the environment during use is therefore negligible.

Lead sheet and terne plate: roofing, flashings, weatherproofings
Lead is one of the most durable materials which can be used for these purposes. However, it has been shown that very small amounts of lead can dissolve in rainwater or be abraded during the lifetime of the roof. An approximate corrosion rate of 5g per m² of exposed area per year has been used in a Life Cycle Analysis performed in the Netherlands: the authors consider this figure may be above the actual rate, as it is based on measurements taken some time ago (Roorda and van der Ven, 1998).

Lead sheet, on exposure to air, rapidly forms a layer of oxide on its surface. Further reaction with carbon dioxide in air results in the formation of lead carbonate, which has an extremely low solubility and gives good protection from further attack. Leaded roofs in areas subject to high levels of sulphur dioxide (the main component of “acid rain”) have very good stability, because a superficial layer of lead sulphate can form, which has a very low solubility in both water and dilute sulphuric acid.

If the design of a roof allows condensation to occur underneath, this can result in corrosion. The condensed water is very pure, having not been exposed to atmospheric carbon dioxide, and a protective patina of lead carbonate does not form on the metal surface - thus any attack on the lead tends to continue. This can be much more serious if the condensate passes over timbers, as it can dissolve chemicals from the wood which can further attack the lead. Good building design
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prevents such condensation occurring, and this is an important feature in modern, well insulated buildings (Blaskett and Boxall, 1990). Further potential for accelerated lead loss from roofing materials may result from lichens on tiled roofs. Water, in contact with lichens, can contain organic acids, which can dissolve lead from guttering etc. (Blaskett and Boxall, 1990).

The combined use of lead and aluminium in roofing materials is not recommended when materials are exposed to a marine environment. Here corrosion of lead has been noted which in turn has caused accelerated corrosion of aluminium (Blaskett and Boxall, 1990).

The use of lead sheeting within buildings, for example for soundproofing or radiation shielding, is not expected to release any lead.

Lead piping
The main sources of lead in drinking water are lead service pipes and household plumbing. Other sources include lead-tin solder and brass fittings. Lead from pipes can slowly dissolve when exposed to some fresh waters, though corrosion rates are usually low. The solubility of lead from pipes is dependant upon the acidity of the water, temperature and residence time; acidic, soft water is generally more plumbosolvent.

In hard waters (i.e. waters containing dissolved lime compounds - more prevalent where water supply is from groundwater) some slow corrosion can occur initially, but a layer of scale quickly forms on the inside of pipes, protecting the lead from further attack. Soft water does not behave in this way, and slow corrosion can occur and continue. Waters containing carbon dioxide, or small amounts of organic acids, cause increased attack (Blaskett and Boxall, 1990). This is particularly relevant in areas supplied with surface waters, which may contain traces of organic matter.

Water from lead piping can contribute to both human intake of lead and to inputs into the environment, via the sewage system. Health concerns together with the introduction of copper pipes, which are cheaper and easier to install, have resulted in the phasing out of lead piping. No new lead pipes have been installed in most countries for over 30 years, but a large number of old lead pipes are still in service. A recent report of the Select Committee of the UK House of Lords on the European Community (1996) concludes that there is no doubt that there are still serious health risks from lead in drinking water particularly to children, infants and foetuses, and that the minimization of lead exposure from drinking water should be an ideal policy objective.

Until recently, the World Health Organisation has recommended that drinking water should contain no more than 50µg of lead per litre, though a provisional figure of 10µg/l has now been agreed (WHO, 1993). Proposed EC legislation to reduce the lead standard for drinking water from 50µg/l down to 10µg/l may well provide difficulties of compliance in many countries within the European
Community. The responsibility for removing lead pipes within the home continues to rest with the householder in the UK.

Nriagu and Pacyna’s 1983 estimates of total global emissions of lead into aquatic ecosystems, found that atmospheric fallout was the dominant contributor. Out of direct anthropogenic inputs to water (not counting atmospheric fallout), domestic wastewater was estimated to contribute between 1,500 and 12,000 tonnes per year, approximately 15% of total direct inputs to water. Dumping of sewage sludge adds a further 2,900 - 16,000 tonnes per year, approximately 30% of direct anthropogenic inputs (Nriagu and Pacyna, 1988). Lead dissolved from lead pipes will contribute to these figures. Nowadays cleaning of community waste water is common practice. Dumping of sewage sludge to aquatic systems has been phased out. More recent estimates (TNO, 1997) show that airborne sources and input to water have fallen considerably since this earlier work.

There is also the potential for lead pipes to slowly corrode in soil, adding to the environmental burden of lead, though this will be very localized. Such corrosion rates again are very low, as evidenced by their long life. Tests performed over periods of 10-11 years in a range of different British soils, showed corrosion rates in most soils ranged from below 2.5 to 10µm per year, with well-drained sandy soils, chalk and moist normal clay showing the lowest corrosion rates. Much higher rates of 150-170µm per year for pure lead, and 80-520µm per year for a lead-tellurium alloy, were found in a moist acid clay, and even greater rates in wet acid peat. Corrosion rates remained constant or slightly increased with time (Gilbert, 1946, cited in Blaskett and Boxall, 1990). Any losses of lead due to corrosion tend to travel only short distances through the soil, being rapidly bound to soil particles.

**Lead cable sheathing**

There is the potential for very small amounts of lead to dissolve during service. The amount will strongly depend upon the exact composition of the water or the nature of the material in which the cable is buried.

The main application of leaded cable sheaths is along the sea bed. Corrosion rates of lead in seawater are low. Tests conducted in harbours in different parts of the world showed losses of 2 to 15µm per year. General corrosion rates of lead in a range of waters, including seawater, have been reported to be between 2 and 20µm/year (Blaskett and Boxall, 1990). However, most lead-sheathed cables have outer layers which isolate them from the environment and preclude any possibility of corrosion.

There have been reports of occasional failure of lead cable sheaths set in soil, which has become waterlogged with strongly alkaline solution from seepage from incompletely cured concrete. Laying the cables in a bed of sand or gravel, to ensure good drainage and allow air to penetrate, can combat this (Blaskett and Boxall, 1990).
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**Lead weights**
Lead weights used as wheel balances, and other uses out of water, are not expected to release more than a minimal amount of lead unless subject to regular abrasion. An analysis of the environmental effects of lead containing vehicle components, using a Life-Cycle Inventory, calculated that each set of lead wheel balances, which has an exposed surface area of approximately 10cm², will lose approximately 0.09g of lead over a lifetime of 12 years (using a corrosion rate of 7.3g/m² per year). This corrosion is reduced by using plastic coated weights now available on the market.

