

# **LEAD**

the facts

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Prepared by  
IC Consultants Ltd  
London, UK

December 2001

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### **Acknowledgements**

The following persons are acknowledged for their help in preparing this book:  
George Kazantzis, Madeleine McMullen, Paul Docx, Thomas Keegan

ISBN: 0-9542496-0-7



Printed on 100% recycled paper

Typeset by RSB, St Johns, Woking, Surrey

Printed and bound in England by Ian Allan Printing Ltd, Hersham, Surrey KT12 4RG

# CONTENTS

<b>1 INTRODUCTION</b>	1
<b>2 PROPERTIES OF LEAD</b>	5
<b>2.1 Physical properties</b>	6
2.1.1 General properties	6
2.1.2 Density	6
2.1.3 Attenuation of X-rays and gamma radiation	6
2.1.4 Resistance to irradiation by thermal neutrons	7
2.1.5 Attenuation of sound	7
<b>2.2 Mechanical properties</b>	7
2.2.1 Ductility	8
2.2.2 Tensile strength	8
2.2.3 Creep behaviour	8
2.2.4 Fatigue	9
2.2.5 Final comment	9
<b>2.3 Chemical properties</b>	9
2.3.1 Extraction of lead from its ore	9
2.3.2 Corrosion of lead	10
<b>2.4 Properties of some compounds of lead</b>	12
<b>3 APPLICATIONS OF LEAD</b>	17
<b>3.1 Historical overview</b>	20
<b>3.2 Specific uses of lead metal</b>	20
3.2.1 Lead-acid batteries	20
3.2.2 General constructional uses of lead – sheet and pipe	24
3.2.3 Sheathing for electrical cable	28
3.2.4 Radiation shielding	29
3.2.5 Lead shot, weights and miscellaneous products	30

## CONTENTS

<b>3.3 Uses of alloys containing lead</b>	32
3.3.1 Tin-lead alloys	32
3.3.2 Leaded bronzes, steels and aluminium alloys	35
<b>3.4 Leaded glasses and ceramics</b>	37
3.4.1 Lead crystal and optical glass	37
3.4.2 Radiation shielding glass, cathode ray tubes, fluorescent tubes and electrical glass	38
3.4.3 Ceramic glazes and enamels	39
3.4.4 Electrical ceramics	40
<b>3.5 Leaded pigments and paints</b>	40
<b>3.6 PVC stabilisers</b>	42
<b>3.7 Petrol additives</b>	44
<b>4 LEAD INDUSTRY PROFILE</b>	47
<b>4.1 The technology of lead production</b>	50
4.1.1 Production of lead mineral from mines	50
4.1.2 Primary production	51
4.1.2.1 Production of metallic lead – smelting	51
4.1.2.2 Lead refining	54
4.1.3 Secondary production	56
4.1.3.1 Secondary smelting	56
4.1.3.2 Secondary refining	58
<b>4.2 Lead production, trade and consumption: current status and trends</b>	58
4.2.1 Lead production	58
4.2.1.1 Production from mines	58
4.2.1.2 Total production of refined lead	58
4.2.1.3 Secondary production	59
4.2.2 World trade in lead	61
4.2.2.1 Overview	61
4.2.2.2 Trade in lead ore	62
4.2.2.3 Trade in lead metal	62
4.2.2.4 Lead stocks	63
4.2.3 Lead consumption	64
4.2.3.1 Global consumption of lead	64
4.2.3.2 Lead consumption in Western Europe	64
4.2.3.3 Breakdown of end uses of lead	64
<b>4.3 Economic value of lead</b>	65
4.3.1 Lead production and transformation	65
4.3.2 Lead-consuming industries	65
<b>4.4 Employment in the lead and related industries</b>	65

<b>5 RECYCLING OF LEAD</b>	71
<b>5.1 Recycling processes</b>	73
<b>5.2 Recycling of major lead products</b>	73
5.2.1 Lead-acid batteries	73
5.2.2 Lead sheet, piping, cable sheathing	75
5.2.3 End-of-life vehicles	75
5.2.4 Electrical and electronic products	76
5.2.5 Cathode ray tubes	77
<b>5.3 National policies and collecting strategies</b>	77
<b>5.4 Future opportunities</b>	79
<b>6 SOURCES, LEVELS AND MOVEMENTS OF LEAD IN THE ENVIRONMENT</b>	81
<b>6.1 Natural occurrences and concentrations of lead</b>	84
6.1.1 Lithosphere / geosphere	84
6.1.2 Hydrosphere	86
6.1.3 Atmosphere	86
<b>6.2 Anthropogenic sources of lead</b>	87
6.2.1 Production of lead	87
6.2.1.1 Mining operations	87
6.2.1.2 Smelting operations	88
6.2.1.3 Refining and other processing	88
6.2.1.4 Manufacture of lead and lead-containing products	88
6.2.2 Uses of lead	89
6.2.2.1 Lead metal	89
6.2.2.2 Compounds of lead	92
6.2.3 End-of-life and disposal of lead and lead-containing products	93
6.2.3.1 Directly dispersive applications: petrol, paints	94
6.2.3.2 Items remaining in-situ after use: lead shot, weights, cable sheathing.	94
6.2.3.3 Items disposed of in the normal waste stream	95
6.2.3.4 Losses from recycling of lead and lead-containing products	99
6.2.4 Other anthropogenic sources of lead in the environment	100
<b>6.3 Chemical speciation of lead</b>	105
<b>6.4 Natural fluxes, transportation and fates of lead in the environment</b>	106
6.4.1 Transport by air	106
6.4.2 Transport in water	107
6.4.3 Movement in soil	108
<b>6.5 Uptake of lead in biota / bioaccumulation</b>	109

<b>7 LEAD EXPOSURE TO HUMANS AND OTHER ORGANISMS</b>	<b>113</b>
<b>7.1 Pathways to the biosphere and humans</b>	<b>116</b>
7.1.1 Lead in air	116
7.1.2 Lead in water	116
7.1.3 Lead in soil and dust	118
7.1.4 Lead in food	121
7.1.5 Estimates of total lead absorbed by humans (adults and children) from air, dust, food and water	122
<b>7.2 Environmental effects and ecotoxicity</b>	<b>123</b>
<b>7.3 Health effects on humans</b>	<b>127</b>
7.3.1 Historical accounts of plumbism	127
7.3.2 Absorption of lead	127
7.3.3 Fate of lead in the human body	127
7.3.4 Measures of lead exposure	128
7.3.5 Health effects of lead exposure	128
7.3.5.1 Effects of lead exposure on mental development and IQ	128
7.3.5.2 Other effects of lead exposure	130
7.3.6 Lead poisoning	133
<b>7.4 Extent of lead exposure in the general population</b>	<b>135</b>
7.4.1 The general population (non-occupational exposure)	135
7.4.2 Exposure of individuals occupationally exposed to lead	137
7.4.3 Trends and health implications	138
<b>7.5 Policy approaches to lead</b>	<b>140</b>
<b>8 INDUSTRIAL EMISSIONS AND CONTROLS</b>	<b>143</b>
<b>8.1 Industrial emissions</b>	<b>145</b>
8.1.1 Sources of emissions	145
8.1.2 Quantities of emissions	146
8.1.3 Nature of emissions	148
8.1.4 Lead deposition	149
8.1.5 Impacts of industrial emissions	150
<b>8.2 Control measures</b>	<b>152</b>
8.2.1 Historical background	152
8.2.2 Measures to control losses of lead to the environment	152
8.2.3 Choice of process	153
8.2.4 Additional measures to protect the health of employees	154
<b>8.3 Examples of the current state of emissions by industry</b>	<b>155</b>
<b>9 IS LEAD A SUSTAINABLE COMMODITY?</b>	<b>159</b>
<i>References</i>	165
<i>Annex – Historical production and uses of lead</i>	177



## CHAPTER 1

# INTRODUCTION

Lead is one of man's most valuable commodities. Occurring naturally in the environment, the metal is mined and processed in some 60 countries. The usage continues to increase and has risen from 4 million tonnes per year worldwide in the 1960s to 6 million tonnes in the 1990s. Of this, nearly 2 million tonnes per year is produced in Europe. Secondary production or recycling is now widely practised and currently accounts for some 70 per cent of usage worldwide.

Lead has some important properties, in particular malleability (i.e. it can be hammered into shape), ease of production, ease of melting and joining, and good corrosion resistance in most common environments. As a result, it has been used for purposes such as roofing, window frames, piping, kitchen/tableware and ornamental uses for many centuries. Its high density has proved effective for weights and anchors for fishing lines, boats, and later for munitions. This property is now utilised in lead radiation screening and soundproofing. The electrochemical properties of lead enable it to be used in storage batteries in all motor vehicles, and for some back-up power supplies. Certain compounds of lead, particularly brightly coloured lead oxides, and leaded glasses and leaded glazes on ceramics, have been used for millennia. The use of most leaded paints has recently been phased out, but lead is still an important addition to some glasses and glazes.

However, it has been known since ancient times that exposure to lead can have serious consequences for health. Accounts of symptoms consistent with chronic lead (and other metal) poisoning dating from the Roman period have been found, and there is evidence that many, in particular the nobility at the time, suffered from high exposure to lead. Up until recent decades, many workers suffered lead poisoning from exposure in the workplace.

Today, it is known that exposure to lead can cause adverse effects on many parts of the body. The organs potentially most affected are the brain and nervous system, kidneys, blood, and the reproductive system of both sexes. Lead in certain forms is also considered a possible carcinogen. Of particular concern is that relatively low levels can affect the developing foetus and young children, impairing their mental development and causing a small but measurable decrease in IQ. However, clinical symptoms are only found in very highly exposed

individuals (who are usually exposed at work) and this is now extremely rare in the Western World.

Although mining, processing, manufacturing and the use of lead-containing products, together with recycling and waste disposal will continue to give rise to small emissions and losses to the environment, responsible action by industry coupled with the development and implementation of appropriate environmental regulations, designed to protect both human health and the ecosystem, keep these losses to a minimum. In a world driven by high technology, the continuing uses of lead which now avoid significant sources of human exposure, present little or no risk.

Nevertheless, the very word lead has, since the 1970s, evoked an emotive reaction in many of the general population and to a degree in the minds of politicians and regulators. They are not necessarily aware of the full scientific facts but are easily swayed by the more biased and articulate lobbyists, some of whom hold extremist views.

This book aims to:

- explain what lead is and to describe its properties;
- detail the present applications, and compare its suitability with other alternative materials and substances (this includes lead metal, alloys containing lead, compounds of lead, and other substances containing lead);
- describe the EU (and, in less detail, worldwide) lead industry as it is today, including the amount of production, consumption, re-use and recycling, and market trends;
- describe the risks of exposure to lead - to the health of the general public, to occupationally exposed workers, and to ecosystems - arising from manufacture, use and disposal of lead and lead-containing substances (and also from natural sources of lead);
- describe the lead emissions from industries which produce and use lead, and detail measures undertaken by the industries to minimise emissions;
- present trends in the use/production of lead, and in levels of exposure to humans;
- critically assess:
  - whether lead is a suitable material for its current uses;
  - whether these products or their manufacture present significant cause for concern;
  - and in the light of these points, whether lead is likely to remain in use in the future.

In summary, this book presents an unbiased account of the present day activities of the lead industry, the production, uses and disposal of lead – and the

potential risks to human health and the ecosystem that still remain. It is prepared on the basis of factual evidence, incorporating the use of state-of-the-art science, using the specialist advice of a team of experts from Imperial College of Science, Technology and Medicine, London. It has been written independently of the lead industry. It aims to provide a source of factual information for policy makers, regulators and scientific advisers in local and national government, the European Community and international organisations, together with non-governmental organisations and industry. In short, its primary objective is to set the record straight and pave the way for the future of lead as a sustainable and safe commodity.



## CHAPTER 2

# PROPERTIES OF LEAD

Lead has the advantages of low melting temperature and extreme malleability, which allow easy casting, shaping and joining of lead articles. Besides this lead is slow to corrode and there are many examples of lead articles which have lasted for centuries. Lead is relatively abundant. Lead concentrates can be easily extracted from the ore and winning the metal from the concentrate does not need much energy. This reflects also in a fairly low price compared with other non-ferrous metals. Lead can be recycled as a secondary raw material from lead-acid batteries, from metallic scrap and from several composite consumer products in conjunction with existing recycling loops, for example for steel, zinc and copper, at moderate costs.

However, compared with other metals, lead has extremely low strength, exacerbated by its creep and fatigue behaviour. Thus it is unsuitable for applications that require even moderate strength. (Some of its mechanical properties are closer to those of higher strength plastics than most metals.)

Lead is rarely used in its pure form, as small alloying additions considerably increase its strength. For applications requiring higher strengths, composites such as lead clad steel can be used.

The very high density of lead lends itself to some quite different applications, such as shielding against sound, vibrations and radiation, for example as protection for users of computer and TV screens. For these purposes lead is used in metallic form or as lead compounds in lead glasses.

Some compounds of lead have their own useful properties, particularly in relation to colour and glass-forming ability.

## 2.1 PHYSICAL PROPERTIES

### 2.1.1 GENERAL PROPERTIES

Freshly cast lead is silvery in colour, but quickly turns dull grey to bluish grey, as the metal at the surface oxidises in the presence of air.

Lead possesses the general physical properties of metals: it is a conductor of electricity and heat (though not as good a conductor as some other metals, such as copper and aluminium), has a metallic lustre, albeit a dull one, and has high density. It has a very low melting point, compared with most other metals, of 327°C. This is useful for ease of casting and joining lead, and also influences some of its mechanical properties, which are described later.

Several different isotopes of lead exist in nature. Their relative concentrations in different mineral deposits can vary; this can be used as a diagnostic tool in identifying sources of lead in soils and sediments.

The physical properties of lead are compared with those of other metals and materials in Tables 2.1(a) and 2.1(b).

### 2.1.2 DENSITY

Lead has a particularly high density, 11.3g cm<sup>-3</sup> compared with many other metals (e.g. iron 7.8g cm<sup>-3</sup>, copper 8.9g cm<sup>-3</sup>, aluminium 2.7g cm<sup>-3</sup>). Lead owes its high density to two factors:

- its high atomic number, and hence high relative atomic mass of 207,
- the metal atoms (or, more precisely, ions) are arranged in a dense, close packed structure (face centred cubic structure).

It should be noted that lead is not the densest element: other denser metals include: gold (19.3g cm<sup>-3</sup>), platinum (21.5g cm<sup>-3</sup>), tungsten (19.3g cm<sup>-3</sup>), tantalum (16.6g cm<sup>-3</sup>) and mercury (13.6g cm<sup>-3</sup>). Three metals with similar densities to lead are molybdenum (10.2g cm<sup>-3</sup>), silver (10.5g cm<sup>-3</sup>) and palladium (12.0g cm<sup>-3</sup>).

The high density of lead has important bearings on other properties, particularly attenuation of X-rays, gamma rays and sound waves.

### 2.1.3 ATTENUATION OF X-RAYS AND GAMMA RADIATION

When X-rays or gamma rays pass through matter, they become attenuated; i.e. their intensity diminishes with distance travelled. There is a huge range in the effectiveness of materials at shielding radiation, but they are described by the following equation:

$$I_x / I_0 = A. \exp -(\mu. \rho. x)$$

- where  $I_0$  is the original intensity of radiation  
 $I_x$  is the reduced intensity after passing through a thickness  $x$  of shielding material  
 $A$  is a constant  
 $\mu$  is the mass attenuation coefficient of the shielding material (which varies with wavelength of radiation)  
 $\rho$  is the density of the shielding material.

This equation shows that the ratio of radiation transmitted to original radiation ( $I_x/I_0$ ) varies inversely and exponentially with the wavelength of the radiation and the density of the shielding material (i.e. as the wavelength of the radiation increases and the shielding material becomes more dense, the amount of radiation transmitted will decrease.)

Lead has a high mass attenuation coefficient, particularly for higher energy X-rays (as have other elements of high atomic number) and high density, so it makes an excellent shielding material. (CRC Handbook of Chemistry and Physics, 1996-7).

## 2.1.4 RESISTANCE TO IRRADIATION BY THERMAL NEUTRONS

Lead has a very small neutron capture cross section (the only metals with lower values are magnesium and beryllium). In consequence it does not absorb neutrons and therefore does not become radioactive and unstable (although any impurities in the lead can absorb neutrons and thus transmutate).

## 2.1.5 ATTENUATION OF SOUND

When sound waves pass through matter they become attenuated, that is, their intensity reduces with distance travelled. Sound attenuation is a complex subject, with different processes (and, therefore, different material properties) being important over different ranges of frequencies. However, for many practical applications, mass per unit area is one of the most important factors in calculating the effectiveness of a solid barrier in sound-proofing. As lead is dense, a relatively thin layer of lead can attenuate sound more effectively than a much thicker layer of other less dense sound-proofing materials. The softness of lead also avoids resonant effects.

## 2.2 MECHANICAL PROPERTIES

Under low loads, all solid materials deform slightly, then return to their original shape when the load is released. This is termed elastic deformation, and is reversible.

At higher stresses, brittle materials fracture and ductile ones (some metals, some polymers) are plastically deformed, i.e. can be stretched, bent etc. and do not return to their original shape when the load is released.

### **2.2.1 DUCTILITY**

Lead is very ductile (or malleable), that is, it can be plastically deformed, and large deformations are possible before the material breaks. In most metals, only very limited deformation is possible before the metal becomes hard and brittle. At this stage, it is necessary to anneal the metal, i.e. leave it to soak in an oven at a suitable temperature (usually a few hundred degrees C) for a suitable time (often around a couple of hours). This softens the metal by allowing processes of stress relief, recovery and sometimes recrystallisation, to occur within the metal. The softened metal can then be further deformed, and the sequence can be repeated.

Lead behaves quite differently to most other metals, because it melts at a much lower temperature. Because its melting temperature is much closer to the temperature at which it is used (normal room or outdoor temperature), some of these recovery processes can occur within the metal spontaneously. This allows extensive deformation before fracture, without the need to anneal the metal. This ability to hammer lead into desired shape is extremely useful for numerous applications, as will be described later.

### **2.2.2 TENSILE STRENGTH**

The tensile strength of pure lead is quoted as 12-17 MPa, which is very much lower than that of the other common metals (mild steel is about 15 times stronger; copper (“as cast”) 10 times stronger; aluminium (“as cast”) about 6 times stronger.) Even less strong materials (soft pine, plastics) have slightly higher strengths than lead (see Table 2.2). However, as lead slowly deforms with time under a static load, it is necessary to specify the exact testing conditions. This phenomenon, termed “creep”, is described below. As with other metals, the strength of lead can be considerably improved by small additions of alloying elements. Antimony, tin and copper are commonly used (see Table 2.3).

### **2.2.3 CREEP BEHAVIOUR**

Creep is the slow plastic deformation of materials under a constant stress. In metals, it can occur at even low temperatures, but the effect is extremely small and only important for the most sensitive applications. This phenomenon is more important at higher temperatures (relative to the melting point),



since displacement of the metal atoms (more precisely, ions) can more readily occur.

Lead is subject to creep at normal temperatures, since its melting temperature is relatively low. This creep can occur at low stresses, leading eventually to failure well below the tensile strength.

The long term “creep strength” of metals is difficult to measure, as tests of many years are required. However, studies have found that creep can occur in lead (of 99.99% purity) at stresses as low as 0.7 MPa (though by a very small amount, elongation of 0.06% after 500 days at 30°C; double the stress produced a 2% extension in the same period (Blasket and Boxall, 1990)). Extrapolation from other tests shows that, under normal conditions, no appreciable creep will be expected at stresses below 1.72 MPa (or if in compression, 2.75 MPa) for 99.9% pure lead (LDA technical notes 1992). Differences in results are assumed to be because of differences in temperature and other test conditions.

Processing conditions and some alloying additions influence the creep behaviour of lead; small additions of copper (widely used for lead sheet) and also silver can improve creep resistance.

#### **2.2.4 FATIGUE**

This phenomenon is the failure of metals, after repeated loading cycles, at stresses below the normal tensile strength of the material. It occurs because of the growth of tiny cracks within the material: stresses at the crack tip are much higher than across the bulk of the specimen. It can be caused by mechanical loading and even cycles of thermal expansion. Lead, like many other materials, is subject to fatigue. As with creep behaviour, fatigue resistance can be improved by certain alloying additions, most importantly copper.

#### **2.2.5 FINAL COMMENT**

For any application, the proposed design must predict the service conditions which the components will experience. Because of the particular mechanical properties of lead, it is important to comply with the standards set out for the specific building or architectural applications.

### **2.3 CHEMICAL PROPERTIES**

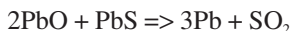
#### **2.3.1 EXTRACTION OF LEAD FROM ITS ORE**

The most common ore of lead is galena, lead sulphide (PbS). Extraction of metallic lead from this compound is relatively easy:

## LEAD: THE FACTS

1. roast the sulphide in air, to convert to the oxide  
e.g.  $2\text{PbS} + 3\text{O}_2 \Rightarrow 2\text{PbO} + 2\text{SO}_2$
2. heat the oxide in the presence of a reducing agent (such as charcoal, coal)  
e.g.  $2\text{PbO} + \text{C} \Rightarrow 2\text{Pb} + \text{CO}_2$

On primitive hearths, such as a pile of charcoal and lead ore, the lead on the surface (open to the air), quickly becomes oxidised. This newly formed lead oxide can react with lead sulphide underneath in a double decomposition reaction to yield lead metal:



The removal of silver and other impurities from lead is also relatively easy, though separate refining stages are required for removing different impurities. These processes are described in more detail in Chapter 4 - Industry Profile.

Thus, metallic lead of high purity can be obtained with simple technologies, requiring much lower temperatures than the preparation of many other metals, including copper and iron. This is undoubtedly an important reason why lead has been known and used since ancient times.

### 2.3.2 CORROSION OF LEAD

Contrary to popular opinion, lead is not a completely inert metal, though it is not very reactive. In general, it is less reactive than iron and tin, but more reactive than copper. Under some conditions, lead can slowly dissolve in water (over a period of many years), consuming oxygen and displacing hydrogen.

The corrosion of lead is usually very slow, because many of its compounds can form protective barriers on the surface of the metal. Lead generally displays good durability when exposed to air and to many aqueous solutions, even in some fairly hostile environments. However, even small amounts of corrosion are important in the case of lead, not just because the metal article can lose its integrity and fail, which is the prime concern to the design engineer, but because even low concentrations of lead dissolved in drinking water, or ingested by other routes, can potentially be harmful to health, as discussed in detail in Chapter 6.

#### Lead in air

In moist air, lead quickly tarnishes, forming a thin layer of lead oxide on the surface. This can further react with carbon dioxide in the air to form lead

carbonate. This surface layer provides a high degree of protection against further reaction under normal atmospheric conditions.

### Lead in water

Corrosion of lead in water, as with other metals, is an electrochemical reaction. Some parts of the surface act as anodes (positive electrodes), while other parts act as cathodes (negative electrodes).

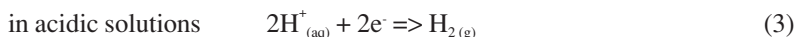
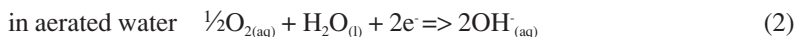
#### *Anodic reaction*

The metal dissolves into aqueous metal ions, and electrons are generated.



#### *Cathodic reaction*

In highly concentrated metal salt solutions, metal can be deposited on the cathode, as in electroplating. However, under normal circumstances this does not occur, and cathodic reactions involve water and oxygen. There are two alternative reactions, which are important:



Both reactions (2) and (3) can occur together. However reaction (2) is generally more rapid than reaction (3), and accounts for most of the corrosion. So, if the water is de-aerated, the corrosion rate greatly reduces by a factor of about ten. Unfortunately, normal waters are almost always aerated.

The rate of reaction (3) on exposed metal surfaces will be greater in more acidic solutions (having lower pH) as the concentration of hydrogen ions is greater. Both an anodic and a cathodic reaction must happen simultaneously. If either is blocked, then the whole reaction stops. The dissolution of lead in water is called plumbosolvency. Whether or not it occurs depends upon the composition of the water and other factors, described below.

#### *Control of corrosion reactions*

In practice, the corrosion of lead is often controlled by its reaction products (lead salts) building up on the surface of the metal. Many of these salts have very low solubilities in water, particularly lead sulphate, carbonate and chromate. If they form a barrier which covers the whole surface, and the barrier is not damaged, the rate of corrosion is greatly reduced.

Table 2. 4 lists the solubility of some lead compounds in water. Most lead salts have low solubilities, and thus have the potential to form protective layers on the

surface. This property gives lead particularly good resistance to sulphuric, phosphoric and chromic acids, making it extremely useful in the chemical and other industries. Notable exceptions are lead acetate, nitrate and chloride which are very soluble and do not offer protection.

It must be stressed that the pH (measure of acidity or alkalinity of a solution) and the presence of other species, can greatly affect the solubility of these products. Lead sulphate is even more insoluble in aqueous sulphuric acid than in water, whereas lead carbonate can be dissolved in both acid and alkaline solutions; the oxides of lead are more soluble in some acids.

Thus, the rate of dissolution of lead depends upon the exact composition of the water to which it is exposed, including dissolved gases and minerals. The hardness of the water is a very important factor, as lead can slowly dissolve in soft water, but generally does not dissolve in hard water. Temperature and rate of flow of solutions can also influence corrosion rates.

Lead alloys will generally have higher corrosion rates than pure lead, because inhomogeneity of composition encourages some areas to act as local anodes or cathodes.

Rates of surface attack by a wide range of natural and industrial waters, including seawater, are quoted as lying between 2 and 20 $\mu\text{m}$  per year (Blaskett and Boxall, 1990). This corresponds to a mass loss of 20 to 230 $\text{gm}^{-2}$  exposed area per year (allowing for the high uncertainty level in these figures). The risk of lead dissolving in certain environments, such as in drinking water and soil, will be discussed in more detail in Chapters 6 and 7.

## **2.4 PROPERTIES OF SOME COMPOUNDS OF LEAD**

Many lead compounds have strong colours, from white to yellow to red and black, most of which do not alter on prolonged exposure to sunlight. The compounds are also relatively stable, and so have found use in paints and other colourants.

Lead oxide is a good glass former and can be mixed in all proportions with ordinary silicate glasses. It improves the appearance of silicate glasses, increases their density, and lowers their melting temperature.

The reactions of lead oxide in dilute sulphuric acid are fundamental to the operation of a lead-acid battery. This is discussed in detail in Chapter 3.2.1.

**TABLE 2.1(a)** Physical Properties of Lead and a Selection of other Metals and Materials

	Pb	Cu	Fe	Al	Zn	Sn
density (g cm <sup>-3</sup> )	<b>11.34</b>	8.96	7.87	2.70	7.14	7.3
melting point (°C)	<b>327.5</b>	1084	1536	660	419.5	231.9
boiling point (°C)	<b>1750</b>	2560	2860	2520	911	2270
atomic number	<b>82</b>	29	26	13	30	50
atomic weight	<b>207.19</b>	63.54	55.85	26.98	65.37	118.69
mean specific heat capacity at 100°C (Jkg <sup>-1</sup> K <sup>-1</sup> )	<b>129.8</b>	386	456	917	394	226
thermal conductivity (at ambient temp) (Wm <sup>-1</sup> K <sup>-1</sup> )	<b>34.9</b>	397	78.2	238	119.5	73.2
coefficient of thermal expansion 0-100°C (10 <sup>-6</sup> ).K <sup>-1</sup>	<b>29.0</b>	17.0	12.1	23.5	31	23.5
electrical resistivity at 20°C, (μ ohm cm)	<b>20.6</b>	1.69	10.1	2.67	5.96	12.6

**TABLE 2.1(b)**

	Pb	Polymers			Ceramic	Glass	
		HDPE	PP	uPVC	porcelain	soda glass	leaded glass
density (g cm <sup>-3</sup> )	<b>11.34</b>	0.94-0.96	0.90-0.91	1.3-1.4	2.3	2.5	3-4
melting point (°C)	<b>327.5</b>	130	60			1200-1500	
mean specific heat capacity at 100°C (Jkg <sup>-1</sup> K <sup>-1</sup> )	<b>129.8</b>		1920	840-1170	~750	~700	
thermal conductivity at ambient temperatures (Wm <sup>-1</sup> K <sup>-1</sup> )	<b>34.9</b>	0.45-0.52	0.12	0.12-0.17	1.5-2.5	0.85 (light flint)	0.55 (dense flint)
coefficient of thermal expansion 0-100°C (10 <sup>-6</sup> ) K <sup>-1</sup>	<b>29.0</b>	100-200	60-100	70-80	2-6	7.5	

(adapted from Smithells, 1992 and Kaye and Laby, 1995)

Pb - lead; Cu - copper; Fe - iron; Al - aluminium; Zn - zinc; Sn - tin  
 HDPE - high density polyethylene; PP - polypropylene; uPVC - unplasticised PVC

**TABLE 2.2** Tensile Strengths of Lead and some other Metals and Materials (All figures are for pure metals in the as cast condition unless otherwise stated. The strength of most metals is higher (approximately doubled) in rolled condition, and also much increased by alloying additions.)

	Pb	Cu	Fe	Al	Zn (rolled)	Sn	soft solder
UTS (MNm <sup>-2</sup> )	12-17	120-170	100-230	90-100	110-150	20-35	55-75

	Pb	glass	leather belt	pine spruce, along grain	oak	HDPE	PP	PVC
UTS (MNm <sup>-2</sup> )	12-17	30-90	30-50	20-50	60-110	20-36	28-40	50

**Explanatory note:** UTS is the ultimate tensile strength of the material, that is, the stress at which the material breaks. It is usually measured in special testing apparatus. Exact values of properties may vary with different testing conditions.

Results of tensile tests on lead, at 20°C, tested at a speed of 0.5mm/min, found the strength was 13.2 MNm<sup>-2</sup>; testing at a higher speed of 25mm/min gave a measured strength of 11.5 MNm<sup>-2</sup>.

For metals, strength is very sensitive to such factors as: temperature, material preparation, rate of cooling, any deformation or further heat treatment, the presence of impurities (even in trace amounts); for glass, the amount of handling has a marked effect (decreasing strength); polymers are sensitive to variables in manufacturing process, and degrade after exposure to heat and ultra-violet radiation (Kaye and Laby, 1995).

*Note:* the creep strength of pure lead, which allows for slow deformation, is much lower, taken as around 1.5-3MNm<sup>-2</sup>.

**TABLE 2.3** Strengthening Effect of adding Antimony to Lead

Antimony content %	Tensile strength (MNm <sup>-2</sup> )
0	17.25
1	23.46
2	29.00
4	39.05
6	47.20
8	51.20
10	52.92
11	52.58
12	57.61

(Blaskett and Boxall, 1990)

**TABLE 2.4** Solubility of some Compounds of Lead in Water and other Solutions

Compound	Chemical formula	Solubility in Water (g/100ml)	Temperature (°C)	Soluble in other solutions?
lead acetate	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	44.3	20	yes
lead bromide	$\text{PbBr}_2$	0.844	20	in acid, KBr
lead carbonate	$\text{PbCO}_3$	0.00011	20	in acid, alkali
basic lead carbonate	$\text{PbCO}_3$ $2\text{Pb}(\text{OH})_2$	insoluble	-	
lead chlorate	$\text{Pb}(\text{ClO}_3)_2$	151.3	18	
lead chloride	$\text{PbCl}_2$	0.99	20	in ammonium salts, slightly in dilute HCl, and ammonia
lead chromate	$\text{PbCrO}_4$	0.0000058	25	in acid, alkali
lead fluoride	$\text{PbF}_2$	0.064	18	in $\text{HNO}_3$
lead hydroxide	$\text{Pb}(\text{OH})_2$	0.0155	18	
lead iodide	$\text{PbI}_2$	0.063	18	in alkali, KI
lead nitrate	$\text{Pb}(\text{NO}_3)_2$	56.5	18	in aq. alcohol, $\text{NH}_3$ , alkali
lead oxalate	$\text{PbC}_2\text{O}_4$	0.000166	18	
lead oxide: litharge	$\text{PbO}$	0.0017	18	in $\text{HNO}_3$ , alkali, ammonium chloride
red lead oxide	$\text{Pb}_3\text{O}_4$	insoluble	-	in hot HCl, acetic acid
lead dioxide	$\text{PbO}_2$	insoluble	-	in dilute HCl, slightly in acetic acid
lead ortho-phosphate	$\text{Pb}_3(\text{PO}_4)_2$	0.000014	18	
lead sulphate	$\text{PbSO}_4$	0.00425	25	very low solubility in sulphuric acid; dissolves in other acids and ammonium salts
lead sulphide	$\text{PbS}$	0.01244	18	in acid, not in alkali
lead sulphite	$\text{PbSO}_3$	insoluble	-	

(adapted from Kaye and Laby, 1995 and Blaskett and Boxall, 1990)





## CHAPTER 3

# APPLICATIONS OF LEAD

Examples of lead use have been known for thousands of years. The Romans used lead on a large-scale for plumbing, tank lining and domestic articles such as cooking pots and tableware, and also in glasses and glazes on pottery. Lead use has continued to grow and, in recent times, has risen from 4 million tonnes per annum in the 1960s to 6 million tonnes in the 1990s, due primarily to an increase in demand for lead-acid batteries.

Present uses of lead and lead compounds are:

### **LEAD METAL**

#### **Lead-acid storage batteries**

The major use worldwide, primarily as a starter battery in motor vehicles, but also as traction batteries for zero-emission electric vehicles and to provide emergency backup power supply, mostly for computer and telecommunication systems. Good rates of recycling are already achieved for starter batteries, though they could be improved upon in some countries; very high recycling rates are achieved for traction and backup batteries. Alternatives are under development for some applications, though at present these could not replace lead at comparable cost, or for technical reasons.

#### **Constructional uses: pipe and sheet**

Lead piping is now a minor application, as it is no longer used for domestic water supplies because of concerns that lead slowly dissolves in soft water and may pose a risk to health, and because of improvements in alternative materials. However, much lead piping remains in place. New lead pipes are used in the chemical industry.

Lead sheet is widely used on roofs for flashings and weatherproofings, and is often used for complete roofs on both historic and modern buildings.

#### **Cable sheathing**

Lead sheaths are used to protect underwater and some underground power cables. This is now a minor application of lead.

### **Radiation screening**

Lead is the most effective of the commonly available materials for screening from X-rays and some other types of radiation. It is widely used in hospitals as part of X-ray equipment, and also in nuclear power stations.

### **Miscellaneous products**

Lead is widely used in shot and other munitions. Some alternatives are available, and are used in situations where lead poses a particular risk to wildlife, especially to birds, as a result of ingestion. Lead is also used extensively in weighting applications.

### **Lead alloys**

Lead-tin solder is widely used, particularly by the electronics industry. Very minor applications are in bearings and ornamental ware (pewter) - though alternative materials are now generally used. Small additions of lead are made to some steels, brasses and bronzes to improve machinability.

## **COMPOUNDS OF LEAD**

### **Batteries**

This is a major use of lead oxide. Lead dioxide is pasted on to the battery grids, and is the active material in the electrochemical reaction.

### **Pigments and other paint additives**

Lead compounds were widely used until a few decades ago. They have been replaced in certain applications following concerns about potential impacts to human health. Leaded paints are still used in specialised outdoor applications as coatings for commercial vehicles and other industrial applications because of excellent rust-proofing properties. Lead dryers are still used in alkyd-based air-drying paints as very efficient and cost effective through-dryers.

### **Glasses and glazes**

Lead additions improve the appearance and cutting properties of crystal glass. Small additions are also made to optical and electrical glass. The major application of leaded glass is in television screens and computer monitors, to protect viewers from the harmful X-rays generated by these appliances. Lead-containing glazes are used for some pottery, tiles and tableware.

### **Functional ceramics**

Lead titanates/zirconates are used in the electronics industry in various functions.

**Additions to PVC**

Small additions of organic lead compounds to some grades of PVC improve durability and heat resistance, both in manufacture and in service. This is a significant market for lead compounds.

**Leaded petrol**

Lead compounds were universally added to petrol to improve its efficiency at low cost. This has been the major source of lead emissions to the environment. It is now being phased out almost universally because of concerns about health impacts.

### **3.1 HISTORICAL OVERVIEW**

Lead has been extracted and used since the earliest periods of history. The oldest known lead article is a metal figure, found in Egypt, believed to date from 4000BC. Other finds from ancient periods have been principally statuettes and figures.

Though lead was well known, the amount used was very small until the time of the Roman Empire. Earlier, it appears that lead was often an unwanted by-product of silver extraction (as the two metals frequently occur together). Being neither strong nor shiny, lead was much less prized than copper, iron or the precious metals. However, the demand for piped water by the Romans resulted in its large scale use for piping, lining of tanks, aqueducts and so on. Lead and lead-rich pewter was also used for domestic articles such as kettles, cooking pots and tableware. Other uses of lead included ornaments, coffins, alloying additions in bronzes used for statues, tankards and some coins; lead tablets were sometimes used for inscriptions; and lead weights. The use of lead for munitions has been known since ancient times.

The bright colours of many lead compounds have been exploited since very early times, for paints and pigments; black, white, yellow and red coloured compounds were also widely used as cosmetics. Lead-rich glazes were used on ceramics by the ancient Egyptians and others; leaded glasses were also known in the ancient world, and used because of their ease of melting and strong colours.

Even though harmful effects of lead were recognised, or at least suspected, lead and its compounds were also considered therapeutic for a variety of ailments, and ointments were believed to work better if stored in lead containers.

### **3.2 USES OF LEAD METAL**

#### **3.2.1 LEAD-ACID BATTERIES**

By far the greatest use of lead worldwide is in lead-acid batteries of which more than 70% are recycled. The principle was discovered in 1850 by Siemens, and patented and first put to practical use by Planté in 1859; lead-acid batteries are now used in motor vehicles, electric powered vehicles, and also in some situations such as computer and telecommunication systems, and smaller numbers in other installations including hospitals, which require instant emergency back up power in case of power failure.

Batteries have been the greatest consumer of lead since the 1960s, but their importance has risen hugely: in 1960 batteries accounted for 28% of lead use worldwide, whereas in 1999 74% of lead consumed was for this application.

(ILZSG 2001a) (Note, this is in countries which are members of the International Lead Zinc Study Group which account for around 80% of world consumption of lead.) In Western Europe, 57% of the lead consumed is used in batteries (1999 data, based on total consumption of refined lead, and consumption of lead for batteries, in most of the countries in Western Europe, which account for 95% of total consumption.) In the USA, over 80% of lead is used in batteries (1999 data). (Calculations are based on lead statistics, ILZSG 2001a)

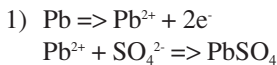
The demand for lead-acid batteries, both for automotive applications and for stationary output, is continuing to increase.

### Principle

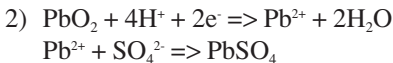
The simplest form of a lead-acid battery would consist of two electrodes immersed in a tank of dilute sulphuric acid. The electrodes are:

- 1) an electrode made of grey metallic lead (negative terminal)
- 2) an electrode made of various lead oxides (positive terminal)

If these two electrodes are connected by an electrical conductor, then an electric current will flow through the conductor - powering any electrical appliance in the circuit - as chemical reactions occur simultaneously at both electrodes:



(electrons generated at the negative electrode)



(electrons consumed at the positive electrode)

This cell produces a voltage of 2V.

As current flows, both electrodes react with the sulphuric acid, to deposit plates of lead sulphate. The reaction continues until the electrical connection is broken, either one or both electrodes are used up, the acid is all used up, or until the accumulated lead sulphate blocks further reaction.

The discharged battery can be re-charged by connecting to a direct current power supply. The plate connected to a positive terminal will undergo the reverse of reaction (1), and turn back into lead metal; while the other will revert to lead dioxide, by the reverse of reaction (2).

### **Design of modern lead-acid batteries**

The commonest type of lead-acid battery consists of the following components:

- a grid of lead alloy, which forms the negative terminal, according to reaction (1)
- the spaces in the grid, which are filled with a mixture of powdered lead and lead oxide, forming the positive electrical terminal, according to reaction (2)
- an electrolyte (solution which conducts electricity) of sulphuric acid, in which the whole grid is immersed
- separators (made of insulating material) and electrical connections, including the terminals.
- the case, normally a heavy duty polypropylene box.

To be ready for use, the newly built battery is “formatted” by charging with electricity, so building up the lead dioxide for the positive terminal.