Weights used for fishing, yacht keels and other underwater applications, will very slowly corrode, though weight loss is only estimated to be of the order of 2 to 25 mg per cm² (the same as 20-250g per m²) of exposed area per year. This assumes a corrosion rate in the range of 2 to 20µm per year (Blaskett and Boxall, 1990).

It is reported that lead weights for commercial fishing nets need to be replaced regularly, perhaps as frequently as every 6 months (Danish Ministry of the Environment and Energy, 1998). Weight loss in such a situation would not only be from corrosion, but abrasion on the sea bed. Such abraded lead would initially fall to the sea bed, and will slowly dissolve, and most will eventually become incorporated into marine sediments.

**Lead shot**
Use of lead shot for hunting and fishing can result in significant localized inputs to soils (Alloway and Ayres, 1997) and contribute to inputs to surface waters (Roorda and van der Ven, 1999), ultimately adding to the lead burden in the sediments. Waterfowl are particularly susceptible, as they can dredge up shot from the mud at the bottom of ponds, and suffer acute lead poisoning (Clarke, et al, 1981), as described in Chapter 7.

**Lead alloys: solder, leaded steels and bronzes**
Minimal loss during use is expected in most cases, though inputs to the environment from disposal of these articles can occur. In the case of lead solders used on pipework, some lead dissolution can occur which would contribute to the lead content of the water, though the inputs from solders are tiny compared to dissolution from the whole of a leaded pipe. However, the use of leaded solders in pipework for potable water has been phased out. Additionally, some evaporation of lead may occur during application of solder, though this is generally minimal because the temperature remains well below 500°C. Exposure in the general community and occupational exposure are discussed in Chapter 7.

**6.2.2.2 Compounds of lead**

**Leaded glasses, and ceramics coated with leaded glazes**
On the whole, these articles remain inert during use. However, very small
amounts of lead can leach out of lead crystal vessels and lead-glazed ceramic ware during use, in particular on exposure to organic acids. Leaded glass and ceramic tableware are subject to standard tests to ensure safe leaching rates from the articles, using a standard solution of 4% acetic acid (which is a similar strength to vinegar). This has potential impacts for human health rather than the environment, and is discussed in Chapter 7.

**PVC stabilised with lead**
Rates of lead leaching from water pipes rapidly fall to a very low value. Information from the European Council of Vinyl Manufacturers suggests that drinking water supplied in lead stabilised PVC pipes falls within the World Health Organisation’s recommended level of 10µg/l lead. Thus, this is a potentially small contribution to lead inputs into the sewage system.

**Leaded petrol**
Until the 1990s, lead from mobile sources, i.e. emissions from vehicles running on leaded fuel, represented the biggest source of emissions, and dwarfed all others. Vehicle emissions increase lead levels in the surrounding air, and lead compounds adhere to dust particles, which settle and increase lead contents of dusts and soils.

Nriagu and Pacyna estimated that in 1983, mobile sources world-wide contributed 248,000 tonnes of lead to the atmosphere. This compares with total estimated emissions to atmosphere, from all sources, of between 288,700t and 376,000t (Nriagu and Pacyna, 1988). Total global use had been reduced to 40,000t in 1997 and is still declining.

Emissions are falling as permitted lead contents of petrol have been lowered, and unleaded petrol has replaced or is replacing leaded fuel in many countries. Projected lead emission from road transport in Western Europe for the year 2010 is 3000t (TNO, 1997). In the USA and in Europe, leaded petrol has already been phased out. However, in other parts of the world, particularly in developing countries, leaded petrol is still in common use.

### 6.2.3 END-OF-LIFE AND DISPOSAL OF LEAD AND LEAD-CONTAINING PRODUCTS

- **Directly dispersive applications**, including petrol and paints.
- **Applications in which recovery is difficult or unfeasible**: leaded glass, PVC additives, alloying additions and small lead containing items, such as lead shot.
- **Recyclable applications of lead**: mainly batteries, and including constructional uses of lead, cable sheathing and many other metallic applications.
It should be noted that these categories are not absolute. For example, some recovery of lead from steel and other lead-containing metals and components does occur (by sending the lead trapped in dust cleaning systems to lead smelters), and recycling of leaded glass, or recovery of its lead content, is conducted by some plants. On the other hand, not all metal from recyclable applications is currently recovered: for example, some cable sheaths and shot are left in the environment after use. (Estimated global emissions of lead resulting from use and disposal of lead containing products are given in Table 6.3."

6.2.3.1 Directly dispersive applications: petrol, paints

The use of these lead-containing products results in the dispersion of lead in the environment, with virtually no realistic possibility of recovery. For example, compounds of lead which are added to petrol are emitted from vehicle exhausts, and widely dispersed in the environment (as described in sections 6.2.2.2 and 6.4). However, this use is declining.

The use of lead in paints has largely been phased out, following technical improvements and concerns about risks to human health. However, many buildings have in the past been painted with lead-based paints, and this paint is still in place, either in a deteriorating condition, or covered by fresh paint. When old paint is sanded down prior to repainting, or flakes off, this greatly adds to lead levels in household dusts and garden soils. Burning of painted wood (in garden bonfires etc.) will produce smoke and ash rich in lead compounds, which will also add to lead levels in soil and air. Some paints used to contain lead-based drying agents. However, these have now been phased out.

A study of lead inputs into the environment in Denmark in 1994 found that releases of lead from red lead, paints and other compounds, are now very minor, contributing less than 1% of total anthropogenic lead inputs into the environment (Danish Ministry of the Environment and Energy, 1998). However, elevated lead levels from previous paint use can persist in soils for a very long time. Indeed the half-life of lead in soil (the time needed for its concentration to fall to half of its initial level) has been estimated at several hundred years (Alloway and Ayres, 1997). Analysis of lead levels in household dusts and garden soils in the United Kingdom, found that urban soils have higher lead levels than rural, and that garden soils and indoor dusts in London - a large city which has been populated since Roman times - had much higher levels of lead than the urban average (Thornton et al, 1994). This is believed to be a result of historic uses of lead, of which leaded paint was a contributor.