Small alloying additions are made to the lead, in order to improve its strength, lifetime (by lowering its corrosion rate) and in the case of batteries for vehicles, resistance to fatigue, caused by vibrations and jolts.

Historically, the usual alloy was basically lead - antimony (0.75 - 5% antimony), which is much stronger than pure lead. Minor additions of other elements, such as copper, tin, arsenic and selenium can also be made to improve grain refinement, ease of casting and impart age-hardening characteristics.

For starter batteries, the more modern sealed maintenance-free batteries use alloys based on the lead - calcium - (tin) system, containing up to 0.1% calcium, and from 0 to 0.5% tin. The tin is added to improve corrosion resistance. These systems are beginning to predominate, particularly in the larger, more mature markets (in the USA and Europe).

### **Applications**

1. The SLI (starting, lighting, ignition) battery used in all motor vehicles.
2. The traction battery, used to power vehicles such as golf carts and airport vehicles, and some indoor vehicles such as fork lift trucks, where quietness and lack of emissions (from the vehicle itself - though of course there are emissions from the power stations which generate the electricity to charge up the battery) are important, and journey distances are short.
3. Backup power supplies in case of power failure. Most are used for computer systems (59% in 1996), and telecommunications (21% in 1996), with 6-7% each for industrial/utility customers, medical (e.g. for hospitals), and military/government users. (Frost and Sullivan, 1996) They can provide instant supply, either alone, or for the brief interval between power cut and a diesel generator starting to supply power.

**Lifetime**

Car batteries typically have a lifetime of approximately 4 years in Europe. Batteries for stationary power supply have longer lifetimes, up to 10 years.

**Advantages of the lead-acid battery**

This is the most economical form of electricity storage. The technology is well-established, and its capabilities and limitations are well known.

**Disadvantages**

Lead-acid batteries are heavy and bulky, and store a limited amount of energy. The average weight of a European car battery is 13 kg, with a lead content of 7.6 kg.

**Recyclability**

Lead-acid batteries are highly suitable for recycling. The EU Directive on batteries obliges Member States to implement systems to achieve high recovery rates. Some states have special collection procedures, and collection rates of over 90% are achieved in many countries. (Refer to Chapter 5, Recycling)

**Alternatives**

There are several other systems which can store electricity. All are more expensive than lead-acid batteries.

Nickel-cadmium batteries are commercially available for some applications. These batteries are more compact than lead-acid, but could not at present replace them in all applications, especially in cars. Also, cadmium is another toxic element and environmental benefits of switching to this system would be questionable.

Other systems are used in very limited applications, or are still at the research stage.

**Emerging/projected applications of lead-acid storage batteries****1. *Electric powered vehicles***

The lead-acid battery is one of a number of technologies which are currently being developed for this application.

Electric powered vehicles are more expensive than ordinary motor vehicles, and have limited journey lengths between re-charging. However, this technology has not had as many decades for development as the traditional motor vehicle technology, and there could be a substantial improvement in prices and performances.

The Advanced Lead-Acid Battery Consortium has demonstrated that advanced lead-acid batteries are capable of routinely powering a car for over 100km per charge in urban driving, can have a dependable lifetime of 500 cycles,

and can be quickly changed in a matter of minutes. Considerable research and development effort is going into improving performance, with short term aims of extending lifetimes to 1000 cycles, and journey lengths to 150km.

Present incentives to pursue alternative vehicle technologies are to improve air quality in the urban environment, to reduce carbon dioxide emissions and to reduce overall fuel consumption. At present some such vehicles are used in California, in an attempt to reduce the smog problems caused by air pollution; some are in use in Europe, and look set to increase in numbers.

Alternatives include nickel-cadmium, nickel-metal hydride, lithium-ion, and polymer-based battery systems, and completely different technologies such as fuel cells, liquid gas (which is a cleaner fuel for the conventional motor vehicle) and hybrids which use a combination of these.

## 2. *Power supply to remote areas*

Diesel generators provide the usual electricity supply in areas not connected to a grid. They have a number of problems: transport of diesel can be difficult; the fuel can be expensive; the generators pollute the air and are noisy; regular maintenance is required. They can also be an expensive way of meeting very small electricity demands.

Solar panels, wind and small hydroelectric generators, with electricity stored in batteries for when there is no sunlight or wind or water, avoid all of these problems. Once installed, there are no transport problems, no pollution and very little maintenance is needed. A highly successful project has been reported in Alaska. (Demarest, et al, June 1997) Investment in this application is in place in Peru; Asia is seen as a very large potential market.

Though lead-acid batteries are by no means the only option, they are the cheapest available batteries.

## 3. *Storage of electricity at power stations*

Banks of batteries at power stations can store electricity produced at times of low demand, and provide extra supply at peak demand. There is currently an example in the USA, and a system installed in 1995 in Puerto Rico is reported to have improved the reliability of electricity supply to the island. (Taylor et al 1995)

### **3.2.2 GENERAL CONSTRUCTIONAL USES OF LEAD - SHEET AND PIPE**

After batteries, the next most important metallic use of lead is for the manufacture of lead sheet and pipe. Lead sheet is widely used in the building, construction and chemical industries, where the versatility of both the material and its applications have created the worldwide annual demand of some 265,000



tonnes (1999). Lead pipe was once a significant product but is now produced only in very small quantities, exclusively for use by the chemical industry.

The UK produces more of these products than any other country (in 1999, 97,700 tonnes), almost 30% of total UK lead consumption. The next largest producers are Belgium and Germany, each using around 30,000 tonnes per year and accounting for 50% and 11% of their total lead consumption, respectively.

### **Lead sheet**

Most lead sheet is used in the building and construction industry, with the highest demand being in the UK, mainly due to the style of buildings, climatic conditions and its traditional usage. Across Europe traditional applications are typically for flashings and weatherings. Some 85% of lead sheet demand is for these types of application, with lead's durability and malleability providing unique properties to weather seal buildings where chimney stacks, windows and abutments are adjacent to roof lines and vertical walls. This is the main application area as it provides a completely watertight seal preventing rainwater ingress and so avoids adverse internal building environments. The material is extremely easy to install, providing basic skill and design techniques are adopted, and once installed it is resistant to wind lift due to its high weight per square metre.

Other important uses of lead sheet are for complete roofing systems and for vertical cladding of walls. Architects have long recognised the unique properties of lead sheet, using it on many cathedrals and historic buildings across Europe. Prominent building designs using lead sheet are also visible in new construction projects and are not solely a feature of this traditional approach. Though more expensive initially than alternatives, its long life - over 100 years is quite feasible for correctly installed lead - and low maintenance requirement, can make the long term costs comparable with, or even lower than, some cheaper alternatives, as other (non-metallic) materials need replacement after about 20 to 50 years. The grey colour of the natural material provides a unique aesthetic appeal, toning in well with a variety of colour schemes and other building materials.

A life cycle analysis performed in the Netherlands (Roorda and van der Ven, 1999) of lead and two alternative polymeric materials for flashings, found that lead compared favourably with the alternatives. This study included the impacts of production of the materials, effects of their use, and eventual disposal. Lead is generally recycled, rather than disposed of. However, it must be noted that this study assumed:

- a) the polymeric materials would need replacing during an estimated 70 year lifetime of a building, but the lead would not. If the polymeric materials proved to be able to last without replacement, then the total impacts of the lead and polymeric alternatives are roughly equivalent.
- b) the lead comes entirely from secondary sources. This is valid in most countries which produce all their lead from scrap, but in some countries, small

amounts are produced from primary lead. Primary production entails considerably more energy consumption, there is greater potential for pollution, and this causes depletion of a non-renewable mineral resource, so the total impacts of the use of lead would be greater than calculated.

c) this study did not include zinc or copper, which are also durable roofing materials, and are more widely used in other countries.

It was noted that lead sheet possessed superior qualities due to its longevity, its recyclable nature, and low energy requirement for conversion. The study concluded that 'the environmental impact of lead sheet is more favourable than that of the alternatives. The main reason is the product lifetime of the alternative materials is expected to be shorter than that of lead' and that 'corrosion products from lead sheet have a negligible impact on the aquatic ecosystem, based on present toxicological data. In fact lead is one of the substances which reaches target levels on water quality in the Netherlands'.

Lead sheet is used to a lesser degree for radiation shielding, noise attenuation and damp proofing. Inside buildings, layers of lead incorporated into walls can be used as part of a system for sound insulation, particularly where space constraints do not allow thicker walls of cheaper materials. The softness and formability of lead allow it to be shaped exactly as required, so an integral sound barrier can be constructed.

Layers of lead sheet can be used to provide watertight linings for tanks and vessels. This application is occasionally used in the building industry, where complete integrity and lack of maintenance are required. However, it is more commonly used by the chemical industry for the lining of tanks and other vessels exposed to corrosive contents such as sulphuric acid, because of its good corrosion resistance compared with other materials.

The pattern of use of lead sheet is considerably different in North America. There is no tradition of using lead sheet in roofing, but it is used in small amounts in building construction, for example to provide maintenance free waterproofing membranes and occasionally for more prestigious projects. The use of lead in radiation shielding is relatively large (27% of sheet consumption in the USA), and it is also used by the chemical industry. Japan has a different pattern of lead sheet use again, using most (70%) for radiation shielding, and the remainder for sound insulation.

**Alternative materials** - Many alternatives are suggested as providing equivalent characteristics to lead. However, this is not found to be the case when all factors are taken into account.

Flashings, weatherproofings etc. - aluminium, lead-clad steel, rubber backed metal could be used, though they may not be as durable for all applications. (Danish Ministry of Environment 1998)

Roofing - many alternatives exist, including lead-clad sheet and galvanised (zinc coated) steel sheet. Zinc and copper are traditionally used in some

countries, and have some of the advantages of lead for this purpose. However, concerns over human and environmental exposure to these materials have also been raised. Many non-metallic materials are in common use. Most alternatives, particularly non-metallic materials, require more maintenance, have much shorter lifetimes than lead and consume more energy during manufacture and recycling.

Listed buildings would require approval for replacement of lead roofs by alternatives.

### **Lead pipe**

Though lead has been used for piping since pre-Roman times, new lead pipe has not been used for domestic water supplies for over 30 years in most countries, and is now a very minor application. Its use has been discontinued because other materials (eg copper and PVC) are cheaper and easier to install. Lead from old pipes can dissolve slowly in soft water, and can thus contribute to human lead intake, with potential adverse impacts on health. (This is discussed in more detail in Chapters 6 and 7.) Considerable amounts of lead pipework are still in service, particularly connecting the street mains supply with individual houses.

Lead piping is still used in chemical plant because of its excellent corrosion resistance. It is particularly useful in some acid plants, particularly for sulphuric acid.

*Alternatives* - For domestic water supplies - copper and plastic piping are now used. For chemical plants, the alternatives are not necessarily obvious as it depends on the design and usage requirements. Stainless steel or other corrosion resistant alloys could be considered in certain cases but these would be more expensive.

### **Leaded window cames**

Traditionally, these consist of H-shaped extruded sections of lead which hold together small pieces of glass which make up a window. Such cames have been used for stained-glass windows in churches and cathedrals. The modern equivalent of this 'H' section is a flat self-adhesive extruded lead tape which is applied to glass windows. This is a cheaper alternative and is very effective in providing the appearance of the traditional lead came.

*Alternatives* - For this application, no viable alternative exists at present (Danish Ministry for the Environment and Energy, 1998).

### **Suitability of lead sheet, pipe and other articles for recycling**

Recycling rates are very high. Lead from these sources is frequently 'clean and soft' (free from major impurities) and therefore extremely suitable for recycling

into similar products. The speed and efficiency of recycling are high, with the whole process of collection through to re-processing and reforming often completed in just a matter of days, making lead a fine example of sustainability and conservation.

### **3.2.3 SHEATHING FOR ELECTRICAL CABLE**

Lead is used as a sheathing material for power cables in several areas, e.g. the petrochemical industry or undersea (for example to supply electricity to islands) and for underground high voltage cables. Alloys are usually designed to provide specific mechanical properties.

The largest consumers of lead cable sheathing in 1999 were France (13,000t), UK (9,600t), Italy (3,300t), India (3,000t) and South East Asia (7,7000t). Most countries in Western Europe use between 1 and 3% of their lead for this purpose.

Lead sheathed electrical cables consist of the following major components:

- electrical conductors to carry the electrical current;
- electrical insulation (usually PVC for low voltage power cables, cross linked polyethylene and paper for medium and high voltage power cables) to protect users and prevent current leakage;
- impermeable protective sheathing, to protect the cable from moisture and corrosion;
- sometimes an additional layer of armouring used to protect the cable from mechanical damage;
- external oversheathing for corrosion protection in general and to protect the cable during installation.

Lead is used as the impermeable sheath in these applications as:

- it is completely impervious to water;
- it has very good corrosion resistance in a variety of media, including marine environments;
- it can be extruded in very long lengths, and also easily jointed by soldering ;
- it is pliable, so can be coiled and uncoiled, without being damaged, during cable preparation, transport and application;
- it can be applied to the cable core at temperatures which do not damage vital cable components.

Concerns about lead used in this application relate to possible corrosion. However, since an external oversheath is always used over the lead, the influence of cable lead sheaths on the environment is regarded as relatively low. This applies also for cables which are not removed at the end of their useful lives, but left in the soil or on the seabed.

**Alternative materials** - As an impermeable sheathing, aluminium sheaths or foils can be used as substitutes in some cases, provided that mechanical or electrical requirements specifically meet the properties of a lead sheath. Thus the use of lead sheathing in some applications has been reduced significantly over the last few years.

At present no alternative has been found for undersea cables, (Danish lead study) as other metallic materials e.g. aluminium, stainless steel, do not have the same resistance to corrosion by salt water. Similarly, lead exhibits resistance to corrosion by oils and is thus used in underground cables by the petrochemical industry. Moreover, due to the lower resistivity of aluminium, eddy currents in aluminium sheaths can be as much as six times greater, compared with lead sheaths. This can reduce the high voltage transmission overall yield by 2 or 3%. Consequently a greater electrical energy loss occurs with subsequently more generation required and thus greater release of pollutants into the environment. Additionally, no equivalent alternative material is known, for lead compounds used as a stabilising element in EPR insulations.

**Suitability for recycling** - Old cable sheaths can be recycled, and sometimes this is done, primarily to obtain the copper. The main difficulty is that it is often not economic to recover them, particularly from the sea bed, and they are often left in place at the end of their useful life. (Refer to Chapter 5.)

### 3.2.4 RADIATION SHIELDING

Throughout the world, lead is the major shielding material used for most screening purposes.

Metallic lead is widely used to provide protection from certain types of radiation, most commonly gamma and X-rays. As described in Chapter 2, the high density and atomic number of lead make it a very effective screening material. Lead finds applications in containers for radioactive materials, and as a component of linings for rooms containing X-ray equipment, such as in hospitals and dental surgeries. Significant quantities of lead are also used in the nuclear power industry.

When exposed to neutrons (a different type of radioactivity typically generated at nuclear power stations and research facilities) lead has the additional advantage of having extremely low levels of absorption. This means that lead, unlike many other elements, does not itself become radioactive to any significant degree, even after prolonged bombardment. Thus it can be used as a durable shielding material. For such applications, pure, unalloyed lead should be used to ensure minimum neutron absorption. (To absorb neutrons, different shielding materials are used; for example, several metres thickness of concrete).

*Alternative materials* would be either:

- less dense materials with weaker screening properties, so greater thickness would be needed to provide the equivalent levels of protection.
- materials of similar or greater density. However there are few of these, and candidates are either precious metals (gold, platinum), or refractory metals, such as tungsten and tantalum, which are difficult to produce and shape and thus are very expensive.

In short, although lead is by no means the only material which can provide screening against radiation, its very high screening ability, combined with malleability and relative low cost, makes it a particularly suitable candidate for many applications. Stability on exposure to neutrons makes it particularly suitable for use in power stations and for the containment of radioactive waste. One special application has been the use of lead-containing concrete to build the sarcophagus around the damaged Chernobyl nuclear reactor.

In some situations, copper and steel (which have fairly high densities) are used in radiation shielding, and cadmium for shielding from neutrons. It has been suggested that concrete or barium could replace lead (Danish Ministry of the Environment and Energy, 1998), though it is conceded that possible technical problems have not been studied. In summary, replacements for lead are largely impractical and certainly more expensive.

### **3.2.5 LEAD SHOT, WEIGHTS AND MISCELLANEOUS PRODUCTS**

#### **Lead shot**

Lead shot remains a minor lead product, accounting for 1-3% of lead consumption in most countries. Italy is exceptional, in that almost 9% of its consumption, 24,000 tonnes, is used for this purpose. Fine lead shot is used for alloying additions to steel, brass and other alloys. Larger shot is used for shotgun cartridges.

#### **Munitions**

Lead has been used in the manufacture of bullets, canon balls and the like for many centuries. It is a favoured choice because its high density means that leaden projectiles have greater momentum, and so greater destructive power and longer range, than similar missiles of less dense materials. Lead also has the advantages that it is relatively cheap, very easy to form, and causes minimal abrasion to the gun barrel.

*Alternatives* - Steel shot is used in some countries, but can cause a number of problems. The shot can become lodged in trees and damage wood saws, can ricochet back towards the hunter from stones etc, and also reduces the lifetime of the gun barrel. Bismuth and tin are also used as shot material, and are commercially available (J. L. Caillerie, Metaleurop, personal communication).

***Suitability for recycling*** - In principle, lead shot can be collected from indoor and outdoor firing ranges, and once collected, could easily be re-melted.

### **Lead weights**

Lead has been used for many centuries for weighting purposes. Apart from its high density, which enables smaller volumes to be used to provide desired weights, the main advantage of lead is its durability. This is particularly relevant in aqueous and marine environments, such as weights for fishing lines and anchors, because iron - itself fairly dense - rapidly corrodes in such environments, unless large additions of alloying materials are used or the weight is covered with a protective coating. Small lead weights are now banned for hunting and fishing in certain areas because of the risk of birds ingesting them. Larger weights are still permitted, as are other uses such as in diving belts.

Lead weights are also found in many other applications including wheel balances on motor cars, curtain weights and yacht keels.

***Alternatives*** - Alternatives are available, though they do not always give the same performance.

For fishing tackle - a number of alternatives exist, including zinc, bismuth-tin and other tin based alloys, and plastic coated iron.

For commercial fishing - iron and stainless steel weights can be used, but there is no immediate alternative to lead for nets. Various manufacturers claim to have developed alternatives but have not marketed them (Danish Ministry of the Environment 1998).

For yacht keels - iron is widely used and is cheaper than lead. However, lead has the advantages that it is more plastic than iron, and may deform rather than fracture in the case of an impact (J. L. Caillerie, Metaleurop, personal communication), though lead also has much lower strength than iron and may break more easily, depending upon the circumstances of the impact. It has also been shown that yachts with lead keels can sail more quickly than those using iron (Danish Ministry of the Environment 1998).

***Suitability for recycling*** - As with other metallic applications, lead weights can easily be recycled. In practice, the degree of recycling depends on the ease with which the weights can be collected. For weights used by the fishing industry, it would be feasible for "used" weights to be returned to the supplier, as these items are regularly replaced. Recycling would never be complete, as considerable loss of material occurs in the water as a result of abrasion and damage to fishing equipment. Wheel balance weights used in vehicles are generally removed from end-of-life vehicles when the tyres are removed, and sent for recycling. Weights which are not removed generally enter the non-ferrous fraction of vehicle shredder material and are recovered along with other non-ferrous metals.

## MISCELLANEOUS APPLICATIONS OF LEAD

### **Figures, ornaments**

These are a very minor use of lead. Many alternatives exist, such as plastic, tin and other metals. The use of lead in “toys” is tightly controlled by toy safety regulations.

### **Security seals**

A very minor use of lead. It could be replaced by aluminium or plastic.

### **Capsules for wine bottles**

Following a 1990 European directive, lead capsules are no longer permitted and tin, plastic or aluminium are used instead.

### **Lead powder**

This is incorporated into several products: a minor constituent in some plastics for protective clothing to screen from radiation; and some paints which protect steel from corrosion.

*Suitability for recycling* - Smaller miscellaneous items could be re-melted if collected. Some probably find their way to scrap merchants, though small items are generally disposed of in the municipal waste stream.

## **3.3 USES OF ALLOYS CONTAINING LEAD**

Lead can be added to a variety of other metals to improve the properties of the resulting alloy for a particular application. The largest consumers of lead for alloys (excluding batteries) are the USA (34,800t), the UK (16,800t) and Japan (11,600t) (1997 data, ILZSG 1999). Other countries in Europe use much smaller amounts of lead for this purpose.

### **3.3.1 TIN-LEAD ALLOYS**

#### **Solders**

Soldering is one of a number of ways of joining materials. While it does not generally give the same strength as welding or mechanical joining, soldering has the advantages that it is easy to apply, does not require very high temperatures, and a completely sealed joint is possible.

Tin-lead solders (a type of soft solder) are the most widely used, because their low melting temperatures and good flow characteristics make them highly suitable for many different applications. They are also cheaper than alternative solder alloys.



Solders are used in many applications, but the largest is in the electronics industry, which consumes approximately 60,000t of leaded solder per year (ILZSG 1999).

Tin-lead alloys have low melting temperatures - a eutectic (an alloy containing two or more constituents, which has a minimum melting temperature at an exact composition) mixture of 38% lead and 62% tin melts completely at 183°C (which is below the melting temperature of either tin or lead.) This liquid can penetrate minute openings, and is suitable for soldering components easily damaged by heat.

Alloys containing between 19 and 97% tin melt over a temperature range, starting at 183°C (for example, 70% lead and 30% tin melts between 183°C and 255°C.) In the melting range, the solder is “pasty”, and can be moulded into a desired shape, which renders it useful for making “wiped joints” on lead pipes and cables, and for filling holes in car bodywork. Lead-rich solders retain solidity to higher temperatures and are suitable for applications requiring joint strength at slightly elevated temperatures such as in car radiators. These applications are dying out.

For joining materials which are particularly sensitive to heat, fusible alloys can be used. These contain lead, but also additional alloying elements such as tin, cadmium, and bismuth to further reduce melting temperature (for example, “Wood’s metal”, consisting of 50% bismuth, 25% lead, and 12.5% each of cadmium and tin, melts at 73°C.) These are rarely used and cadmium-containing alloys would not be preferred because of the potential toxicity of that metal.

**Alternatives** - A great deal of work is in progress to find suitable lead-free alternatives. Some are already used commercially and utilise mainly tin, silver and copper. Other approaches include the use of conductive glue (particularly for lightbulbs and electronic equipment), although technology is still at the evaluation stage. Welding or brazing can be used where the application would not be damaged by the higher temperatures involved.

There is no single replacement suitable for the diverse range of applications of lead-tin solder; alternatives are generally specific to a certain application. It is not known whether these alternatives could be satisfactory for all applications. (Danish Ministry of the Environment 1998)

**Suitability for recycling** - As solder is only used in small amounts in an article, the recycling of solder alone is not possible (though residues from *solder production* can easily be recycled). If the whole article undergoes recycling, the solder is recovered from the non-ferrous metal fraction along with copper, tin and precious metals.

Some recovery of solder from electronic products is already performed in Europe (ILZSG, 1998); substantial recovery may be required by law in the future. (See Chapter 5, Recycling)

The presence of alternative solder materials could complicate non-ferrous metal recovery operations. The mixture of metals obtained from the scrap is treated to separate it into different fractions (iron-rich, copper-rich and so on); these fractions then undergo further treatments to remove impurities and to recover valuable minor constituents. The whole process involves many stages. Additions of different solders could introduce large quantities of materials which are difficult to separate (for example, bismuth, which is difficult to remove from lead) and extra purification steps may be necessary. This would increase costs, may increase the amount of waste generated, and could make the process of non-ferrous metal recycling from waste electronic equipment uneconomic.

### **Terne plate**

This is a thin layer of lead-tin alloy bonded on to steel sheet. The product has the corrosion resistance of lead, combined with the mechanical strength and durability of steel. Vehicle petrol tanks are often lined with such a lead alloy to give corrosion resistance.

## **SOME MINOR USES OF LEAD-CONTAINING ALLOYS**

### **Bearing materials**

Bearings are used to provide low-friction interfaces between moving parts. In general, bearing materials contain a soft component, so that any misalignments do not cause very high local pressures.

One group of such bearing materials is lead-tin based alloys. Such bearings can withstand light loads, but have poorer fatigue resistance than tin-based bearings and other alternatives. Lead based bearings have the advantage of good lubrication, however their chief advantage is their low cost. (Rollason, 1973)

Other bearing materials include bronzes, which may contain up to 20% lead. These are used for some heavy-duty applications. (Blaskett and Boxall, 1990) An aluminium-lead alloy is also used.

*Alternative materials* - At present the number of lead based bearings used is very small compared with other alloys based on tin and copper and standard bearings which use hardened steel components.

Alternatives for applications which currently use leaded bearings may need to solve lubrication problems, and a change of design may be necessary. (Danish Ministry of the Environment 1998)

### **Pewter**

Pewter is a tin based alloy, which can contain up to 50% lead. It was widely used for centuries for ornamental purposes and tableware. It is soft, easy to cast and shape, has a dull metallic lustre, and does not tarnish under normal circumstances.

Pewter can also be made from tin with only very small additions of copper and antimony to improve strength. The non-lead pewter is shiny and harder. Leaded pewter is no longer manufactured in significant amounts, though some old pewter articles, such as tankards and ornaments, have traditional appeal and are still in use.

Leaded tableware has the potential to contaminate food and drink, particularly when used for acidic beverages such as wines or fruit juices. This is discussed in Chapters 6 and 7.

### 3.3.2 LEADED BRONZES, STEELS AND ALUMINIUM ALLOYS

Small additions of lead in bronze and other copper alloys found at archaeological sites, are believed to have been added as a diluent to the more precious copper, and/or to reduce the melting temperature.

Some modern copper, aluminium and steel alloys use small additions of lead to improve machinability.

Some aluminium alloys are formulated with a lead addition of less than 4% for improved machinability. These are mainly used by smaller specialised companies for 'niche' machined products for the automotive industry. The market share of these products is estimated at 0.3% (maximum) of the aluminium used in automotive applications, with a decreasing trend with time.

The current European standard for aluminium casting alloys (EN 1706, 1676) includes a few alloys with a lead content of up to 0.35%. The lead content in the majority of the casting alloys is significantly lower, typically 0.1%. Lead is not an alloying element for casting alloys or for the majority of wrought alloys but is a tolerated impurity. Higher lead content cannot be accepted because it would reduce quality of the final product. Lead is not necessary to reach specific properties of the alloys mentioned above.

The term "machining" of metal covers several operations, including drilling, boring and turning, but generally involves cutting the material towards the desired final shape and size. Machining of ductile materials can be difficult, because a thick swarf (strip of material which is removed from the main body) builds up, obstructing and putting pressure on the cutting tool. "Free machining" steels contain small additions of lead (up to 0.35% by weight) which form insoluble globules of metal in the steel. These make the swarf break off into small pieces during machining. Lead additions are reported to improve machinability by 30%, allowing higher cutting speeds and longer tool life, and so increased production rates; this also improves the surface finish of the machined material, and the machining consumes less energy and is quieter. (EUROFER statement, 1998)

European leaded steel production figures are quoted as well over 1 million tonnes per year, containing 2000 tonnes of lead (late 1990s), with British Steel alone producing half a million tonnes in 1997. (EUROFER, 1998)

Small additions of lead (1.5 - 3.5%) are added to some bronzes for the same reason.

Such additions generally have detrimental effects on the strength and ductility of the material. However with small, well controlled additions, this effect can be small.

**Alternatives** - The steel industry has investigated a number of potential alternatives over a period of more than 15 years.

Calcium-treated carbon and low alloy engineering steels can have improved machinability; they are widely available in Europe, and are being investigated in Japan as alternatives to some leaded steel automotive components. However, calcium additions are not beneficial in all grades of steel (low carbon free-cutting steels).

Bismuth enhances the machinability of steel. However, it has a significant adverse effect on the ductility of steel at hot-rolling temperatures. Its cost is almost ten times that of lead and it arises as a by-product of lead extraction. Current annual world production of bismuth, at a little over 5,000 tonnes, would not suffice if lead in free-machining steels were to be replaced by bismuth.

Resulphurised steel gives good machinability under certain machining conditions. This could potentially replace some, but not the majority of, applications of leaded steel.

Other elemental enhancers of steel machining include tellurium and boron, but their applicability is also limited. Selenium has been discounted for a number of reasons, including its toxicity.

It is concluded that, at present, no viable alternative to lead exists as a steel machinability enhancer. Though the environmental impact of leaded steel is negligible, the search for a replacement for lead is likely to continue.

### **Recovery of lead**

Fumes generated by electric arc furnace steelmaking plants, which may use some leaded steel scrap in their charge, typically contain 1-4% lead and 15-30% zinc. These fumes are collected in high-efficiency bag-house dust extraction systems, which have to meet stringent air quality standards. The collected dust may be enriched by recycling, the zinc and lead-rich product being sent to smelters for recovery.

Fume generated at the point of steel leading, captured in dedicated extraction systems, may contain lead at levels greater than 50%. These are also recovered by smelting.

### **Compounds of lead**

These cover lead used in glasses, glazes, pigments and other paint additives, stabilisers in PVC and petrol additives.

All the above - excluding petrol additives and lead oxide used in lead-acid batteries - have made up 9-10% of worldwide lead consumption since 1960. The total used in 1997 was half a million tonnes. (ILZSG, 1999b)

The most commercially important applications are as additives to glass for cathode ray tubes, and additives in PVC.

### 3.4 LEADED GLASSES AND CERAMICS

Lead oxide has been added to glasses and glazes since ancient times.

The main advantage to early glass-makers would have been the large reduction in melting temperature. Additions of lead compounds to silica-based glasses can reduce the softening temperature considerably (e.g. 20-30% PbO glass has a softening temperature of approximately 660-670°C, compared to pure silica, which softens at around 1600-1670°C. However, addition of alkali has a similar (though not quite so strong) fluxing effect, and a “typical” soda-lime glass (based on silica, with a total alkali content of about 30%) softens at around 700°C. (Bansal et al, 1986)

Additions of lead oxide also change other properties of the glass. Leaded glass has an increased refractive index giving it a more attractive appearance in crystal and making it suitable for certain optical glasses. The application of lead glass for radiation shielding, including TV-tubes, is based on the much higher absorption coefficient of leaded glass to X-rays.

The relatively low specific electrical conductivity and dielectric losses are the basic properties for the important application of lead glass in many electrical and electronic devices.

#### 3.4.1 LEAD CRYSTAL AND OPTICAL GLASS

Additions of lead oxide to glass have a number of advantages. Most importantly, it increases the refractive index of the glass, making it more sparkling in appearance. It also decreases the melting temperature of the glass, and makes the glass softer and easier to cut.

Full crystal glass normally contains 24-36% lead oxide; cheaper “semi-crystal” glass contains about 14-24% PbO. Smaller additions of lead are made to some optical glass, such as binoculars and telescopes, and to ophthalmic glass for spectacles.

*Alternatives* - Additions of some other oxides, such as barium or zinc, can give similar optical properties to glass. (Danish Ministry of the Environment and Energy, 1998)

Much research has concentrated on reducing the rate of lead leaching from the product, for example, by composition control or surface treatment. However, some crystal manufacturers are working to reduce lead contents of their products. One UK company developed a lead-free product for the Californian

market where there is great concern about leaded products. This glass, which contained some alternative additives including barium, was found to have equally good optical properties. It also did not give problems in manufacture, because the glass had similar melting behaviour and could easily be cut. The full scale manufacture of this glass was not pursued for economic reasons - chiefly the higher cost of the alternative raw materials. (M. Marshall, British Glass, personal communication, 1999)

As lead oxide imparts excellent optical properties to the glass, at reasonable cost, it is not expected to be replaced without strong economic or legal incentives.

It should be noted that some of the alternatives, particularly barium, can be toxic themselves. Also, many special glasses contain small amounts of other additives, some of which (arsenic, selenium) are also potentially toxic. There is relatively little data on the toxicity, and therefore the health and environmental impacts, of many of the alternatives.

Current EU regulations define qualities of lead crystal glasses in terms of their lead contents: lead-free glass could not be sold as "full lead crystal". (Information from M. Marshall and J. Stockdale, British Glass, personal communication)

### **Recyclability**

Lead crystal items generally have high value and will last indefinitely. They are usually kept, or perhaps sold as antiques, and only disposed of when broken.

No scheme is in place for collecting these items, and for the small number involved, it would not be economic. Also, as these glasses span a wide composition range - both of lead and also of other additives - adding large amounts of glass to the recycling process could affect product quality and melting behaviour. However, some leaded glass could be processed in some lead furnaces in Europe. (A. Bush, personal communication)

These glasses are not wanted in the normal waste stream of recycled container glass, because lead would act as an unwanted contaminant.

A large amount of waste generated in the factory, by cutting etc., is recycled in-house. Some of the lead dissolved into etching and polishing solutions is recovered by the glass industry, or returned to smelters for lead recovery.

### **3.4.2 RADIATION SHIELDING GLASS, CATHODE RAY AND FLUORESCENT TUBES, ELECTRICAL GLASS**

This is the largest current application for lead compounds.

The high density and good optical properties of leaded glass make it useful for these applications.

A television set or computer monitor incorporates a cathode ray tube, which produces X-rays when switched on. Thus, a high density glass is needed to protect the viewer. The visible front screen (panel) does not contain any lead in order to avoid the browning-effect that occurs when leaded glass is exposed to x-rays. The radiation shielding is accomplished by using barium in combination with a high wall thickness. The rear part of the picture tube, the funnel, contains around 22% of lead oxide. A substitution of lead by barium for the funnel is not possible due to the requirement of low wall thickness, especially in the yoke-area, in combination with high radiation protection.

Leaded glass is also used in hospitals, laboratories and nuclear power stations, for viewing X-ray equipment and radioactive materials from behind a safe screen.

**Alternatives** - Lead additions give excellent shielding properties to glass. No economically viable alternatives exist for current lead glass applications (M. Marshall and J. Stockdale, British Glass, personal communication). Some research indicates that it could be possible to replace the lead in cathode ray tubes with alternatives such as barium, strontium and zirconium, (which also shield from X-rays, though not as strongly) though no such glass is commercially available. (Danish Ministry of the Environment and Energy, 1998) Any alternative would certainly be much more expensive to produce, and it is questionable whether these materials could be supplied in sufficient quantities to meet demand.

It has been suggested that lead in fluorescent tubes could be replaced by strontium and barium, though the manufacturing process would be more difficult. (Danish Ministry of the Environment and Energy, 1998) Again, manufacture of alternatives would be far more expensive.

**Recyclability** - It is technically possible to recycle TV screens, or to recover the lead from them. This is currently not being done in Europe to any significant degree because of the lack of economic incentive. This situation may change with future EU legislation. However, some of these items are recycled in the USA (see Chapter 5). Leaded glass should not be recycled with ordinary bottle glass, as this would cause contamination.

### 3.4.3 CERAMIC GLAZES AND ENAMELS

There is an extremely long history of the use of lead compounds for glazing. Lead is still used in a wide range of glaze formulations for items such as tableware, wall and floor tiles, porcelain and some sanitary ware (toilets, washbasins etc). Lead compounds are also added to some enamels used on metals and glasses.

Lead compounds have the advantages that they have relatively low melting temperatures, good compatibility with substrate material, a wide temperature range for softening, good electrical properties, and give a hardwearing and impervious finish. They show good chemical durability under a range of both acidic and alkaline conditions (which occur in dishwashers). Lead compounds also have a relatively low cost.

*Alternatives* - There are alternative glazing systems available, though they may not perform so well under all conditions for all products. The ceramics industry in general is aiming towards voluntarily phasing out the use of leaded glazes in the long term, not because they consider there is any problem with the product, but primarily to avoid the need for leach tests on the products, and particular workplace health and safety procedures, which are legally required if lead is used. (J. Cope, Wedgewood Ceramics, personal communication)

*Recyclability* - Glazes and enamels are not suitable for recycling, as they represent a very small proportion of the final product and would be difficult to separate from the substrate.

#### **3.4.4 ELECTRICAL CERAMICS**

Some lead-containing ceramics, namely lead zirconate/lead titanate, have piezoelectric and other useful properties. They find applications as spark generators, sensors, electrical filters etc.

### **3.5 LEADED PIGMENTS AND PAINTS**

Many compounds of lead are strongly coloured and highly durable, so they have a long history of application in paints, pigments, and even cosmetics (see Annex). Some lead compounds are also added to paints as drying agents. These are very efficient through-dryers in alkyd-based air-drying paints. Typical lead contents are 0.1-0.5% in paints ready for use. Lead compounds were widely used before 1950; there was then a rapid move to alternatives so that they were virtually eliminated by 1960 in sectors such as household paints.

At present, the use of lead compounds has significantly been reduced, though they are still used for a few specific applications.

The main compounds of interest are:

#### **Powdered lead metal**

This used to be added to some paints for heavy duty corrosion protection.



**White lead**

White lead or basic lead carbonate, is an intimate mixture of lead carbonate, lead hydroxide, and sometimes lead oxide, and has an “ideal” composition  $\text{PbCO}_3 \cdot 2\text{Pb(OH)}_2$ . White lead can be formulated into paint which is very easy to work with. The product is very durable and has good external weathering properties. This was one of the major bases for white paint although its use was largely phased out in the 1950s. The only remaining and legally permitted uses are for certain historic buildings and in artists’ colours for restoration work.

**Oxides of lead**

There are four forms of lead oxide:

- Litharge,  $\text{PbO}$ , has two forms with different crystal structures: red and yellow
- Lead dioxide,  $\text{PbO}_2$ , which is brown
- Minium, or “Red lead”,  $\text{Pb}_3\text{O}_4$ , has a composition between the above.

The main present uses of lead oxides are in additives to glass and PVC, described separately; a mixture of litharge and lead dioxide is used in lead-acid batteries, as described earlier.

Red lead was historically used in paints because of its colour and as an anti-corrosive pigment in rust inhibiting primers used for the protection of steelwork. Its use today is very small.

**Other compounds**

Calcium plumbate used as a pigment in paints is very effective on galvanised steel, as it gives good corrosion resistance.

A quite important compound technically is basic lead silicate, used in cathodic electrodeposition primers for motor vehicles to improve throwing power and corrosion resistance. Non-lead systems with satisfactory performance are now available, but leaded systems are still in the large majority.

Lead is present as a naturally occurring impurity in a large number of pigments and fillers. Examples of raw materials used in the paint sector with impurities of lead are: talc, calcium carbonate, china clay, iron oxide black, perylene reds, anthraquinone reds, quinacridone reds and violets, phthalocyanine blues and aluminium pastes.

**Lead chromate pigments**

Chrome yellows and molybdate oranges are part of a whole group of inorganic pigments still in modern use. Chrome yellows and molybdate oranges are not single compounds but are solid solutions of lead chromate and lead sulphate, with the addition in the case of the oranges of lead molybdate, the colour properties depending on the proportions of each constituent and on the crystal form.

Lead chromate yellow and molybdate oranges/reds are, from a technical point of view, among the best and cheapest pigments for paints and plastics where opaque, bright end-colour is required.

They can, in many applications, be substituted by opaque organic pigments in mixture with other inorganic types, but at high cost and often with loss of brightness, opacity, flow, gloss or other technical properties.

The use of lead in lead chromate pigments represents approximately 1% of total worldwide use of lead. The global market of lead chromate pigments will be around 90,000 tonnes a year. Based on an average content of 60% of lead, the total lead consumption due to lead chromate pigments is around 55,000 tonnes a year. Market studies made in 1980/81 indicated a steep decline in the lead chromate market in the USA and Europe, to be followed by a flattening and subsequent modest increase in the later 1980s. Present indications now support this view. The recent market development shows a yearly decline of about 3-5% in Western Europe, and a decline of about 5-10% in the USA. For the former Eastern Europe and for Far-East countries the market-size will also vary depending on general industrial growth.

**Alternatives** - For rust-proofing primers, alternatives exist, such as paints containing compounds of zinc, although it appears that they are not so effective as lead, and more frequent repainting can be needed. (Danish Ministry of the Environment, 1998)

Although there are alternatives to lead for pigments, there is no replacement for some of the colours at comparable cost and with similar durability. For applications using coloured compounds, the final choice of paint depends on the precise colour required, and costs (Danish Ministry of the Environment, 1998).

**Recyclability** - Red-lead rust-proofing primer could, in principle, be recovered from steel structures by sand blasting, if present in large enough amounts, and if there was a large enough economic or other incentive to do so. In practice most of the lead is captured in steelworks flue dust when lead-painted steel is recycled.