6.2.3.2 Items remaining in-situ after use: lead shot, weights, cable sheathing

Significant amounts of these products remain in place after use and can have important environmental impacts. For example, soils in heavily used firing
ranges can accumulate several percent of lead, and also high concentrations of antimony (Alloway and Ayres, 1997). A life cycle analysis study of lead sheet in the Netherlands quoted estimates that hunting and fishing were the most important sources of lead inputs direct to surface waters and sediments (not including via the sewage system) adding an estimated 35 tonnes per year, over half of the total lead emitted directly to water (64 tonnes per year). Total inputs to water from all sources, including the sewage system, were estimated at 119 tonnes per year (Roorda and van der Ven, 1998).

In France, an estimated 6,500t of lead is used annually for hunting, which becomes dispersed in the countryside in uncultivated and in agricultural areas. This is now a much more important dispersed source of lead than petrol (Académie des Sciences, 1998). To protect waterfowl, the use of lead shot for hunting was banned over English wetlands from September 1999, under provisions made under the Environmental Protection Act 1990. Several other countries have made similar provisions.

The previously mentioned study of lead uses and environmental effects in Denmark concluded that, in 1994, abandoned cables were the major source of lead inputs into soil (not including landfill), estimated at between 400 and 2000t per year. However, as these cables remain intact for long periods of time and the lead is in any case encapsulated under other materials, this source is unlikely to be environmentally significant. Lead shot and other ammunition contributed a further 195-270t per year; these categories together account for approximately 95% of lead inputs to soil. Almost all lead inputs to water are from fishing tackle (quoted as 105-275t per year) and abandoned cables (50-300t per year); inputs from other sources total an estimated 6-13t per year (Danish Ministry of the Environment and Energy, 1998). Much of this lead will remain inert for a long time, but will slowly weather and, in due course, add to lead levels in water, soils or sediments (see section 6.4 for descriptions of movements and fates of lead in the environment). These findings do not necessarily represent the situation in other countries, which have different patterns of industry and lead usage.

Not all these items are left in place after use; some are recovered, such as lead shot from some firing ranges, particularly in the Netherlands where lead is recycled from some 20,000 tonnes per year of contaminated soil (cited in Danish Ministry of the Environment and Energy, 1998). Lead cable sheaths are also reclaimed when economically feasible. Abandoned fishing weights are often the result of accidental loss.

### 6.2.3.3 Items disposed of in the normal waste stream

These include: small miscellaneous items containing lead, which are not generally recovered; some solder; leaded glass (from TV and computer screens, and broken lead crystal, optical and electrical glass); ceramics; and leaded PVC. Some items which are normally recycled, such as batteries, may occasionally
LEAD: THE FACTS

find their way into the waste stream, particularly during times when the price of lead is low (refer to Chapter 5 Recycling of Lead, for a description of the recyclability of various lead-containing products, and how well this works in practice).

The normal disposal routes are to landfill or by incineration. The fate and any impacts of the lead will depend upon the disposal route taken, and the original form of the lead.

**Disposal of lead-containing wastes to landfill**

The behaviour of lead compounds in landfills will depend upon:
- the form which it is in (e.g. metal, ash, in glass, etc.)
- the nature of the material which surrounds it
- the construction of the landfill.

Lead as a component in leaded glasses and PVC is relatively stable, and migration is expected to be extremely slow. Lead in metal or alloy form will slowly weather and form compounds, which may or may not be soluble in water. Some of the lead compounds from incinerator ash are chemically active and water soluble and may migrate, both within the landfill and into underlying geological strata if leakages occur.

In this respect, the most important characteristic of the landfill is its pH (measure of acidity or alkalinity), because lead compounds are in general more mobile in acidic conditions. Also, the type of landfill is very important. In some countries, only relatively inert mineral material is placed in landfill. Others have a policy of landfilling mixed waste. Organic components which slowly break down over a number of decades produce acids which in turn can dissolve lead, and thus may favour leaching and migration.

Old landfills consisted of little more than large holes in the ground, produced by quarrying, and filled with refuse. The paradigm in some countries up until the 1980s of “dilute and disperse” was that landfills would gradually leak their contents into surrounding soil and water, but in concentrations which would be too low to cause concern. This school of thought has been abandoned as it has become clear that leachate from uncontrolled landfills can irreversibly contaminate groundwater, which is a very valuable water resource in some areas. (Not all old landfills release harmful contents into surrounding water: for example, many landfill sites are in areas of thick clay which acts as a good natural barrier to water movement.) Attempts have been made to improve the safety of some old landfill sites by encapsulating the area with a protective material, or by covering the surface and pumping out the leachate which is then handled in a wastewater treatment works.

In contrast, modern landfills are usually treated as large engineering projects and incorporate state-of-the art technology. They are generally lined with a
Sources, Levels and Movements of Lead in the Environment

Waterproof liner (such as thick plastic sheeting, and/or a clay liner) and leachate (the liquid which drains down from the landfill) is pumped out, to limit its penetration into surrounding soil. Aftercare is now a legal requirement, including the maintenance of the cap to prevent water ingress.

Disposal of lead-containing wastes to landfill would seem to be the best option, when recycling is not practical. However, over the long term, landfill liners can fracture and if pumping is not maintained, leachate (potentially containing toxic metals and organic substances) can migrate through surrounding soil with the potential to contaminate soil and underground water resources.

Leachates from 15 landfills in the UK had concentrations of lead below 50-220µg/l (Robinson et al (1982) and Lisk (1991), cited in Alloway and Ayres, 1997). Concentrations of lead and other substances in leachates have also been found to vary with the age of landfill: “young” - 50-920µg/l; “medium” - 40-80µg/l; “old” - 30-120µg/l (Lisk, 1991, cited in Alloway and Ayres, 1997). Leaching of metals can occur during all stages, but is greater in newer landfills, when there are large amounts of organic acids present from decomposing organic material (Williams, 1998). Longterm monitoring is now required in all current sites in the EU.

However, a number of studies carried out on modern landfill leachates in several countries found that lead leachate levels were well below safe limits (AWD Technologies, 1990). One study even found that leachate levels were so low that they met the drinking water standard for lead (NUS Corporation, 1990). In the absence of evidence to the contrary, it must be assumed that waste products disposed of in controlled landfills do not represent a significant source of stress on the environment and, providing they are correctly managed, will not in the future either.