### **3.6 PVC STABILISERS**

This is the second most important application for compounds of lead (after cathode ray tubes). (European Council of Vinyl Manufacturers, 1997)

All thermoplastics (plastics which soften on heating) require small amounts of additives, called stabilisers, to prevent the material degrading rapidly during manufacture, or in service.

All lead stabilisers are based primarily on nine basic lead compounds, which are all of low water solubility. A typical formulated lead stabiliser system comprises:

- lead compounds - two or more
- lubricant system - a combination of say stearic acid, calcium stearate and esters such as glycerol esters of fatty acids
- phenolic antioxidant system, to deal with oxygen attack on the carbon backbone
- organic costabilisers - often polyhydric molecules.

For PVC, lead salts are the most cost-effective stabilisers, and used for around three quarters of PVC applications. They are principally used in rigid PVC products, for example building profiles such as window frames, guttering, pipes and other products used outside. The incorporation of lead compounds can give excellent stability to heat and UV light, good electrical and mechanical properties, and good processing behaviour to the plastic. Flexible PVC cable used for insulation of electric wires is almost entirely made from PVC stabilised with lead. In this application, the lead stabiliser improves the dielectric properties of the insulation and is an efficient stabiliser, especially if the cable is exposed to higher temperatures.

The amount of formulated lead stabilisers used in Europe in 1998 was 112,383 tonnes, of which 98.55% was used in three main applications:

- pipes 35,902 tonnes (approx 13,000 tonnes of lead metal)
- cables 20,418 tonnes (approx 12,000 tonnes of lead metal)
- profiles 54,427 tonnes (approx 25,000 tonnes of lead metal).

(European Stabilisers Producers Association). Lead contents of PVC are in the range: 0.5 - 2.5 % lead.

**Alternatives** - Lead based stabilisers are technically very effective, and it takes the plastics industry a long time to develop alternatives which have equivalent performance at comparable cost. However, PVC manufacturers in several countries in Europe have begun to develop and produce PVC stabilised with alternative systems. This is chiefly for marketing reasons. Substitution in window profiles began in Austria, spread to other countries in the European Union, and is currently at about 15%. Alternatives for insulated cable are now produced in France, Italy and Scandinavia, following marketing pressure from Sweden, and substitution for this product is estimated at 25-30% in the EU, though mainly for less demanding applications. Substitution for pipes is low, because this is a much more demanding application. (Donnelly, P., 1999)

Several alternative stabilising systems are in use:

**Organo-tin compounds** have been used commercially for over 40 years. They can give good heat stability and outdoor weathering properties. These

grades of PVC are commonly used for rigid bottles and sheet. Organo-tin compounds are the next most widely used stabilisers after lead, but there is also concern about potential risks: Sweden plans to phase out the more hazardous organotin stabilisers by 2000, a position paper in Holland states that organotin levels should not rise above 1995 levels, and in Germany, discussions between the industry and authorities are taking place, since finding low levels of organotin stabilisers in sewage sludge. (Donnelly, P., 1999)

**Calcium-zinc stabilisers** impart good electrical and mechanical properties to the material, and also good weathering properties for outdoor applications. This system is considered non-toxic, and so is used for drinking water bottles, food packaging, and toys. Pipes for potable water in France and Belgium also use these stabilisers for the same reason. Calcium-zinc stabilisers are more expensive than other options, but research and development work is underway to increase their use in other applications.

**Cadmium-based stabilisers** also impart good properties to PVC, but these are being phased out for environmental reasons.

Electrical cable can be insulated by cross-linked polyethylene, as an alternative to PVC, but this is very little used at present. It is more expensive than PVC.

### **Recycling and end-of-life**

There is no current practice to extract lead from PVC residues. However, PVC pipes are recycled and in Holland 85% of what is available is recycled back to pipe. Germany has a window profile recycling plant. New windows are made from this material which incorporates a surface layer of virgin material to ensure the colour properties are correct. However, manufacturers are generally reluctant to use recycled material in view of problems of unknown feedstock, possible contamination, collection problems, and small price difference between virgin and recycled PVC.

PVC has a reasonably high calorific value, and can be disposed of by incineration; however, if lead stabilisers are used, these would add to the lead content of the incinerator ash. However, the voluntary commitment of the PVC industry is developing the use of alternatives to lead stabilisers (ECVM 2001). The presence of lead in this ash causes disposal problems. There is the potential for volatile lead oxide or chloride to escape as a gas, causing contamination of the environment (though in a well run incinerator, these should be collected in gas cleaning apparatus). Emissions are discussed more fully in Chapter 6.

## **3.7 PETROL ADDITIVES**

Since the 1920s, organic compounds of lead - tetraethyl lead and tetramethyl lead - have been added to petrol as an inexpensive way to improve performance.

However, these have drastically been reduced in recent years, particularly in the USA and Western Europe, and now account for only 1% of lead consumption. For comparison, in 1960 leaded gasoline accounted for over 9% of lead used, and in 1972 its use peaked at approximately 11% of total lead use. (Roskill Information Services, 1975)

### **How lead additions work**

Petrol, or gasoline, consists of a mixture of volatile hydrocarbons, suitable for use within a spark-ignited internal combustion engine, and having an octane number of at least 60. (Irwin et al, 1997)

The octane number is a measure of the burn rate of the fuel, and is defined as lying between 0 and 100. Petrol of higher octane number burns well and smoothly; low octane number petrol can cause “knocking” during combustion, giving poorer performance and causing some engine damage. The addition of the lead compounds to petrol increases the octane number. For petrols used in the EU, the increase is typically from octane number 89 to 97.

The addition of lead to petrol from the 1920s was hailed as a great success at the time, as it allowed good performance from fuel, without the need for sophisticated refining, which would make the fuel much more expensive. An additional benefit was that metallic lead deposited on the valve seats can act as a lubricant.

Amid mounting concern that the lead dispersed in the environment was causing damage to human health and the environment, a series of regulations and directives have been adopted in Europe since the 1980s, in order to phase out the use of leaded petrol. The maximum lead content of petrol has been reduced from 0.4g/l to 0.15g/l, (following the Lead In Petrol Directive 85/210/EEC) and further regulations on air quality - which limit the amount of lead in air - came into force in 2000, with an attainment date of 2005. Virtually all western European countries have now phased out the use of lead in gasoline.

However, in some countries in eastern Europe, higher levels of lead are permitted, up to 0.4g/l. In most of the newly independent states and the Russian Federation, permitted lead levels are 0.15-0.37g/l. Various strategies for reduction of lead in petrol have been made in these countries, though it is expected that some will have difficulty in achieving these targets.

Use of petrol is increasing in many other parts of the world, in particular the rapidly expanding economies in Asia. Higher lead levels are permitted in some countries, (though in China, the authorities have recently restricted the use of leaded petrol in Beijing).

In the USA, phasing out of leaded petrol began in the 1970s. This was instigated by the demand for catalytic converters, in order to reduce photochemical smog problems in the cities - catalytic converters are “poisoned” by the use of lead-containing petrol.

## *LEAD: THE FACTS*

The phasing out of leaded petrol is described in more detail in chapter 8: Emissions and Controls.

***Alternatives*** - Unleaded petrol is widely available in Western Europe as leaded petrol is being phased out. Modern vehicles operate on it without problems.

Older vehicles, designed to use high-octane rating leaded fuel, can have problems operating on unleaded petrol if the octane level of the unleaded fuel is too low. The production of high octane unleaded fuel requires either a more exact refining procedure (difficult in countries which do not have modern refineries, though this is not a great problem in western Europe), or addition of aromatic compounds, such as benzene, to the fuel. Some of these compounds are carcinogenic and can cause other problems to human health and the environment.

Some older vehicles with soft valve seats would not operate so well on unleaded petrol, because they require the lubricating effect the lead has on the valves.

# LEAD INDUSTRY PROFILE

## LEAD PRODUCTION

About 60% of lead produced world-wide is derived from ore. Lead ore is mined in many countries around the world, though three quarters of world output comes from only six countries: China, Australia, USA, Peru, Canada and Mexico. Small amounts are mined in several countries in Europe, with the biggest producer being Sweden. Total production has been at a similar level since the 1970s; new mines open or are expanded to replace old mines. (Note: all these mines contain at least two metals (also zinc, sometimes silver, gold and copper) so lead extraction is not the only reason for the mining.)

The production of refined metallic lead from minerals dug out of the ground involves a number of steps which are outlined below.

**Mineral extraction** - mining and separation of the lead-rich mineral (ore) from the other extracted materials to produce a lead concentrate.

**Primary production** - production of metallic lead from lead ore concentrates involves the following process steps:

**Smelting** - reacting the lead rich mineral with other ingredients, to yield impure metallic lead. This is traditionally done in two stages:

- roasting in air, turning the lead concentrate (usually lead sulphide) into lead oxide;
- heating the lead oxide in a blast furnace with coke to yield metallic lead.

Alternative single stage methods offer many potential advantages in terms of overall efficiency, energy consumption and lower emissions (e.g. QSL, Kivcet, Isasmelt, TBRC).

**Refining** - the removal of impurities and other metals from the crude lead (S, Cu, Ni, As, Sb, Bi, Ag, Au, etc.). The refining process is applied in several steps in kettles with addition of specific agents, or alternatively, smaller quantities are processed by electrolytic refining.

Total production of refined lead (from all sources) has a different pattern, with the highest production rates being in the more industrialised countries. North America and Western Europe produce over half the world's refined lead, and the trend is for slowly rising production. The world-wide trend is for a slow increase in production, though there have been short-term falls in production in the 1970s and 1980s, as a result of oil crises and economic recession.

**Alloying** - of refined lead with other metals to give the desired composition.

**Secondary production** - the production of refined metal by processing lead scrap. It is often possible to simply re-melt scrap lead, with very little extra processing. However, compounds of lead (such as battery pastes) require smelting. Refining is often needed to remove any unwanted contamination and alloying additions in the feed material. The procedures are similar to those outlined for primary processing, but in general, fewer operations are required.

The proportion of lead produced from secondary sources (i.e. scrap metal), which represents about 60% of total world-wide production, is also higher in the more industrialised countries. North America produces 70% of its lead from secondary sources, and Western Europe 60%. In contrast, Chinese production is almost entirely from ore.

In Western Europe the lead producing industry consists of:

- Primary production - eight smelters in five countries with a total capacity of 600,000 tonnes and a labour force of 2,000.
- Secondary production - 30 smelters in 12 countries with a total capacity of 750,000 tonnes and a labour force of approximately 3,000.

Secondary production requires much less energy (less than half) than producing lead from ore. (Primary production 7,000-20,000 MJ/t lead, secondary production 5,000-10,000 MJ/t lead).

## TRADE IN LEAD

Lead is bought and sold by many countries on the world market, in the forms of ore, impure metal and refined metal, as well as final products. The USA, South East Asia, and Western Europe are the largest importers of lead in its various forms, though many of these countries also export refined metal. The main exporters of lead are the countries which mine large amounts of lead ore.

## CONSUMPTION OF LEAD

Lead is used by all industrialised nations. The USA is by far the biggest consumer, with some countries in Asia (China, Japan, Korea) and Europe (UK, Germany, France and Italy) also using large amounts. Most of the lead is used for



batteries, an application which has grown enormously in importance. The use of lead pipe has declined, as it is no longer used for potable water supplies, though lead sheet is used in roofing and other applications, particularly in the UK. The use of lead in chemicals remains at about 10% of European consumption; much of this is used in glass for TV screens and stabilisers in PVC. Lead cable sheathing, shot and alloys are minor uses of lead. The addition of lead compounds to petrol was at one time a significant market, but this has already been phased out in the USA and most of Europe, and is declining in many other countries. It now represents a minor market segment with less than 1 percent of total consumption worldwide\*.

## **ECONOMIC VALUE OF LEAD**

It is impossible to calculate this accurately. The battery market is chosen as an example as the major lead-based product sold world-wide. Data for 1999 suggest that the automotive battery market had a turnover of \$6-10 billion, and batteries for back up power supplies \$2.85 billion, with the latter expected to expand rapidly.

### **Employment in lead and related industries**

Though there are no precise figures, estimates by the lead industry suggest that between 70,000 and 90,000 people are employed in lead mining, smelting and refining, and over 2,000 more in lead oxide manufacture. Battery manufacture is estimated to employ about 60-70,000 people. Many more work in industries which use small amounts of lead in their products.

*\*In countries which are members of the ILZSG, including: Australia, Austria, Belgium, Canada, Finland, France, Germany, India, Italy, Japan, Republic of Korea, Mexico, Netherlands, New Zealand, Scandinavia, South Africa, South East Asia, Spain, Switzerland, United Kingdom, United States.*

## 4.1 THE TECHNOLOGY OF LEAD PRODUCTION

### 4.1.1 PRODUCTION OF LEAD MINERAL FROM MINES

Lead has been mined in much of Europe for centuries, and even in the last century lead production in Britain, Germany and Spain was significant (Pulsifer, 1888). However, in most of the region, economic reserves have been exhausted. At present, the main lead mining countries are: China, Australia, USA, Peru, Canada, Mexico, and Sweden. Smaller quantities of lead are extracted from several countries in Africa, Asia, other Latin American countries and Europe. Lead extraction from the Russian Federation and Commonwealth of Independent States has greatly declined following economic change (ILZSG, Lead and Zinc Statistics, 2001).

It is extremely rare that lead is found in its native form as lead metal; as with most metals, it almost always occurs as a mineral, chemically combined with other elements, such as sulphur and oxygen. Although there are a host of different naturally occurring minerals which contain lead, the most important ore (mineral suitable for the extraction of the metal) is galena (lead sulphide,  $PbS$ ); other ores include cerrusite (lead carbonate,  $PbCO_3$ ) and anglesite (lead sulphate,  $PbSO_4$ ), which are generally found in small amounts nearer the surface of sulphide deposits. Lead-rich minerals frequently occur together with other metals, particularly silver, zinc, copper and sometimes gold. Thus lead is also a co-product of zinc, copper and silver production making the extraction of lead more economic than if it occurred in isolation.

#### Ore Concentration

The lead-rich ore, with a typical concentration range of 3-8% lead, must first be separated from other material (the gangue). The principle of using flowing water to wash away the lighter gangue particles, leaving the denser ore behind, has also been used since ancient times (e.g. Laurium, Greece, 5th century BC. Healy, 1978, cited in Blaskett and Boxall, 1990). More sophisticated methods which utilise differences in densities of the materials include jigging devices and rotating and shaking tables. These methods were in use by the end of the last century.

The modern method of ore concentration is froth flotation which allows much higher extraction efficiencies to be achieved. Also, both lead and zinc can be separated. The ore mixture is ground to very fine particles, preferably less than a quarter of a millimetre in size. The ground material is made into a suspension or pulp by adding water and other chemicals. Air is blown into the suspension and the addition of frothing agents allows a stable froth to form on the surface. Other additions can make mineral components become attached to the froth (for example, non-wetting agents), or sink to the bottom (termed depressants) as the process requires.

In the case of lead-zinc ores, the metals are usually separated in a two-stage process. First the zinc sulphide is depressed while the lead sulphide is floated off and removed. In a separate stage further additions are made to activate the zinc ore, and it is floated off. The froths are then broken down by water sprays and the mineral suspensions filtered to remove the water. A number of chemical reagents can be used in this process. They include zinc sulphate, sodium cyanide or sodium sulphite to depress the zinc, and copper sulphate to activate it.

## 4.1.2 PRIMARY PRODUCTION

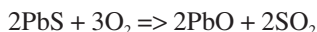
### 4.1.2.1 Production of Metallic Lead - Smelting

The next stage is to convert the lead ore into lead metal. The general name given to this type of process is smelting.

Historical accounts of lead smelting are described in the Annex - *Historical production and uses of lead*. Old lead workings are a current source of lead in the environment, and will be discussed in Chapter 6. Some of these early slags have proved to be a profitable raw material for lead extraction by more modern methods.

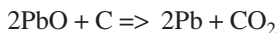
#### Traditional two-stage process

The first stage is to remove the sulphur from the lead ore by roasting the ore in air. The lead mineral is converted to lead oxide, and sulphur dioxide gas is released:



This is performed in a Dwight Lloyd Sintering Machine which allows continuous processing of ore. A mixture of finely divided ore concentrates and flux (the flux is required later), diluted with returned sinter fines or blast furnace slag, are placed on a moving grate and ignited. As the grate moves the charge forward, air is forced through the charge either from above, or in more modern plants, from below. The reaction is exothermic (i.e. heat is released). The lead sulphide is mostly converted to lumps of the oxide as shown above. The exhaust gases used to be vented to air but now they are routed to gas cleaning equipment to remove metallic fume and sulphur dioxide. The metallic dusts are returned to be re-processed. The sulphur dioxide generated can be used in the manufacture of sulphuric acid.

The second stage is to reduce the lead oxide to metallic lead using carbon (coke) as both the reducing agent and heat source. The lead oxide rich sinter from the first stage is placed in a blast furnace along with coke and limestone or some other flux (such as silica or iron oxide). A series of reactions take place in the blast furnace, but overall the effect is:



The lead is molten at blast furnace temperatures and is tapped off from the bottom of the furnace. The fluxes form a molten slag of metal oxides / silicates which floats on top of the liquid metal. The composition of this slag is chosen to enable it to collect most of the impurities from the lead. The slag generally contains a small amount of lead (around 2 or 3%, according to Blaskett and Boxall, 1990), and most of any zinc present (zinc containing slag can be processed to extract metallic zinc).

The lead obtained from the blast furnace contains small amounts of some metallic impurities also contained in the ore. These can include the metals: copper, arsenic, antimony, bismuth, tin, silver and gold. This lead is called lead bullion because of the presence of precious metals (molten lead has been used to extract silver and gold from other metals, such as copper, since ancient times). Separate refining operations are required to remove these metals from the lead, which are described later.

Besides processing ore, modern plants add small amounts of flue dusts (obtained from dust extraction systems treating exhaust air) and other lead-containing residues from their works and from other industries which produce dusts containing lead.

A variation of the traditional blast furnace is the **Imperial Smelting Process**. This operates in a similar way, but allows lead and zinc to be removed simultaneously, the lead in liquid form, and the zinc distilled off as a vapour. Lead and zinc usually occur together in ore bodies (and also some flue dusts), and this type of furnace has the advantage that it extracts these metals effectively, without the need for separation processes to be performed on the ore.

### **Alternatives to the two-stage process**

Although the above processes are effective in producing lead, they have some major drawbacks:

- there is much opportunity for pollution to occur during the operations and therefore extensive gas cleaning equipment is necessary;
- operating these two separate stages is inefficient in terms of energy consumption and plant required.

For these reasons, much research has been devoted to developing methods of extracting lead directly from its ore, without a separate intermediate stage. The main difficulty is that, if extraction is performed in a single vessel, either the metal obtained will have an undesirably high sulphur content, or the slag has a high lead content. (Some processes produce a slag rich in lead oxide, into which coke is added to reduce it to the metal, which is then returned to the furnace.)

However, a number of direct smelting processes are in operation or under development, including the Isasmelt, Kivcet, QSL, and Outokumpu processes. They employ differing furnace designs, methods of heat input and process control. In general emissions from such processes are much lower because:

- there are fewer handling stages of lead-containing material (during which dusts can escape)
- the smelting processes themselves are carried out within closed furnaces. In some cases the furnaces are maintained at pressures slightly below atmospheric pressure to limit dust and gas egress
- some processes use oxygen gas or air enriched with oxygen, rather than air, which reduces the volumes of gases that need to be handled and also increases the sulphur dioxide content of waste gases, enabling more economic production of sulphuric acid.

Most of the new processes can also process secondary materials such as lead sulphates, lead ashes etc.

Although these direct smelting processes all have advantages compared to the conventional sinter - blast furnace route, they still only account for about 20% of primary lead production (ILZSG World Directory of Primary and Secondary Lead Plants, 1997). However, this has increased from about 10% in 1992 (LDA Technical Notes, 1992) and is likely to increase further. The Imperial Smelting Process accounts for another 12% of primary production (ILZSG, 1997).

**Hydrometallurgical Processes** (which include **electrolytic processes**) are an alternative approach to obtaining and purifying metallic lead. These offer the advantage that, unlike traditional smelting operations, harmful lead fume and sulphur-containing gases are not evolved (although in modern plants, pollution control systems can reduce emissions to low levels. Industrial emissions are discussed in Chapter 8.) Hydrometallurgical processes always produce waste solutions that are rich in metal salts, which could be regarded as a useful resource for the recovery of metals, or as a problematic waste.

Hydrometallurgical methods are generally regarded by the industry as a much cleaner approach than pyrometallurgy, and may become important in the future (LDA Technical Notes 1992). (For comparison, copper is now produced and refined by hydrometallurgical methods, rather than pyrometallurgical.)

The principle for all such methods is that anodes of impure lead are dissolved into an electrolyte (a suitable solution or liquid which allows the passage of electrical current) and pure lead is deposited on the cathode. At present, this approach is not economical for primary production, except possibly in rare cases where there is a very cheap source of electricity (LDA Technical notes 1992; A. Bush, LDA, private communication, 1999). Electrolytic methods are sometimes used to refine lead which contains relatively small amounts of impurities, as described later.

#### 4.1.2.2 Lead Refining

##### **Pyrometallurgical Refining**

Refining involves the removal of metallic impurities from lead to yield a pure product. Lead often contains traces of several different metals, and separate stages are needed to remove these.

##### 1. *Copper*

The bullion is heated to just above its melting point and held at that temperature. Solid copper and copper sulphide, possibly mixed with sulphides of lead and other metals, rise to the surface of the melt and can be skimmed off. Sometimes sulphur is added to allow more effective removal of the copper. This impure copper is sent to be purified or is used to make copper-lead bearing material.

##### 2. *Arsenic, Antimony and Tin*

These elements are more chemically reactive than lead and can be removed by preferential oxidation. There are two methods available:

###### *The softening process*

Lead is melted and stirred with an air blast. The impurities are preferentially oxidised (along with some of the lead) and form a molten slag, which is skimmed off. "Softening" derives its name from the fact that these impurities harden the lead.

###### *The Harris process*

The molten lead is churned with an oxidising agent such as molten sodium hydroxide or sodium nitrate. After several hours the impurities have left the lead and are suspended in the flux as sodium arsenate, antimonate and stannate (tin); any zinc is removed as zinc oxide. The flux and lead are separated and impurities may be extracted from the flux. The major product, sodium antimonate, is refined. The tin is also refined and the arsenic is landfilled.

##### 3. *Silver and Gold*

Separation of silver from lead was performed in ancient times by the process of cupellation, which was effective but extremely inefficient. Cupellation is used primarily to produce silver. The lead metal was heated and stirred in air, eventually turning it completely to lead oxide, leaving behind metallic silver (and any gold present). If the lead itself was required, the oxide would have had to be re-smelted.

However, modern methods (the Parkes process or the more recent Port Pirie process) extract these precious metals with molten zinc. The lead is melted and

mixed with zinc; the precious metals form an alloy with zinc, which floats to the top and can be removed as liquid or cooled to allow the zinc to solidify. The zinc is removed from the precious metals by heating it under reduced pressure, which makes the zinc evaporate (vacuum distillation). The zinc is condensed and re-used; the silver is refined and sold.

#### 4. *Zinc*

The lead is now free from precious metals, but contains traces of zinc which must be removed. The usual method is, again, vacuum distillation. The lead is heated for several hours in a large kettle under vacuum and the zinc evaporates under the combined effects of temperature and low pressure. The zinc then condenses on a cooled lid.

#### 5. *Bismuth*

The only impurity likely to be left in the lead is bismuth, although this is not always present in the first place. Bismuth cannot be removed by selective oxidation as it, like silver and gold, is less reactive than lead. For years, it could only be effectively removed by electrolytic means (described below). As a result, ores rich in bismuth (particularly those found in Canada) have usually been refined using these methods. Electrolytic processes, such as the Betts process (described below), still remain the best way to obtain lead of very high purity. Alternatively bismuth can be removed by the production of stoichiometric  $\text{CaMg}_2\text{Bi}_2$  compound by adding calcium and magnesium as an alloy or as individual metals. Crystals form which can then be skimmed off.

The degree of purity finally aimed for is a balance between customer demand (i.e. added value of high purity lead, as traces of bismuth are acceptable for some applications) and the additional costs of removing further traces of this impurity.

### **Electrolytic refining**

This is an alternative to the refining stages described above and can be performed after copper removal and softening. Successful electrolytic refining has been possible since the Betts process was developed at the beginning of the 20th century.

**The Betts Process** uses large cast anodes (positive terminals about  $1\text{m}^2$  in area) of lead bullion (from which copper has already been removed), and thin starter sheets of high purity lead used for cathodes, (or negative terminal) onto which the new lead is deposited. The electrolyte used is a fluosilicate acid; (solutions of simpler electrolytes, including nitrate and acetate, did not allow successful deposition of lead.) When an electrical current is switched on, the lead anode slowly dissolves and purified lead is deposited upon the cathode.

A more recent variation on the above (developed in Italy in the 1950s) uses a sulphamate electrolyte which is easier to prepare and works equally well.

The main advantages of the electrolytic route are:

- any bismuth present is effectively removed (this process was favoured in Canada, where lead ores contained bismuth)
- higher levels of purity are possible
- dust and fume are not evolved as high temperatures are not needed.

However, drawbacks include:

- a separate treatment is needed to remove all of the tin
- extracting the mineral contaminants from the residues can be complex and difficult
- disposal of the solutions, which are rich in metals, can present environmental problems (though arguably less than the problems of fume)
- it is more expensive than pyrometallurgical methods.

### 4.1.3 SECONDARY PRODUCTION

Secondary production - the production of lead from scrap, rather than ore - is distinct from primary production. There are many plants which are dedicated to production of only secondary lead, while other plants are designed to produce primary lead. However, the processes involved are very similar, and a number of primary production plants now take some scrap as part of their feed material, i.e. produce part secondary lead, a trend which is likely to increase. Secondary lead can be indistinguishable from primary lead provided it is subjected to sufficient refining steps.

In Europe at present, approximately 50% of the lead produced is secondary lead. Most of this comes from scrap lead-acid batteries; lead pipe, sheet and cable sheathing are also significant sources. Scrap lead from the building trade is usually fairly clean and is re-melted without the need for smelting, though some refining operations may be necessary.

Of course, it is necessary to collect the waste materials, sort and remove other components and contaminants and prepare it in a form suitable for further processing. These operations are described in more detail in Chapter 5. Production of lead from secondary sources requires far less energy than producing lead metal from ore. It is estimated to use less than half of the energy used in primary production (LDA). A description of the smelting and refining processes follows.

#### 4.1.3.1 Secondary smelting

Only compounds of lead or very crude lead mixtures (such as pastes from batteries, or oxidised lead dust and dross obtained from other operations) need to be smelted. Smelting is not required for clean scrap lead.



Smelting was traditionally performed in a **blast furnace** in a similar way to the extraction of primary lead. The furnace is charged with lead-rich feed, metallurgical coke and possibly hard rubber battery casing. The lead bullion produced is usually high in antimony and requires subsequent refining steps.

In Europe, smelting is now generally conducted in smaller **rotary furnaces**. The principle is the same, but a greater degree of process control is possible. Adjustment of the charge can allow production of a “hard” (high antimony) crude lead, or a two stage process which yields a “soft” (more pure) lead product. In addition, greater flexibility in operation allows for better treatment of occasional batches of unusual composition. High throughputs of material are not necessary for economic operation, unlike blast furnace operation.

As with primary smelting, large volumes of gases are produced consisting mainly of air enriched with carbon dioxide, sulphur dioxide from contaminated feed (and also any sulphur present in the fuel), small amounts of other gases (depending upon the charge material used) and dusts. Dust filtering to a very low outflow concentration (less than 5mg Pb/m<sup>3</sup>) is now common practice in modern plants in the EU. The dusts are returned to the smelter. For the SO<sub>2</sub> reduction, iron can be added to the charge, or sometimes soda (with the disadvantage that it forms a slag with soluble components). Other solutions to reduce SO<sub>2</sub> emissions are leaching or alkaline scrubbing of the flue gases.

An example of a more modern approach to secondary smelting is the **Isasmelt process** (which can also be used for primary production). This process can deal with charge in any form including slurry, powder and wet or dry agglomerates making the process suitable for treating residues from batteries. The battery paste (a mixture of lead oxides and lead sulphate) is treated, for example with an alkaline solution, to remove most of the sulphate, yielding a lead rich paste which is low in sulphur. This paste is charged to the furnace and oxygen and fuel are injected through a lance causing heating and stirring which facilitates rapid chemical reaction. The furnace is continually charged with wet paste and coal and tapped every 3 hours to produce soft lead. After a suitable length of time (18-36 hours) the feed stops and reduction of the slag yields antimonial lead. There are difficulties in marketing the sodium sulphate so the choice of the sulphur removal process is site-specific (Note, the same opportunities for processing secondary materials are offered by some other modern smelting technologies such as the QSL). Off-gases are cooled and passed to a baghouse to remove dust and fume, which are returned to the furnace.

This process claims a number of advantages over traditional rotary furnaces: higher thermal efficiency; lower operating costs; direct production of both soft and antimonial lead alloy, which allows for blending to suit some applications; slags of low lead content, which reduce disposal problems; and good process hygiene. However, in reality some of these advantages can be very difficult to achieve.

All these processes are still in use. All have some advantages and disadvantages and it is not possible to place them in an order of preference.

#### **4.1.3.2 Secondary Refining**

The lead is either cast into blocks and re-melted in refining kettles or, in more modern plants, refining is performed on the hot lead bullion immediately after production.

Copper is removed in a similar manner to that already described (i.e. it is allowed to float to the surface of molten lead and is skimmed off.) A variation on this is to add iron pyrites and sulphur; this works at higher temperatures and also removes any nickel present. Other elements are removed by a modified Harris process using a flux of molten sodium hydroxide and nitrate to oxidise antimony, arsenic and tin. Bismuth and silver levels are normally very low and the metals rarely need to be removed.

### **4.2 LEAD PRODUCTION, TRADE AND CONSUMPTION: CURRENT STATUS AND TRENDS**

(All figures are for 2000, source ILZSG statistics, (2001), unless otherwise stated.)

#### **4.2.1 LEAD PRODUCTION**

##### **4.2.1.1 Production from Mines**

The main producers of lead mineral are: China, Australia, USA, Peru, Canada and Mexico. These six countries produce three quarters of world output. However, smaller reserves of lead are exploited elsewhere, as shown below, and in Figure 4.1.

Mine production in Western Europe accounts for a small proportion (8%) of global mineral production. The largest producer by far is Sweden (109,000t). Smaller amounts are extracted in Ireland (57,000t), Spain (51,000t), Greece (18,000t) and Italy (7,000t).

##### **4.2.1.2 Total Production of Refined Lead**

Total production includes both lead from ore (primary lead) and secondary lead, produced from scrap batteries and other lead-containing products.

Refined production is performed in more countries than mineral extraction. Countries not endowed with mineral deposits import ore or impure lead metal, scrap lead or produce lead from their own scrap. Some countries, such as Denmark, do not produce any of their own lead. The largest outputs of refined lead are in highly industrialised countries, which have a high demand for this commodity (see Figure 4.2).

**TABLE 4.1** World-wide Production of Lead Ore by Region

	Mine production in 2000 (lead content, in thousand tonnes)
Western Europe	242
Central and Eastern Europe	121
Africa	181
North America	607
Central and South America	446
China	560
Rest of Asia	135
Australia	650
<b>TOTAL</b>	<b>2942</b>

In Western Europe, in 2000, 12 countries produced refined lead and two others have produced small amounts earlier this decade. However, production by four of these countries, UK (394,000t), Germany (388,000t), France (262,000t) and Italy (228,000t), together account for over three-quarters of production (see Figures 4.3 and 4.4).

**TABLE 4.2** World-wide Production of Refined Lead Metal by Region

	Mine production in 2000 (lead content, in thousand tonnes)
Western Europe	1578
Eastern Europe	309
Africa	135
North America	1705
Central and South America	478
China	1051
Rest of Asia	1017
Australia and New Zealand	261
<b>TOTAL</b>	<b>6532</b>

#### 4.2.1.3 Secondary Production

World-wide, production of refined lead from scrap and other secondary sources now accounts for approximately 60% of total lead production.

Rates of secondary production are again higher in the more highly industrialised countries. In North America, processing of lead scrap accounts for the bulk (just over 70%) of metal output. In Western Europe secondary production accounts for 60% of lead output, in Africa 50%, in Latin America a

little under 50% and in Asia less than 30%. The Asian figure is dominated by Chinese production which is entirely primary.

In addition, some scrap is simply re-melted and used without further treatment. This is not included in any of the above figures, but world-wide is estimated at just under 400,000t per year. In comparison to total world output, this is a very small figure (less than 7% of total metal output). Even adding this to production figures, the world-wide proportion of lead produced from secondary sources, with or without refining, is 48% (1999 figures).

In Western Europe, the lead produced by each of the four major lead producers (UK, Germany, France and Italy) is between 50 and 75% secondary. Some other countries, namely Austria, Ireland, the Netherlands, Spain and Portugal, produce only secondary lead. Belgium was the only country to produce most of its lead from ore until 1998, but has recently made alterations to its plant and now produces most of its lead from secondary sources (G. Deckers, U.M. Hoboken, personal communication). (See Figure 4.3.)

It is likely that the proportion of secondary lead produced will continue to increase as patterns of lead use change. The phasing out of the major diffuse applications of lead (particularly in paints and petrol additives) from which lead is virtually impossible to recover, began in the 1950s and is still continuing. Applications which lend themselves to recycling (in particular batteries) are increasing.

**TABLE 4.3** Production of Secondary Lead in Western Europe in 2000

	Production (thousand tonnes)	% of total refined production
Austria	24	100
Belgium	108	92
France	139	53
Germany	213	55
Greece	5	83
Ireland	10	100
Italy	171	75
Netherlands	21	100
Portugal	5	100
Spain	97	100
Sweden	47	61
Switzerland	9	90
UK	179	54
<b>TOTAL</b>	<b>1028</b>	<b>65</b>

(ILZSG, 2001)

**TABLE 4.4** Location of Lead Smelters in the EU

	Primary	Secondary
Austria	0	4
Belgium	1	3
France	1	6
Germany	3	6
Greece	0	1
Ireland	0	1
Italy	0	6
Netherlands	0	1
Spain	0	5
Sweden	1	1
UK	1	6
<b>TOTAL</b>	<b>7</b>	<b>40</b>

Plants for production of primary lead are usually larger than secondary plants.

*Note:* figures separating primary and secondary production should be treated with some caution, as many primary facilities increasingly use secondary raw materials as part of their feedstock.

## 4.2.2 WORLD TRADE IN LEAD

### 4.2.2.1 Overview

Lead is mined in many countries, in every continent around the world, though the bulk is in China, Australia and the Americas.

Some countries have mineral reserves and produce lead entirely or largely from this source, in particular China, Australia, Mexico, Iran, Turkey. However relatively few countries are self-sufficient in lead, and many large consumers of this metal have few mineral reserves. These countries must import lead metal or ore, or use their own scrap to add to any mineral reserves they have. The largest producers in this category are the USA, most of Western Europe, Japan, Republic of Korea; there are also many other such smaller producers of lead world-wide.

There are a number of stages between mineral extraction and production of refined metal ready for use. These processing steps can be carried out:

- in the producer country (such as in China, which refines almost all of its lead) for overseas markets after domestic demand has been met,
- in a consumer country primarily for its own needs (such as in Japan, Austria), or
- in a country which imports ore, impure metal or scrap, refines the metal, then exports a higher value commodity (performed in many countries in Europe, including Belgium, France, UK).

Thus there is a large international trade in lead: as mineral, smelted but unrefined metal, refined metal ready for use, scrap metal, and lead products.

A detailed breakdown of imports and exports of the different grades of metal is not easily available. It is also complicated by the fact that many countries import from, and export to, up to a dozen or more other countries; also many states both import and export lead metal, and some even lead ore. However, figures for imports and exports of lead ore and metal provide information given below. All figures refer to 1999 imports and exports, unless otherwise stated, because information about 2000 flows is incomplete.

#### **4.2.2.2 Trade in lead ore**

##### **Exporters of lead ore**

The largest exporters in 1999 were Peru (147,000t), Australia (256,000t), followed by South Africa (66,000t), Canada (49,000t), Sweden (71,000t), Ireland (40,000t), the USA (93,000t), Poland (46,000t), Morocco (26,000t) and Spain (23,000t).

##### **Importers of lead ore**

The most recent figures (for 1999) show that the largest importers are France (115,000t) and Japan (122,000t), with significant imports being made into China (102,000t), Republic of Korea (90,000t), Canada (56,000t), Germany (111,000t), the UK (37,000t), Bulgaria (115,000t), Italy (110,000t) and Belgium (58,000t).

#### **4.2.2.3 Trade in lead metal**

The world-wide trade in lead metal is much larger than the trade in lead ore.

##### **Exporters of lead metal**

The largest exporters of lead metal are nations which mine large quantities of lead ore: China, Australia and Canada. In 1999 they exported 450,000t, 255,000t and 166,000t respectively.

Significant exports also occur from Europe, in particular from the UK (81,000t), Belgium (71,000t), France (76,000t), Germany (80,000t), Sweden (57,000t) and Italy (23,000t).

World-wide, other important exporters are Mexico, the USA, Peru, Morocco and South East Asia.

##### **Importers of lead metal**

The largest importer of lead metal is the USA, at 311,000t in 1999. However, this is a small quantity compared to the country's total production. Asia and Western Europe import very large quantities of lead with the largest importers being

Korea (117,000t), Taiwan (121,000t), Malaysia (117,000t), Singapore (90,000t), Italy (91,000t), Germany (87,000t), France (67,000t) and Spain (100,000t). The quantities of lead imports are generally rising slowly in the western world, and very rapidly in eastern Asia.

A summary of the main imports and exports of lead ore and metal is given in Table 4.5. This is derived from the above statistics for imports and exports from individual countries and is intended for use as a guide, as the information is not entirely complete.

It should be noted that there will be some other omissions, for example some countries; such as New Zealand, produce lead metal, but there is no record of their import of lead mineral or metal, or mine production. However, it is expected that such inaccuracies are relatively minor compared to total metal flows.

**TABLE 4.5** Worldwide Trade in Lead Ore and Metal in 1999

	Lead ore and concentrates (thousand tonnes)		Lead Metal (thousand tonnes)	
	Imports	Exports	Imports	Exports
Western Europe	430	195	477	394
Central and Eastern Europe	46	46	20	85
Africa	12*	94	15	57
North America	68	142	322	189
Central and South America	Not known	170	62	128
Asia	314	20	552	529
Australia	0	256	0	255
<b>TOTAL</b>	<b>870</b>	<b>923</b>	<b>1448</b>	<b>1337</b>

\* Data for 1998

#### 4.2.2.4 Lead stocks

Many countries have very small stocks of lead. There is an estimated global total of 471,000t held by producers, consumers and the London Metal Exchange (1999 figures). This is equivalent to 4 weeks of consumption. The only country with significant stocks is the USA, which had a strategic stockpile of 252,000t in 1999.

### 4.2.3 LEAD CONSUMPTION

#### 4.2.3.1 Global consumption of lead

Lead consumption world-wide has grown since the 1960s, and is currently at an all-time high of over 6 million tonnes (ILZSG 2001). This is almost double the consumption in the early 1960s. This growth in lead use has not been smooth. Drops in world demand followed the oil crises in 1973/4 and 1979, and again in 1989 to the early 1990s following the end of the Cold War and economic collapse in the former Soviet Union. However, the overall trend in consumption is slowly rising in spite of the phasing out of lead in paint, petrol additives and water pipes.

The largest growth in consumption has been in Eastern Asia due to increases in automobile production and use. There have also been small increases in demand in the USA and, to a lesser extent, in parts of Eastern Europe and Latin America.

All industrialised nations use lead. The USA is by far the greatest consumer, most of it being used for batteries. Other major consumers are: China, UK, Germany, Japan, Republic of Korea, France and Italy. Spain, Mexico and Brazil use less, but still more than 100,000t of lead each in a year. Smaller amounts of lead are used in most other countries around the world. (See Figure 4.2.)

**TABLE 4.6** Consumption of Refined Lead by Region

	Consumption of Refined Lead 1999 (in thousand tonnes)
Western Europe	1699
Central and Eastern Europe	300
Africa	127
North America	1859
Central and South America	392
China	524
Rest of Asia	1286
Australia and New Zealand	64
<b>TOTAL</b>	<b>6251</b>

#### 4.2.3.2 Lead consumption in Western Europe

The largest consumers are: UK (19%), Germany (22%), France, Italy and Spain. These countries consume 84% of all the lead in Western Europe (ILZSG, 2001). The consumption of lead in Eastern Europe is much smaller, in total less than the UK consumption.