Landfilling is the disposal method currently used for 70% of the municipal solid waste in the EU (Alloway and Ayres, 1997). However, many countries are aiming to reduce the proportion of waste disposed of in this way, and to use more sustainable alternatives, in order to reduce volumes of waste, attempt to gain some useful product from the waste, and reduce some of the long term liabilities of landfilling (such as production of flammable landfill gas, and the possibility of long term leaching). Alternatives include incineration of combustible waste, with recovery of heat and/or electricity, and composting or other biological breakdown of organic matter.

Disposal of lead-containing wastes in incinerators

A number of countries in Europe now incinerate much of their municipal solid waste. This has the advantage of a huge reduction in the volume of waste (very important in countries such as Denmark and Austria, which simply do not have the space for landfill) and it is possible to generate electricity from such
incinerators, thus making a small reduction in the need for fossil fuels. The ash from the incinerator is landfilled, or used for roads etc. It is biologically inert (so does not give problems of methane generation, unlike conventional landfills) but can be chemically active because of its high mineral content, and the form which the metals are in.

Incineration, under stringently controlled conditions, is the recommended method of dealing with certain wastes, particularly those contaminated with some organic substances (such as PCBs), which can be destroyed by incineration at high temperature. Incineration with energy recovery is the preferred disposal route for the “fluff” fraction (non metallic fraction, consisting of shredded seats, plastic interior parts, etc) from old vehicles (EU Directive 94/67), because of the high loading of organic compounds. However, this fraction (in total 200-250kg per vehicle) contains up to 0.5kg of lead per vehicle (contained within the plastic materials and coatings).

The presence of lead (and other metals, particularly cadmium and mercury) in waste streams which are destined for incineration, presents a much more severe problem than in waste directly disposed of in landfill. The chemical form of the lead is very important. Leaded glasses and glazes are unlikely to be greatly affected by incineration, as they are fired at higher temperatures, for longer durations, during manufacture (J. Cope, personal communication). However, lead present in metallic form or as other compounds, such as additives in PVC, is much more reactive. There is always the potential for lead, and some of its compounds formed at the high temperatures in the incinerator (particularly lead oxide and lead chloride) to escape as vapour and dust from the stack. In a well-run incinerator this should not occur, as gas cleaning systems should trap the metallic vapours and dusts, together with other undesirable combustion products to a level of <0.5 mg/m³ as the sum of Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V (see EU directive 1142/99).

Incinerator ash must then be disposed of in a landfill. This can be rich in metals and residues from acidic gases. Some incinerator wastes are in the form of slag which can be used as a construction material for roadways etc. under certain conditions. However, other wastes derived from incinerators may contain chemically active, water soluble forms of lead, which have the potential to migrate and be taken up by biota. In Belgium, this ash has to be solidified, if lead solubility exceeds existing standards, before placing in landfill, thus considerably reducing the solubility of lead.

The majority of incinerator output in Denmark is recovered. In the case of the slag or bottom ash fragments, more than 90 percent is utilised in such applications as granular sub-base for car parks, bicycle paths and paving for roads. Certain residues from waste incineration can contain high concentrations of lead and other heavy metals. However, these materials represent only a small fraction of total incinerator output and are routinely disposed of in managed
waste sites without causing any harm to the environment (Chandler, 1997) (The International Ash Working Group, 1995).

**Lead in compost**

In some countries (particularly Portugal, Spain, Denmark, Belgium, Italy and Germany), a significant amount of organic waste is composted (or broken down by anaerobic digestion, allowing collection of methane gas). Advantages of this practice are reduced landfill space occupied, reduced long term liabilities of mixed landfills (in relation to organic compounds in leachate, and flammable landfill gas generation) and, finally, an end product which can usefully be applied to gardens and agricultural land.

In Denmark, improved sorting procedures (sorting at source) have reduced levels of lead in compost to around 30mg/kg TDS (total dried solids), well within Agency for the Protection of the Environment limit levels (120mg/kg TDS for agricultural land, and 60mg/kg TDS for garden use). In contrast, lead levels in composts made in Sweden and Norway, where mechanical sorting is standard practice, are reported to frequently exceed 300mg/kg TDS. The use of source-based sorting, and monitoring of compost lead (and other metals) content, is reported to cost the Danish public 2-10 million Danish Krøner per year (Danish Ministry of the Environment, 1998).

Typical values for concentrations of lead in compost produced in Germany have been reported as: biowaste compost 84-260mg/kg (dm); bio-waste compost with paper 98mg/kg; green material compost 50-129mg/kg; compost from household waste 300-500mg/kg; general compost 50-90mg/kg (KTBL Darmstadt, 1995).

**6.2.3.4 Losses from recycling of lead and lead-containing products**

Recycling is by far the best end-of-life option for most lead products. Theoretically, the lead used in applications which are easily recyclable should continue to circulate within the industry, rather than require storage or disposal, which could possibly find their way into the environment. However, some small losses of lead occur during part of the recycling process. Most of the loss is emission to air, and some very small emissions are made to water.

An industry based assessment of end-of-life analysis of lead in cars, based on “state-of-the-art” processing technologies, concluded that the following emissions occurred:

**Battery**

During the 12 year lifetime of an average car, two batteries are recovered for scrap, and a further battery is recovered from the dismantled car. During battery recycling the following emissions will occur: to air - 15g lead per tonne of lead produced (0.015% loss); to water - 1g lead per tonne of lead produced (0.001%
loss). So recycling of three 10 kg batteries, plus 1 kg of wheel balance weights, will result in 0.47g emission to air, and 0.03g emission to water.

Assuming equally high standards in all lead smelting factories (which is unlikely to be the case), this would suggest that total emissions from production of lead from scrap in Western Europe (at total production of 961,000t in 1998) are 15t to air, and 1t to water.

Emissions to soil have not been calculated. However, some losses occur from batteries resting on the ground at scrap yards – indeed, soils at scrap yards often contain high concentrations of metals. The study of lead in the environment by the Danish Ministry of the Environment (1998), concluded that between 7 and 26 tonnes of lead reached the soil by this route in 1994.

**Non-ferrous fraction**

Besides the battery, each vehicle contains approximately 75kg of non-ferrous materials, which are processed to recover approximately 60kg aluminium, 10kg copper and 5kg zinc. Total emissions from recovery of these three metals are estimated as 1.35g of lead to air, and 0.01g to water.

**Iron and steel production**

Iron and steel works which process leaded steel, are another source of lead emissions in the environment. Almost all the lead contained in steel evaporates in the furnace, and ends up in the flue dust, which is often recycled, leading to a recovery of some 2 kg of lead per vehicle. Nevertheless, the total weight of free machining steel components found in a typical European car is less than 30 g per vehicle. Using an emission factor of 200g per tonne of lead to air, emissions to air are calculated to be approximately 0.4g per vehicle. Input to water is estimated as 0.002g lead per vehicle.

**6.2.4 OTHER ANTHROPOGENIC SOURCES OF LEAD IN THE ENVIRONMENT**

**Disposal of sewage sludge**

In urban areas, most of the rainfall eventually reaches the sewage system, together with domestic and industrial waste waters. This water can be contaminated by lead from lead particles in the air, lead dust in the environment, from lead dissolved from lead pipes and corrosion of lead roofs etc., and industrial effluent. Some of this lead remains in solution, and is eventually discharged with the treated water fraction into the aqueous environment; however, most is contained in the sewage sludge. The practice of applying sewage sludge to agricultural land thus can, and sometimes does, cause elevated lead levels in soils. Control measures to regulate this include the setting of standards based on limiting the maximum concentration of lead (and certain
other metals) in sludge, and a maximum concentration of lead in the soil of 300mg/kg, above which sewage sludge cannot be applied, regardless of its lead content (EC Directive 86/278).

A study of the impact of lead sheet upon sewage sludge levels in the Netherlands, found that corrosion of this product was a major contributor to the sewage system, comprising about 75% of all inputs to sewer and 40% of inputs to surface water (almost all via the sewage system). However, water quality in most (90%) surface waters was within limit concentrations, and some (25%) met target concentrations. The report concluded that ecological damage caused by the metal was negligible, and compared favourably with other metals (Roorda and van der Ven, 1999). The concentration of lead in the sewage sludge was, on average, double the maximum level which would permit application to agricultural land and, as a result, sewage sludge in the Netherlands is usually incinerated or landfilled. The report did point out that other metals (cadmium, copper, mercury and zinc) also exceed the limit values by at least this factor, nickel on average exceeds its limit value by 25%, and only chromium and arsenic remained, on average, within the limit values. Thus, eliminating lead alone from the sludge would not make it fit for agricultural use. It must be noted that only average concentrations were given and there could be local variations in metal inputs to sewer (particularly if industrial sources are significant).

Coal combustion, oil combustion, wood burning and cement manufacture
Fossil fuels naturally contain traces of metals, which are released to the environment on combustion (Table 6.4).

Lead-containing pesticides
The historic use of lead arsenate as a pesticide in orchards is a minor source of lead in the environment (Alloway and Ayres, 1997).
### TABLE 6.1  Total World-wide Emissions of Lead from Metal Extraction and Manufacturing Processes

<table>
<thead>
<tr>
<th>Source</th>
<th>Emissions to atmosphere in 1983 (t/y)</th>
<th>Emissions to water (t/y)</th>
<th>Emissions to land (t/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mining</td>
<td>1,700 - 3,400</td>
<td>250 - 2,500</td>
<td>130,000 - 390,000</td>
</tr>
<tr>
<td>Pb production</td>
<td>11,700 - 31,200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-Ni production</td>
<td>11,050 - 22,100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn-Cd production</td>
<td>5,520 - 11,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>secondary non-ferrous production</td>
<td>90 - 1,440</td>
<td></td>
<td></td>
</tr>
<tr>
<td>total non-ferrous smelting and refining</td>
<td>28,360 - 66,240</td>
<td>1,000 - 6,000</td>
<td>195,000 - 390,000</td>
</tr>
<tr>
<td>iron and steel manufacturing</td>
<td>1,065 - 14,200</td>
<td>1,400 - 2,800</td>
<td></td>
</tr>
<tr>
<td>metals manufacturing processes</td>
<td></td>
<td>2,500 - 22,000</td>
<td>4,100 - 11,000</td>
</tr>
<tr>
<td>chemical manufacturing processes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pulp and paper manufacturing</td>
<td></td>
<td>10 - 900</td>
<td></td>
</tr>
<tr>
<td>petroleum products manufacturing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>31,125 - 83,840</td>
<td>5,560 - 37,320</td>
<td>329,100 - 791,000</td>
</tr>
</tbody>
</table>


### TABLE 6.2  Emissions from Use and Disposal of Lead-containing Products

<table>
<thead>
<tr>
<th>Source</th>
<th>Emissions to atmosphere in 1983 (t/y)</th>
<th>Emissions to water (t/y)</th>
<th>Emissions to land (t/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mobile sources</td>
<td>248,030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>wastage of commercial products</td>
<td></td>
<td></td>
<td>195,000 - 390,000</td>
</tr>
<tr>
<td>urban refuse</td>
<td>incineration of 1,400 - 2,800</td>
<td></td>
<td>18,000 - 62,000</td>
</tr>
<tr>
<td>municipal sewage sludge</td>
<td>incineration of 240 - 300</td>
<td>2,900 - 16,000</td>
<td>2,800 - 9,700</td>
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<tr>
<td>domestic waste water</td>
<td></td>
<td>1,500 - 12,000</td>
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</tr>
<tr>
<td>TOTAL</td>
<td>249,670 - 251,130</td>
<td>4,400 - 28,000</td>
<td>215,800 - 461,700</td>
</tr>
</tbody>
</table>