#### 4.2.3.3 Breakdown of end uses of lead

The applications and uses of lead metal and lead compounds are detailed in Chapter 3 of this volume.



## **4.3 ECONOMIC VALUE OF LEAD**

### **4.3.1 LEAD PRODUCTION AND TRANSFORMATION**

Lead ore is currently produced at a rate of over 4 million tonnes a year of concentrate, having a lead content of 3.1 million tonnes. This has a market value of \$2.2 billion (1998 figures). In 1998, 6 million tonnes of refined lead were produced, which was worth almost \$4 billion. Consumption of 6 million tonnes of lead in this year was estimated to have a total market value of \$4.5 billion. It has been estimated that all mining, smelting and refining operations world-wide are worth around \$15 billion per year (ILZSG, 1999b).

### **4.3.2 LEAD-CONSUMING INDUSTRIES**

#### **Batteries**

Automotive SLI lead-acid batteries are the largest use of lead. Available data suggests that in 1999, approximately 270 million SLI batteries were produced, which had a market value of between \$7 and \$10 billion. There are currently 500 manufacturers of lead-acid batteries world-wide. Currently, 41% of the market is in the USA, 27% in Europe, 16% in Japan and the rest of the world uses the remaining 16%.

#### **Lead compounds**

Half a million tonnes of lead compounds were sold in 1996. The majority of this total was lead oxide with sales of \$650-680 million. Most were used in the manufacture of cathode ray tubes and PVC additives. Sales of lead oxide to cathode ray tube manufacturers are worth around \$250 million a year. In 1995, 127 million television sets and 57 million monitors were sold, each of which incorporated a cathode ray tube, accounting for sales worth around \$70 million. The market for leaded PVC is worth approximately \$4 billion a year.

## **4.4 EMPLOYMENT IN THE LEAD AND RELATED INDUSTRIES**

It is estimated that world-wide employment provided by lead mining, smelting and refining, is around 72,000 - 89,000, with a further 2,400 employed in lead oxide production. Many more people are employed in industries which use lead as a component in manufactured products. The lead-acid battery industry provides employment for about 60,000-70,000 people world-wide.

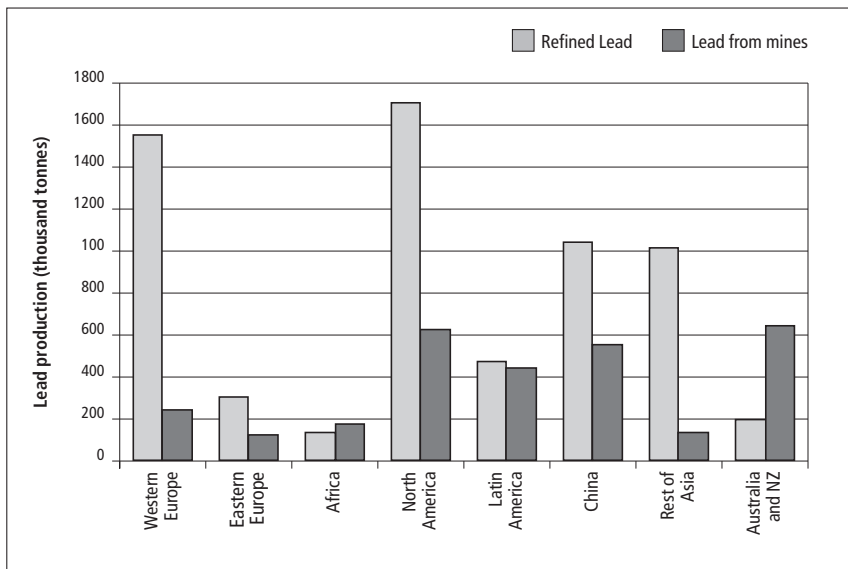


Figure 4.1 Lead Production by Region in 2000

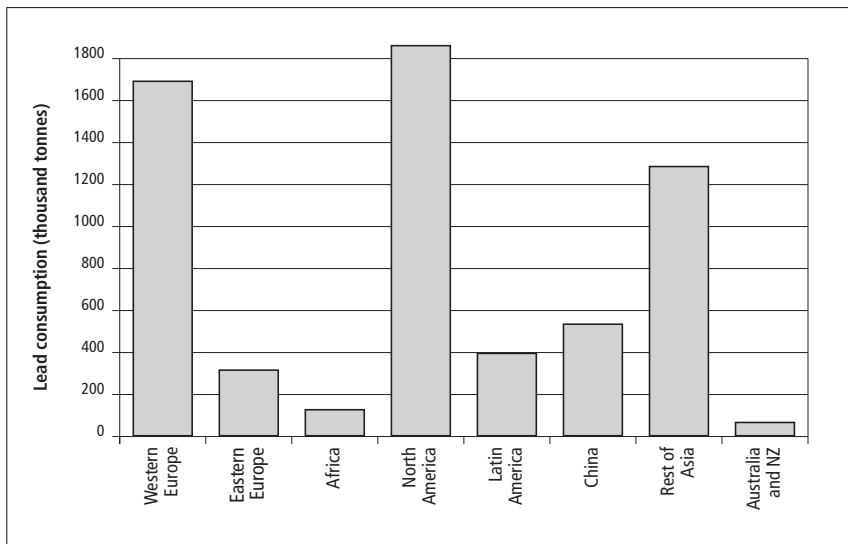
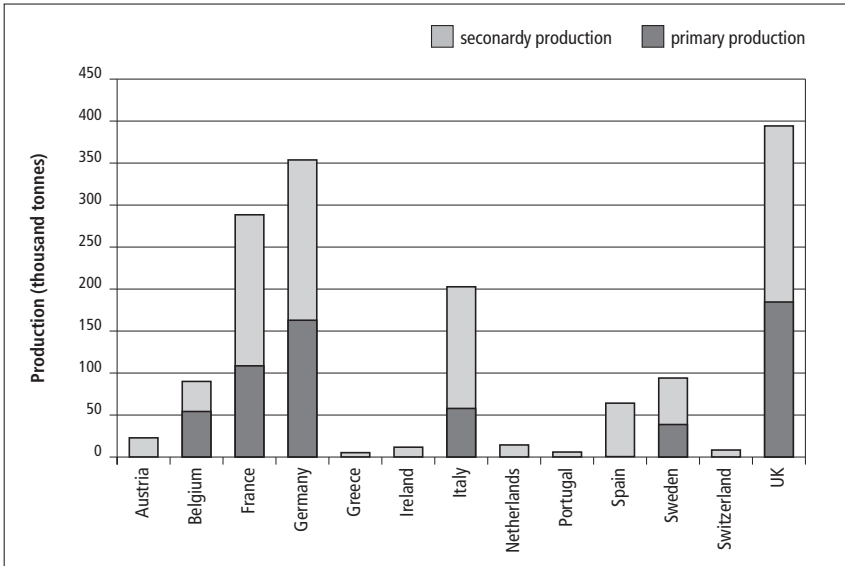
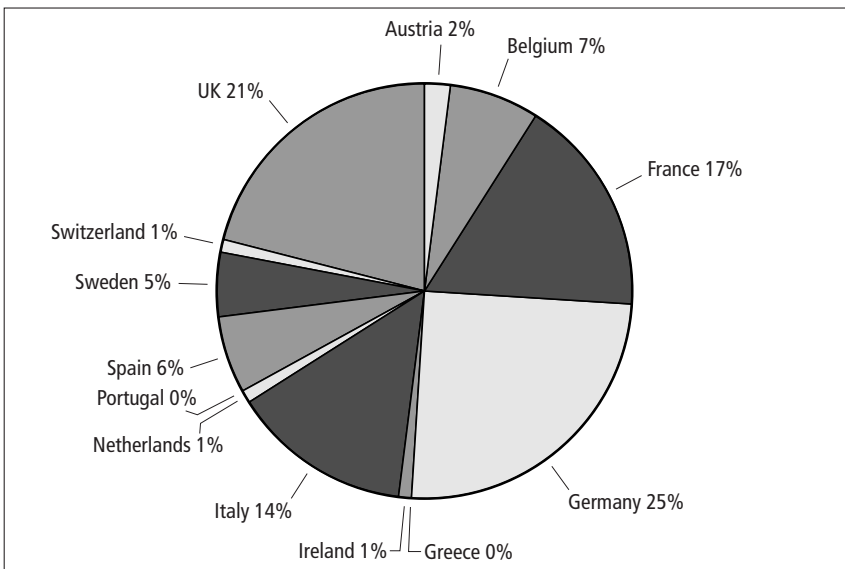


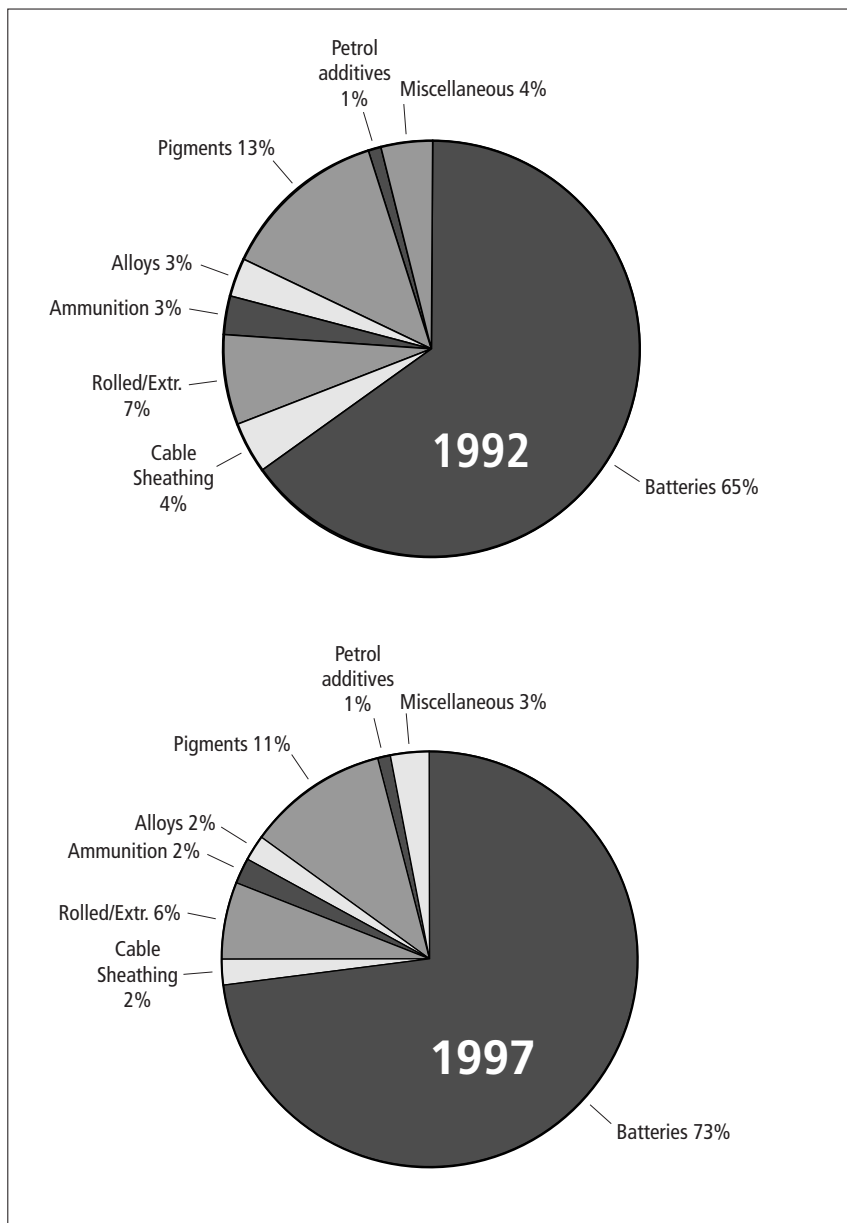
Figure 4.2 Lead Consumption by Region in 1999



**Figure 4.3** Primary and Secondary Production of Refined Lead in Western Europe in 1998

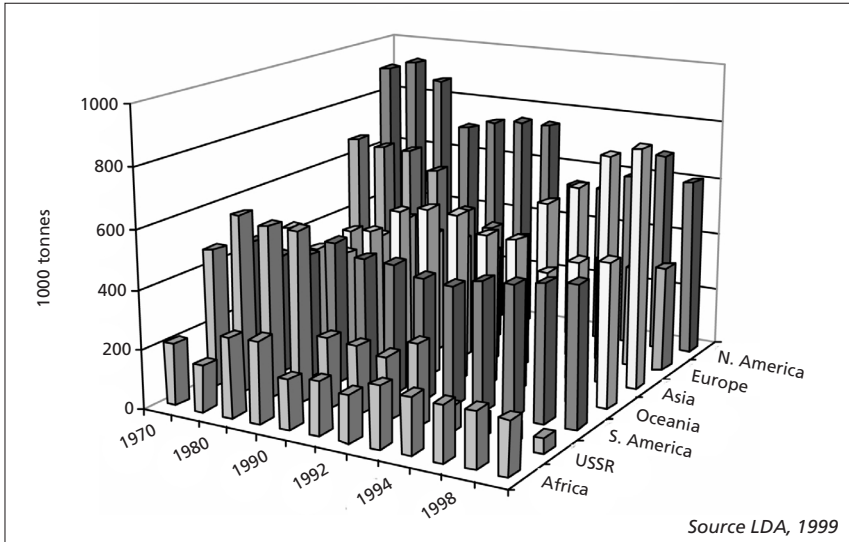


**Figure 4.4** Refined Lead Production in Western Europe in 2000

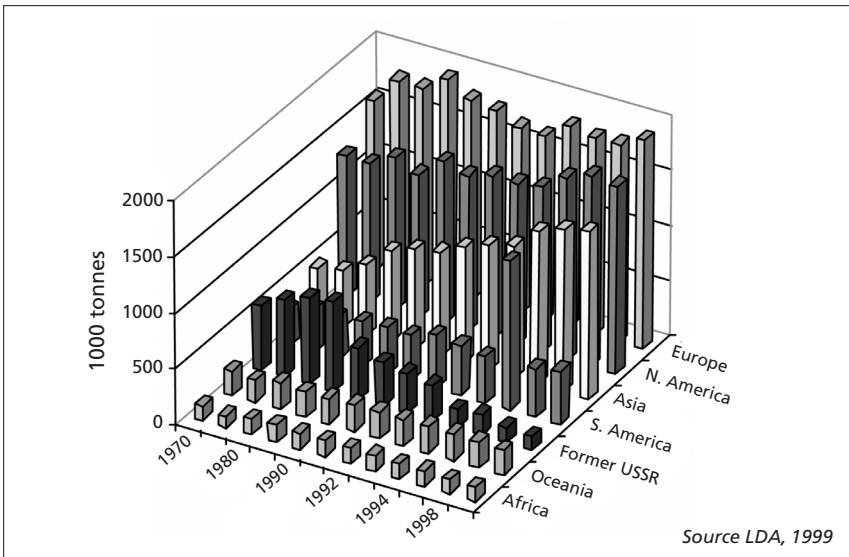


**Figure 4.5** Comparative Uses of Lead in 1992 and 1997

This data refers to the total use of lead in countries which are members of the ILZSG, together accounting for over 80% of the total global consumption of lead.



**Figure 4.6** World Lead Mine Production 1970-1998



**Figure 4.7** World Refined Lead Production by Principal Producers, 1970-1998



## CHAPTER 5

# RECYCLING OF LEAD

Lead is a material which is very easy to recycle. It can be re-melted any number of times, and provided enough processes to remove impurities are performed, the final product (termed secondary lead) is indistinguishable from primary lead produced from ore.

The amount of lead recycled as a proportion of total production is already fairly high worldwide. Over 50% of lead consumed is derived from recycled or re-used material; the figure is higher in Western Europe (60%) and the USA (70%). Secondary production rates compare favourably with other metals.

The long lifetimes associated with some applications of lead coupled with steadily increasing production mean that secondary production as a proportion of total production is not a good indicator of the actual recycling rate for lead (defined as lead recycled as a proportion of end-of-life material).

Recycling rates of lead and other metals are estimated to be much higher than for other materials such as paper, plastics and glass. Disincentives to recycle these materials include: low costs of raw materials to make virgin products, relatively high collection and transportation costs for a low value product and, particularly for plastic and paper, problems with inferior product quality.

Factors influencing high collection rates of lead are:

- the biggest consumer of lead is the battery industry which has a very high rate of collection and return of scrap batteries in most EU Member States;
- many other products used in much smaller amounts are suitable for recycling, and may be returned via scrap merchants;
- in conjunction with the iron and steel industries, zinc, copper and lead are recovered within the recycling processes of these industries;
- some applications which result in its unrecoverable dispersal into the environment, in particular as petrol additives and some paint uses, are being drastically reduced.

Recycling is performed where the industry finds it economic to do so. Recovering scrap metal has the advantages that it is easier and much less energy intensive than producing primary lead from ore (the production of recycled lead

## *LEAD: THE FACTS*

requires 35-40% of the energy needed to produce lead from ore.) Recycling also reduces dispersal of lead in the environment and conserves mineral resources for the future.

It is estimated that at least 85% of lead consumed could potentially be recycled. However, in practice the amount that is recovered is lower.

Some lead products are not recycled, either because it is not economic to do so at present, or simply because it is not practical to do so. However, recycling rates are generally increasing. Legislative and economic factors are two key incentives for this increase.

Any figures for recycling rates of lead must be treated with caution. Figures for recycling rates of lead batteries are available in a few countries, such as Italy, where collection systems involve recording this information. However, for lead recycling in general, quoted recycling rates are usually based upon estimates from lead consumption and secondary production. These figures can be distorted by:

- international trade in both scrap and refined lead;
- long time lags as a result of the long service life of some products;
- changes in lead consumption, which is generally rising world-wide, so that even a total recovery of lead would not be sufficient to meet demand for new lead products.

Improved waste management systems, such as incentives for battery recovery, guidelines for handling old building materials, old vehicles, electronic scrap, stricter quality demands for dumping materials and also progress in production techniques tend to generate higher recycling rates.



## 5.1 RECYCLING PROCESSES

The main stages of the recycling process are:

**Collection and transportation** - via one of several routes to scrap dealers, or in the case of batteries, to battery wholesalers, then to producers of secondary lead.

**Material preparation/sorting** - generally involves breaking or grinding the articles into small pieces, which can be separated. This can be done immediately after collection, such as at car scrap yards, or as an initial preparation stage at the smelters.

**Melting and smelting** - to recover metallic lead. Clean metallic scrap such as pipe and sheet is simply melted; other scrap, especially where lead compounds are involved, requires smelting.

**Refining** - to remove the metallic impurities from lead metal.

**Alloying** - to form the desired composition of the product.

Where no dedicated collection system operates, most collection and return of material is via scrap merchants, with the scrap value of the metal providing the incentive for recycling. For the special case of lead acid batteries, some countries operate formal collection systems, which are discussed later.

Smelting and refining procedures for lead scrap have already been described in section 4.1.3 Secondary Production. Smelting of metal scrap is often not necessary if the metal comes from a “clean” source such as lead sheet or piping. However, refining may be needed to remove any unwanted metals present in the scrap material.

Smelting and refining of secondary lead can often be performed in a plant designed to produce primary lead as the processes are very similar. However, secondary lead is generally produced in dedicated works, as this allows for more efficient processing.

## 5.2 RECYCLING OF MAJOR LEAD PRODUCTS

### 5.2.1 LEAD-ACID BATTERIES

#### **Collection of batteries**

The collection rate of scrap batteries is very high in most highly industrialised countries, and has been for many years. In the European Union a Batteries

Directive looks set to oblige Member States to ensure a high rate of battery collection. Some Member States already have organised collection schemes to increase collection rates, with obligations for retailers and producers to accept batteries returned to them. A levy is imposed by several countries, which is used for such purposes as: to help fund collection, transportation and return of batteries to smelters; administration of collection schemes; publicity and information; inspection of secondary smelters to ensure low emissions; and research into cleaner methods of recycling.

Stated collection targets range from 100% in France and 99.9% in Denmark, to 75% in Portugal. (Bied-Charreton, 1997) Some Member States, including the UK, have not set up any formal system as a high (estimated at >90%) recycling rate is already achieved by existing routes using scrap dealers. However, this relies purely on the scrap value of lead providing an economic incentive, so at times of low value, there is less incentive for collection.