### SOURCES, LEVELS AND MOVEMENTS OF LEAD IN THE ENVIRONMENT

#### TABLE 6.3  Total World-wide Emissions of Lead from other sources

<table>
<thead>
<tr>
<th>Emissions to atmosphere in 1983 (t/y)</th>
<th>Emissions to water (t/y)</th>
<th>Emissions to land (t/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>coal combustion electricity generation</td>
<td>775 - 4,650</td>
<td></td>
</tr>
<tr>
<td>coal combustion - industry and domestic</td>
<td>990 - 9,900</td>
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</tr>
<tr>
<td>coal combustion - total</td>
<td>1,765 - 14,550</td>
<td>45,000 - 242,000</td>
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<tr>
<td>oil combustion - electricity generation</td>
<td>232 - 1,740</td>
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<tr>
<td>oil combustion - industry and domestic</td>
<td>716 - 2,150</td>
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<tr>
<td>wood combustion</td>
<td>1,200 - 3,000</td>
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</tr>
<tr>
<td>cement manufacture</td>
<td>18 - 14,240</td>
<td></td>
</tr>
<tr>
<td>steam electric</td>
<td>240 - 1,200</td>
<td></td>
</tr>
<tr>
<td>agricultural and food wastes</td>
<td></td>
<td>1,500 - 27,000</td>
</tr>
<tr>
<td>animal wastes, manure</td>
<td></td>
<td>3,200 - 20,000</td>
</tr>
<tr>
<td>logging and other wood wastes</td>
<td></td>
<td>6,600 - 8,200</td>
</tr>
<tr>
<td>miscellaneous organic waste including excreta</td>
<td>20 - 1,600</td>
<td></td>
</tr>
<tr>
<td>peat</td>
<td></td>
<td>450 - 2,600</td>
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<tr>
<td>fertiliser</td>
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<td>420 - 2,300</td>
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<tr>
<td>miscellaneous</td>
<td></td>
<td>3,900 - 5,100</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>7,886 - 41,054</strong></td>
<td><strong>240 - 1,200</strong></td>
</tr>
</tbody>
</table>


#### TABLE 6.4  Total World-wide Emissions of Lead from all sources

<table>
<thead>
<tr>
<th>Emissions to atmosphere in 1983 (t/y)</th>
<th>Emissions to water (t/y)</th>
<th>Emissions to land (t/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total from metals and mining industry</td>
<td>31,125 - 83,840</td>
<td>5,560 - 37,320</td>
</tr>
<tr>
<td>Total from use and disposal of lead</td>
<td>249,670 - 251,130</td>
<td>4,400 - 28,000</td>
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<tr>
<td>Total from other sources</td>
<td>7,886 - 41,854</td>
<td>240 - 1,200</td>
</tr>
<tr>
<td>Total</td>
<td>288,681 - 376,024</td>
<td>10,200 - 66,520</td>
</tr>
<tr>
<td>Atmospheric fallout</td>
<td>87,000 - 113,000</td>
<td>202,000 - 263,000</td>
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<tr>
<td><strong>TOTAL</strong></td>
<td><strong>288,681 - 376,024</strong></td>
<td><strong>97,200 - 179,520</strong></td>
</tr>
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</table>

### TABLE 6.5  Anthropogenic Emissions of Lead

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a) Figures for Belgium are for Flanders only, except 1995 where it includes Wallonia (EMEP Report- July 1999)
b) Emissions from petrol/gasoline are not included
e) Estimated figures
6.3 CHEMICAL SPECIATION OF LEAD

It is impossible to consider the presence of lead and its compounds in the environment and its potential toxicity to the ecosystem and to the human population without considering its chemical and mineral form, or species.

Lead exists in the environment in many different forms. In addition to naturally occurring minerals such as galena (lead sulphide, PbS) and lead metal (from sources already described), inputs into the environment can be in many other chemical forms.

Residues from lead mining tend to be in the form of the ore (largely PbS, possibly some PbSO$_4$ or PbCO$_3$), and emissions from smelting works would be expected to be a mixture of lead oxides, sulphates and metallic lead. These forms all have very low solubilities in water.

Lead emitted from other sources can be in other forms. Ash from incineration of waste or combustion of fossil fuel is likely to be in the form of any of the oxides of lead, depending on the combustion conditions; fly ash (from pollution control apparatus) in municipal solid waste incinerators can contain lead chloride, if significant amounts of chlorine are present in the waste (such as in PVC, salt, paper and organic matter). Other industries can emit lead in characteristic species. Lead compounds emitted from vehicle exhausts are generally as halogenated compounds (chlorides, bromides).

Exposure to the atmosphere, water, and other elements present in soil and water, act to weather the lead and its compounds. In general, lead is changed by natural processes from more soluble compounds such as lead chloride, to less soluble ones such as lead sulphate, carbonate and phosphate. Lead in contact with soil is largely adsorbed onto clay particles and organic matter and in these forms is only sparingly soluble. However, natural processes can also act to increase the solubility of lead. For example, changes in river conditions can result in sediments being stirred up and absorbed lead being re-dissolved; a decrease in pH (an increase in acidity) increases the solubility of most compounds of lead; metallic lead is not stable in the very long term and slowly corrodes, generally into soluble lead compounds, which later weather into largely insoluble salts and other phases. For example, examination of former smelting works in the UK found lead largely in the forms of PbO, PbSO$_4$ and PbCO$_3$ (Li and Thornton; cited in Thornton, 1995) whereas one would expect the lead to have originally been emitted as a mixture of lead oxides, metallic lead, and lead sulphate; at old mining sites in Britain most of the lead was in the form PbCO$_3$, and chemically adsorbed onto iron-manganese oxide particles (Thornton, 1995).

The halogenated compounds of lead (such as lead bromochloride) emitted from vehicles are highly soluble in water, and fairly rapidly react to more stable compounds such as lead sulphate.
Knowing the species of the lead is vital, not only to predict its mobility and bioavailability, but also in the assessment of risk to living organisms. In general, insoluble forms of lead cannot easily be absorbed by biota, whereas soluble forms are readily taken up. This is discussed in section 6.5.

6.4 NATURAL FLUXES, TRANSPORTATION AND FATES OF LEAD IN THE ENVIRONMENT, WITH REFERENCE TO MAJOR LEAD-CONTAINING PRODUCTS

6.4.1 TRANSPORT BY AIR

As already described, emissions to air from mobile sources dwarf all other sources put together, though such emissions have now been reduced and are in the process of being phased out in many Western countries, though this trend is not global. The other major sources of lead emissions are the production of lead, copper-nickel and zinc and cadmium; mining; combustion of wood and fossil fuels and refuse incineration are smaller, but significant sources.

The dispersion of lead in the atmosphere depends strongly upon the nature of the source, and thus the sizes and chemical forms of particles. Smaller particles remain airborne for longer, and thus travel much further, than larger ones. Particles larger than about 10mm generally settle out under gravity fairly rapidly and do not travel far. Smaller particles can stay in the air for 10-30 days before settling; in this time they can travel many thousands of kilometres and cross continents. Increased levels of lead and other metals measured in southern Norway, have been attributed to emissions from industrial areas in Europe (Alloway and Ayres, 1994.) Deposition can be induced by rainfall/snowfall etc (either by dissolving any lead which is in a soluble form, or by physically carrying particles down in raindrops). This is an important mechanism contributing to levels of lead in Arctic ice which reached a maximum in the 1960’s and have subsequently fallen, probably as a result of reductions in atmospheric emissions from gasoline additives (Boutron, 1998). Deposition can also be the result of particles settling out under gravity or impacting upon surfaces (Thornton, 1995).

Leaded particles emitted from petrol engines are very small, but quickly agglomerate to form larger ones. These particles have been found to remain in the air for up to 7 to 24 days, during which time they can travel long distances. However, the majority of lead from these sources is deposited within 30-100m of the road, and significant increases in lead levels in soils are not found further away (Davies and Thornton, 1989). Particles from fugitive emissions from industry are generally larger, and thus settle out within a short distance of source (Thornton, 1995).
Based on estimates made from 1983 data, deposition from the atmosphere was by far the largest contributor to inputs of lead to water (Nriagu and Pacyna, 1988) and was also a major source of input to land, being responsible for between 10% and 25% of the total (Nriagu and Pacyna, 1988). However, this situation has since changed significantly following the widespread reduction in the use of lead in gasoline.

Information on measured rates of lead deposition is limited. A recent study of deposition of lead (and 22 other elements) onto agricultural land in the UK, based on monitoring at 34 locations over a period of 3½ years to 1998, showed a range of 19.5 - 139.0 g/ha/y, median 43.3 g/ha/y and average 54.4 g/ha/y (Alloway et. al., personal communication).

6.4.2 TRANSPORT IN WATER

As noted above, the largest input of lead to water world-wide in 1983 was deposition from the atmosphere. Nriagu and Pacyna estimated world-wide inputs by this route were between 87,000 and 113,000t per year, compared to between 10,000 and 67,000t from all other sources put together (Nriagu and Pacyna, 1988). Much of this deposition would be on to the world’s oceans and would in due course be incorporated into the sediment.

The other main sources of lead inputs to water were manufacturing industry involving metals, smelting and refining of metals (including iron and steel), and sewage sludge and domestic waste water (Nriagu and Pacyna, 1988). Acid mine drainage can contain dissolved lead, and water from ore washing etc can contain lead-rich particles (Alloway and Ayres, 1997). In countries such as Denmark with little metallurgical industry, the inputs from dissolution of cable sheaths and fishing tackle have been reported to be the most important ones (Danish Ministry of the Environment, 1998).

Coastal waters can receive significant inputs of lead from industry, sewage and natural mineralisation of the watersheds, and lead concentrations in them can reflect these inputs. As a result, lead levels in harbours, estuaries and inland waters are usually higher than in open oceans (Fergusson, 1990) though of course there is large variation from place to place.

Lead can enter water as dissolved ions (Pb^{2+}) or as particles. In fast flowing rivers, even fairly large particles can be carried long distances, before being deposited on the bed of the watercourse, perhaps on entry to slow moving water in lakes or estuaries or deltas (Thornton, 1995). The long term route of lead is from rivers to estuaries to oceans. High levels of enrichment of lead and other metals in estuarine sediments have been noted (Forstner 1983). However, monitoring of dissolved metals in UK estuaries has shown maximum levels of lead to fall well below the Environmental Quality Standard of 25µg/l over the period 1992-95, with significant reductions in those with large industrial inputs over the 4 year period (DETR, 1998).
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Lead particles which fall into lakes are likely to sink to the bottom, and to become incorporated into the sediment. Particles falling directly into oceans can have long residence times, and may undergo physical and chemical changes. However, the long term sink for lead and its compounds is incorporation into sediments on the sea bed (Thornton, 1995).

Whatever the form the lead is in initially, it eventually reacts with other species in the water or sediments, and is converted into forms which are largely insoluble, such as adsorption onto clay minerals in bottom sediments (Alloway and Ayres, 1993) or, in anaerobic conditions, conversion to lead sulphide. Thus, natural processes tend to remove lead from solution and deposit it in sediments where its availability is very low (Thornton, 1995).

Sediments disturbed by dredging can have significant lead concentrations and would warrant further study (Académie des Sciences, 1998). It has been suggested that the lead could be mobilised by such dredging, by changes in ecosystems (Canadian Environmental Protection Board, 1999) or could be stirred up by water movements and creatures living on the bed, though these lead compounds are expected to settle again quickly, and in time to be overlain with deposited material (Danish Ministry of the Environment and Energy, 1998).

Lead inputs to waters in some countries are falling, following the banning of small lead weights for fishing because of the dangers these pose to waterfowl. It is difficult to predict long term trends of lead levels in seawater or sea bed sediments, and measurements are not available to quantify any trends. Estimated lead inputs (direct and riverine) to control waters around the UK continued to fall over the period 1990 to 1996 (DETR, 1998).

6.4.3 MOVEMENT IN SOIL

Soil constitutes a sink for lead which has a strong tendency to be adsorbed on to particles of clay or organic matter, and in this form is largely immobile and biologically inert. The half life of lead in soil (the time interval for its concentration to fall to half of its original value) is very long, estimated as 740 - 5900 years (Alloway and Ayres, 1997).

Sources of contamination of surface soil in urban areas are from petrol, old lead paint (particularly near houses, by deposition of flakes of old paint, and any bonfires where painted wood was burnt) and in mining and industrial areas, from tailings, emissions and wastes from metal extraction.

Unlike organic pollutants, which decompose with time, lead (and any other metal or non-metallic element) will never disappear. Its chemical form may change, particularly as the compounds binding them break down, or soil conditions change (Alloway and Ayres, 1997). This may increase lead mobilisation and removal to a different sink.
Very high levels of lead (up to 1% or more) in topsoils occur in some urban areas but usually very little migrates to lower horizons. For example, a survey of ca. 580 surface soils (0-15cm) in London, UK, showed a geometric mean lead content of 654µg/g (Culbard et al, 1988). Similarly, studies of lead migration in old lead smelting sites have found very little movement of lead. Even where surface soils and slags contained up to 10% lead, vertical penetration of lead through a sandy rock-soil matrix, during a period of over 200 years, was found to be no more than 70cm (Maskell and Thornton, 1993).

The mobility of lead depends upon many factors: the original form which the lead is in, the type of soil, soil pH (acidity) and moisture content of the soil, and water infiltration from rainfall or other drainage. As already described, in the long term lead weathers into mineral forms which have low solubilities in water, and is adsorbed on to clay particles, where it is generally insoluble.

Old lead shot is expected to fully corrode and some will pass into solution over 100-300 years (Jorgensen, 1987, cited by Davies, 1995); old lead sheathed cables, dug up after 70 years, were reported to show visible corrosion if buried in acid sandy soils, but those buried in boulder clay did not appear to be significantly affected (Danish Ministry of the Environment and Energy, 1998).

Corrosion tests upon lead specimens in soil (British Non-Ferrous Metals Technology Centre, cited in Blaskett and Boxall, 1990) show that after a period of 11 years, the worst cases of corrosion were to depths of 0.14 to 0.18mm wall thickness (in moist acid clay soil, and wet acid peat, respectively) and samples in other soils corroded much more slowly, from less than 0.005 to 0.01mm wall thickness. This would suggest that the time interval required to corrode through 0.5cm of shot, cable wall, etc., would be at least 2000 years - assuming linear reaction kinetics (not always the case: if the reaction rate is controlled by diffusion, the reaction will proceed more slowly with time) and no changes in conditions.

6.5 UPTAKE OF LEAD IN BIOTA / BIOACCUMULATION

As already stated in section 6.3, it is not possible to generalise the uptake of lead from the environment by living organisms. The chemical species in which the lead is present is an all-important factor: lead in some forms (such as lead dissolved in organic acids, as a food contaminant) is very easily absorbed; in other forms it appears to have no effect on biota. There are some examples of soils with very high lead contents causing no apparent effects on plants, animals, or humans, and it is believed to be because the lead is in an insoluble, unavailable form. For example, lead in soil in a mining village in Derbyshire, UK, present in concentrations exceeding 1%, was mostly in the form of the mineral pyromorphite (resulting from natural weathering), but local residents did not
show any significantly increased levels of lead in their blood - a standard test for lead exposure - compared to control populations (Thornton et al, 1994).

Unfortunately, there is no single standard test which can tell how much lead is “bioavailable”, though solubility in water and acid can be used as a guide. In general, plants will only take up minerals which are dissolved in soil water (soils generally have pH between 5 and 7.5), though some absorption of lead falling as atmospheric particulates on leaves can occur in some plants. Animals can directly ingest lead in soil, either in compound or metallic form, and some dissolving in the gut can be absorbed. (In some species, including humans, the stomach juices are strongly acidic and can dissolve many (though by no means all) compounds of lead which would not dissolve in water.) Animals can also absorb lead by inhalation, and possibly through the skin, e.g. from lead-based cosmetics (Alloway and Ayres, 1997), though these could alternatively be absorbed by hand-to-mouth activity (Healy et al, 1982, and Healy 1984, cited in Chaney et al, 1988). Thus, lead absorption varies considerably between different living species; even individuals of the same species can absorb lead to different extents. The importance of this for human exposure is discussed in Chapter 7.

Lead which accumulates in soil in metallic form, or as some compounds of lead, will slowly weather and disperse within the soil-plant system, and therefore a proportion of this will be potentially bioavailable (Alloway and Ayres, 1997). Soil can also be contaminated by dissolved (and therefore bioavailable) lead from contaminated surface water, sewage sludge, drainage from mine wastes (which is often very acidic) and in the long term, from leachate from landfill sites. Lead emissions from smelters and petrol engines are often in relatively bioavailable forms, though these will weather into less soluble, less available species.

Lead uptake by plants from soil is usually limited, because most of the lead in the soil binds to soil particles and is not available (Alloway and Ayres, 1997; Académie des Sciences, 1998; Thornton and Jones, 1984). There is however variation in uptake between plant species, including vegetable crops grown for home consumption. Studies have indicated that sludge application to soil increases metal content in plants in the order Zn>Cd>Ni>Cu>Pb = Hg = Cr (B. Hansen, University of Washington, 1997).

Plants growing in soils with high lead contents can also be contaminated with soil particles on their leaves etc., which can be ingested by animals which eat them (Thornton and Abrahams, 1983). A large proportion (up to 70% or more) of such lead on the leaves of food plants such as vegetables can be removed by careful washing (Thornton and Jones, 1984). This pathway to human exposure will be discussed in Chapter 7.

Animals can absorb lead which is dissolved in drinking water, present in contaminated plants and other foodstuffs and, in the case of grazing animals, direct ingestion of soil. Humans, in particular young children, also ingest soil and
dust which can contain fragments of leaded paint. This exposure route is discussed in greater detail in Chapter 7.

As already mentioned, stomach acids can dissolve some lead compounds which would remain insoluble in water. However, there is some evidence that lead ingested with soil, though it may dissolve in the strongly acidic conditions in the stomach, can be re-adsorbed onto the clay particles in the intestine (where the pH is much higher), and thus be rendered insoluble. Thus most ingested lead can pass through the gut without being absorbed. Ingestion of metallic lead has been shown to cause acute lead poisoning, sometimes fatal, in waterfowl which may ingest lead shot in areas affected by fishing and shooting. Factors influencing uptake of the individual include nutrition and other food eaten before or with the lead-contaminated feed; these factors are discussed in the following chapter.

A further factor which can influence the bioavailability of lead is the particle size. This is a critical factor for absorption by inhalation, as particles bigger than about 10µm are largely filtered out in the bronchial tract and do not penetrate deep into the lung: smaller ones which reach the alveoli will potentially remain there indefinitely, and may slowly dissolve into the bloodstream. Particle size can also have an important influence on uptake of ingested lead. Where lead is ingested in slightly soluble compounds, small particles were found to be much more bioavailable than larger ones, presumably because larger ones did not fully dissolve. A test involving feeding finely divided lead sulphide to human volunteers (who were fasting - this increases uptake) found the lead in this form was highly bioavailable (Rabinowitz et al, 1980, cited in Chaney et al, 1988). The conclusion was that larger particles of lead ore, dispersed by mining, grinding and smelting, would generally have low bioavailability, but grinding of these particles at home by shoes could produce a housedust containing fine particles of lead sulphide which are more bioavailable (Chaney et al, 1988).

Some aquatic organisms can bioaccumulate lead, i.e. concentrate lead to very high levels compared with their surroundings (Académie des Sciences, 1998). There is no evidence for biomagnification occurring through food chains (Académie des Sciences, 1998, and Alloway and Ayres, 1997), unlike mercury and some organic substances, including certain pesticides.
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