### **Preparation of lead-acid batteries**

The batteries are broken open, crushed and automatically separated into their different components: case materials, metal grids and poles, and “pastes” of lead oxides and lead sulphate. The acid is collected and rendered harmless prior to disposal or reuse by other industries. The plastic material is separated into polypropylene and other plastics (hard rubber, PE etc). The latter are discarded or used as a fuel. The polypropylene is cleaned, composited with additives and molten to produce a PP-compound of desired quality for various applications (e.g. car parts, video cassette casings, plant pots etc.). The metallic components are sorted ready for smelting. The pastes, consisting of a mixture of lead oxides and sulphate, are usually treated to remove most of the sulphur (for example, with an alkaline solution). The components are then ready for smelting.

### **Smelting of battery pastes, grids and other materials**

The battery pastes (consisting of lead oxide/hydroxide/carbonate, with a small amount of sulphate), perhaps together with oxidised lead dross obtained from other processes, are fed into the furnace together with coke or other carbon-rich reducing agent and the mixture is smelted. The lead compounds are reduced to yield a lead metal which is low in antimony. Grid metal is smelted in the same furnaces to produce an antimony containing lead. The crude metals are ready for refining.

### **Refining/composition control**

The lead can be refined to produce soft lead suitable for any application using processes previously described. However, more commonly, recovered battery lead is used to produce new battery alloys. This has the advantage that less refining may be needed, provided the charge consists predominantly of lead

batteries. Extra refining may be needed if other scrap is included in the charge material. Some impurities can be tolerated at low levels, though quality demands for modern battery alloys require some impurities to be present in concentrations of <0.1 ppm. The tolerable limits for elements are set according to the effects of the elements upon the electrochemical or physical behaviour of the lead, i.e. how it functions in a battery. (A. Bush, LDA, personal communication)

### **Addition of other types of scrap**

Lead used for roofing, cable sheathing etc. generally has a different composition to battery-lead. Small additions of such scrap can be tolerated in battery production; again, larger additions could necessitate more refining steps. In a modern secondary plant, lead battery alloys are produced from all types of scrap.

## **5.2.2 LEAD SHEET, PIPING, CABLE SHEATHING**

Although there is no formal system in place, most metals are stripped from old buildings before demolition and sold on to scrap merchants. The recovery rate is not known accurately, but is estimated to be very high (Lead Sheet Association). This scrap is “clean” and is generally sold on to facilities producing similar products, so that the same alloying additions are required as are present in the scrap.

Cable sheathing is sometimes recovered after the end of the useful life of the cable. However, it is often not economic to collect old cable, as collection can be more expensive than the value of the metals. The lead sheathing has a relatively low commercial value; however, cables are recovered primarily for their more valuable copper. Cables are more likely to be recovered if they are in accessible locations (e.g. in soil, rather than on the sea bed) and have high copper contents (for example high power cables). Once a cable has been recovered, it is fairly easy to separate the different components and deliver them to scrap dealers.

## **5.2.3 END-OF-LIFE VEHICLES**

Motor vehicles contain small amounts of lead besides the battery. Lead alloy is often used to coat the vehicles’ petrol tanks (which are made of steel) to prevent corrosion. Some of the car components are made of leaded steel, the lead being added to improve machinability as previously described. Other parts which can contain lead include balance weights on wheels and vibration dampers, some brake linings, electric and electronic solders, aluminium casting alloys, brass alloys, sliding bearings, stabilisers in plastics, ceramic coatings, glass and glass coatings, lamps, piston coatings, hot dip galvanised steel and printed circuit

boards. For the purposes of a study of the environmental impacts of these lead-containing components, it was estimated that the battery had a lead content of 10kg (the highest content known in any vehicle batteries) and all other components together contributed 2.5kg lead.

Some of this lead can be returned to lead smelters via the vehicle recycling chain. Scrap vehicles are shredded and separated into ferrous (iron and steel), non-ferrous metallic and the non-metallic fluff fractions. It is estimated that, of the 2.5kg lead in the car (after battery removal), 1.0kg is contained in the ferrous fraction, 1.0kg in the non-ferrous fraction, and 0.5kg in the fluff (though less than 0.5g derives from leaded machining steels). The ferrous fraction is returned to the steelworks. When charged to the furnace, almost all the lead present is evolved as fume. The vapour, which condenses to a dust, is collected in pollution control equipment together with all the other dust components, particularly zinc. Where this dust is rich in lead (and also zinc) it is recycled by the Waelz-kiln process and Imperial Smelting Process to recover both zinc and lead. It is also possible to recover lead from the non-ferrous fraction and some companies routinely do this.

The lead contained in the fluff may be passed to an incinerator, and potentially contributes to lead emissions to the environment, though pollution control equipment should reduce such emissions to very low levels. (See Chapter 6.)

#### **5.2.4 ELECTRICAL AND ELECTRONIC PRODUCTS**

Lead-tin solder is the most widely used material for electrical connections in electrical and electronic goods. If such end-of-life articles are collected and recycled because of their copper value, then lead (and tin) can be recovered simultaneously. At present, some recycling of smaller electrical and electronic parts is done in Europe (examples of such facilities are in Boliden, Sweden, and the UM-Hoboken plant in Belgium). Although the practice is not widespread at present, and they generally enter the waste stream at the end of their lives, recovery rates are expected to increase in the future. The main driving force for this in Europe is the EU directive on waste electrical and electronic equipment, which is currently in preparation. This is expected to set targets for the recycling of such material.

Scrap electrical and electronic equipment can be treated in a broadly similar way to vehicles: ground up into fine particles and separated into different fractions. In this case, most of the lead would be collected in the non-ferrous metallic fraction. This fraction would then be processed to separate the different metals.

The main monetary value of this recycling lies in any precious metals present. However, lead is also routinely recovered in the process.

### 5.2.5 CATHODE RAY TUBES

The main source of cathode ray tubes is TV sets and computer monitors. Again, very little recycling is done in Europe at present, though considerable amounts are recycled in North America. However, European practice looks set to change in the future as recycling rates for electrical and electronic equipment are predicted to increase. The practice of recovering these items in the USA may be regarded as an example to aim for.

Because of lead's intrinsic properties there is no substitute available for its use for radiation protection in the cone-glass in cathode ray tubes. The draft EU Directive on electric and electronic waste takes these facts into account by making an exemption from a ban.

Leaded glass could be returned to glass manufacturers for recycling. At present, the glass industry is not doing this because there is no economic incentive to do so. If economic conditions were to change in favour of recycling, it is believed that an operational scheme could be set up within 3-5 years. (M. Marshall, British Glass, personal communication.) The glass industry is also concerned about impurities present in old glass, such as metals, enamel and porcelain, which can damage furnace linings.

In some countries television screens from different manufacturers have significant differences in compositions, which could cause some difficulties for manufacturers, though the difficulties are not insurmountable. Television screens sold in some other countries have very similar compositions, so recycling would be easier.

Alternatively, lead can be recovered by returning the tubes to lead smelters for lead recovery. The glass can be ground up and added to the furnace. This glass consists largely of silica, which is necessary to produce the slag, (the non-metallic material which floats on top of the metal during smelting, and is essential for removing some impurities from the metal, as mentioned in section 4.1.2.1 Primary Smelting) and is usually added anyway for this purpose. Most of the lead from the glass ends up in the metal fraction. The economic margin is less than for recycling into new glass as the lead content of cathode ray tubes is typically around only 8% (average of all parts of the tube - M. Marshall, British Glass, personal communication). However, separation of the front panel (screen) would result in a higher average lead content.

## 5.3 NATIONAL POLICIES AND COLLECTING STRATEGIES

This section is based on a summary paper by B. Bied-Charreton, METALEUROP, published in the Proceedings of the 12th International Lead Conference, 22-25 September 1997.

### **EC Directive on Batteries and Accumulators**

Council Directive no. 91/157 of March 1991 on batteries and accumulators containing certain dangerous substances covers batteries and accumulators containing more than 0.4% lead by weight (and also more than 0.025% cadmium by weight, alkaline batteries containing more than 0.025% mercury by weight, and other batteries containing more than 25mg mercury per cell).

The Directive offers the opportunity for a legal framework for battery recycling, for batteries to be considered as “clean” products because of their recyclability, and for their acceptance by Member States even though they do contain heavy metals. Member States may set up disposal or collection systems and use measures such as economic instruments to encourage collection (after appropriate consultation, provided such instruments could be justified on ecological and economic criteria, and that they avoid distortion of competition).

Some Member States had their own regulations in place prior to the Directive. National regulations in Member States include:

**Sweden** - to address transportation problems, a number of measures have been introduced. The producer or importer pays a fee, which is used to fund collection, transportation and information/PR, to keep the recycling rate above 95%. Batteries can be returned to retail outlets where they were purchased, to municipality recycling yards or to scrap collectors.

**Italy** - the customer pays a fee on each battery, which is used to fund a consortium which buys, collects and delivers old batteries to smelters. The consortium also carries out research into cleaner methods of battery treatment and ensures that recycling is performed under clean conditions. The recycling rate is reported to be above 95%.

**Austria** - there is an obligation on all retailers of batteries and accumulators to take back used batteries returned by the customer.

**Denmark** - a fee is imposed on all producers and importers of lead accumulators, and all retailers are obliged to accept used accumulators free of charge. This fee is given as a bonus to collectors who deliver used accumulators. The authorities aim to reach a collection and recovery rate of 99.9%.

**Germany** - an obligation is placed on retailers of batteries to accept old ones from consumers, and on battery producers to accept them from retailers. A deposit of DM 15 per lead battery is levied on the buyer of a new battery if an old battery is not returned. This is a special regulation for starter-type lead batteries.

**Netherlands** - collection of end-of-life vehicles is organised and financed by Auto Recycling Netherlands BV, with a fee on every new car.

**United Kingdom** - high rates of collection and return of lead-acid batteries are already achieved (estimated at greater than 90%). Old batteries are usually returned to garages or suppliers of new batteries, or they are separated from waste at municipal dumps and from there returned to scrap merchants who sell them to lead smelters. It was deemed unnecessary to implement a formal system of battery collection: the only change in law was to require labelling. The effectiveness of this scheme is discussed below.

**France** - a network exists which allows the return of lead-acid batteries from the public to smelters; a minimum acceptable recycling rate of 85% has been set, with a commitment to reach 100% “as soon as possible”. A committee exists to organise publicity and information, to secure commitments from all parties, to calculate recycling yields and to set economic instruments if goals are not reached.

**Belgium** - collection and recycling rates are estimated to be around 50%.

## 5.4 FUTURE OPPORTUNITIES

### Improvements in battery collection

Though some countries have implemented formal collection systems, with resulting excellent collection rates, this is not yet universal. Even in the EU, most countries are still relying on existing informal collection routes.

#### Example: UK system

The system already in place achieves collection rates estimated at over 90%. This has been described as “a working but fragmented collection system, which can and does have weaknesses, particularly when the market value of lead is low” as in 1993, when the collection rate fell below an estimated 80% - an opinion from within the recycling industry itself (Ainley, 1996). There was then support from the lead industry to introduce a more formal collection system to ensure high collection rates even when the market price of lead is low.

A further difficulty now faced in Britain is that UK Waste Regulations now require documentation and a fee to be paid for battery movement (£10 for 5 or more batteries): some small scrap dealers have stopped collecting batteries. The effect of this on overall recycling rates is not known.

Even when the collection rate is over 90%, considered high by most, with an annual consumption of 100,000t of lead in batteries in the UK, this would mean

that up to 10,000t of lead from this source is unaccounted for per annum. However, rather than being disposed of, most of this shortfall is believed to be stored in private garages etc., and should eventually enter the recycling system.

There is clearly room for improvement. An organised collection scheme could improve return rates, though such a scheme would entail administration costs. Economic instruments, such as a levy on batteries produced, could ensure a reasonable price can be paid for scrap lead, even at times of low lead price on the world market; these would also be expected to improve collection rates. The lead industry would eagerly welcome any such development, because at times of low lead price, secondary production is not profitable (can even operate at a loss) and there can be shortages of batteries available for smelting.

### **Collection of other items**

For products containing smaller amounts of lead, any economic incentive to recycle will depend on the economic value and recyclability of other materials. The economic value of the lead content alone will never be enough to ensure increasing collection rates.

Cathode ray tubes are an example of a product for which the technology to recycle is available (or would be after a small amount of development), but at present there is insufficient incentive to recycle. This situation is expected to change in the future when new legislation comes into force: however, this could still be a number of years away.

### **Dispersed applications of lead**

A significant proportion, about 10%, of lead is still used in compounds (this does not include the large amount of lead oxide used in batteries, as this is included in the totals for batteries). Much of this is used in cathode ray tubes, already described, but other uses include crystal glass, ceramics and PVC stabilisers. Much smaller amounts are used in paint for specialised applications, and for other leaded glasses. Recovery of lead from some of these products does not appear likely, although closed loop recycling of PVC includes recovery of stabilisers.

Complete recovery of metallic lead from applications such as sea-bed cable sheaths, shot and minor uses appears unrealistic.



# 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.

## 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 km<sup>2</sup> 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

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/m<sup>3</sup> air (1ng is one billionth of a gram). For comparison, measurements of lead in air in Europe range from 55-340ng/m<sup>3</sup>. Near volcanoes, levels of 28-1200ng/m<sup>3</sup> 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 m<sup>2</sup> 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

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 10 $\mu\text{m}$  per year, with well-drained sandy soils, chalk and moist normal clay showing the lowest corrosion rates. Much higher rates of 150-170 $\mu\text{m}$  per year for pure lead, and 80-520 $\mu\text{m}$  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 15 $\mu\text{m}$  per year. General corrosion rates of lead in a range of waters, including seawater, have been reported to be between 2 and 20 $\mu\text{m}/\text{year}$  (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).

### **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 10cm<sup>2</sup>, will lose approximately 0.09g of lead over a lifetime of 12 years (using a corrosion rate of 7.3g/m<sup>2</sup> 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 cm<sup>2</sup> (the same as 20-250g per m<sup>2</sup>) 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

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



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 50-220 $\mu\text{g/l}$  (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” - 50-920 $\mu\text{g/l}$ ; “medium” - 40-80 $\mu\text{g/l}$ ; “old” - 30-120 $\mu\text{g/l}$  (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  $<0.5 \text{ mg/m}^3$  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

	Emissions to atmosphere in 1983 (t/y)	Emissions to water (t/y)	Emissions to land (t/y)
mining	1,700 - 3,400	250 - 2,500	130,000 - 390,000
Pb production	11,700 - 31,200		
Cu-Ni production	11,050 - 22,100		
Zn-Cd production	5,520 - 11,500		
secondary non-ferrous production	90 - 1,440		
total non-ferrous smelting and refining	28,360 - 66,240	1,000 - 6,000	195,000 - 390,000
iron and steel manufacturing	1,065 - 14,200	1,400 - 2,800	
metals manufacturing processes		2,500 - 22,000	4,100 - 11,000
chemical manufacturing processes		400 - 3,000	
pulp and paper manufacturing		10 - 900	
petroleum products manufacturing		0 - 120	
<b>TOTAL</b>	<b>31,125 - 83,840</b>	<b>5,560 - 37,320</b>	<b>329,100 - 791,000</b>

(Source: Nriagu and Pacyna, 1988, cited in Thornton, 1995)

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

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

(Source: Nriagu and Pacyna, 1988, cited in Thornton, 1995)

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

	Emissions to atmosphere in 1983 (t/y)	Emissions to water (t/y)	Emissions to land (t/y)
coal combustion electricity generation	775 - 4,650		
coal combustion - industry and domestic	990 - 9,900		
coal combustion - total	1,765 - 14,550		45,000 - 242,000
oil combustion - electricity generation	232 - 1,740		
oil combustion - industry and domestic	716 - 2,150		
wood combustion	1,200 - 3,000		
cement manufacture	18 - 14,240		
steam electric		240 - 1,200	
agricultural and food wastes			1,500 - 27,000
animal wastes, manure			3,200 - 20,000
logging and other wood wastes			6,600 - 8,200
miscellaneous organic waste including excreta			20 - 1,600
peat			450 - 2,600
fertiliser	55 - 274		420 - 2,300
miscellaneous	3,900 - 5,100		
<b>TOTAL</b>	<b>7,886 - 41,054</b>	<b>240 - 1,200</b>	<b>57,190 - 303,700</b>

(Source: Nriagu and Pacyna, 1988, cited in Thornton, 1995)

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

	Emissions to atmosphere in 1983 (t/y)	Emissions to water (t/y)	Emissions to land (t/y)
Total from metals and mining industry	31,125 - 83,840	5,560 - 37,320	329,100 - 791,000
Total from use and disposal of lead	249,670 - 251,130	4,400 - 28,000	215,800 - 461,700
Total from other sources	7,886 - 41,854	240 - 1,200	57,190 - 303,700
Total	288,681 - 376,024	10,200 - 66,520	602,090 - 1,556,400
Atmospheric fallout		87,000 - 113,000	202,000 - 263,000
<b>TOTAL</b>	<b>288,681 - 376,024</b>	<b>97,200 - 179,520</b>	<b>804,090 - 1,819,400</b>

(Source: Nriagu and Pacyna, 1988, cited in Thornton, 1995)

**TABLE 6.5** Anthropogenic Emissions of Lead

	UN/ECE reported official emission data (t/y)						
	1991	1992	1993	1994	1995	1996	1997
Austria				24.3	39.5		
Belgium <sup>a</sup>	303	526	315	238	435	281	
Denmark				45.6	43	20.1	8.47
Finland	259	150	99	60	67		
France	4350					2813	
Germany					624		
Greece						470	
Iceland	8.9	6.8	5.3	4.6	3.9	1.7	0.4
Ireland						92	
Italy	4300			2174		870	
Luxembourg				52.5	27.8	26.2	
Netherlands	251	233	213	164	152	106	
Norway	183	149	106.6	21.7	15.5	8.3	6.3
Portugal						209	
Spain	4674					2435	
Sweden		365		37	37.8		
Switzerland	461	401	341	287	226	200	174
UK	2562	2348	2129	1860	1541	1357	1207
Belarus					122		42.4
BiH						250	
Bulgaria	436				297.5	278.8	231
Croatia	466				285.6	291.6	190
Cyprus	63	66	69	68	67	67	72
Czech Rep	567					387	
Estonia	154	78	69	70	52	43	33
Hungary	523	242	218	190	154	126	119
Latvia	10.1 <sup>b</sup>	7.9 <sup>b</sup>	6.2 <sup>b</sup>	10.3 <sup>b</sup>	4.7 <sup>b</sup>		
Lithuania	48.8	32.4	28.2	33	30.2	17.8	19.3
Macedonia						113	
Moldova	196	106	63	48	77	40	122
Poland	1336	986	997	966	937	960	896
Romania						1153 <sup>e</sup>	
Russia	3553	3095	2376	2643	2426	2304	2247
Slovakia		182		90.5	83.8	97	84.3
Slovenia	386	390	398	412	204	86	70

a) Figures for Belgium are for Flanders only, except 1995 where it includes Wallonia

b) Emissions from petrol/gasoline are not included

e) Estimated figures

(EMEP Report- July 1999)



### 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<sub>4</sub> or PbCO<sub>3</sub>), 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<sub>4</sub> and PbCO<sub>3</sub> (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<sub>3</sub>, 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).

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 654 $\mu$ g/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.





# LEAD EXPOSURE TO HUMANS AND OTHER ORGANISMS

Lead can reach the biosphere, including humans, by a number of routes. The main exposure routes to humans are:

- **Food** – This is a major source of lead intake for the adult population. Produce can be contaminated from airborne deposition and lead-rich soil, though this can be reduced with careful washing. Previously, leaded solders in cans and wine bottle capsules contributed to lead intake in the general population, but these have been phased out. In the home, the use of lead crystal or ceramic tableware glazed with leaded glazes can cause a small contribution, but such articles manufactured in the Western World are tested to ensure that leaching is acceptably low.
- **Water** – Old lead pipes, which are still in place in many dwellings, can slowly dissolve in some soft and acidic waters. Improved water treatment to reduce plumbosolvency, reduces the lead content of water to acceptable levels in the majority of dwellings. However, the problem is not eliminated without replacement of lead pipes within the home, which incurs expense to the homeowner. A WHO guideline of 10µg/l for drinking water is complied with in most cases.
- **Air** – Direct absorption by inhalation is a minor exposure route for most people, though it can be significant to individuals occupationally exposed. Airborne lead-containing particles fall to earth, most within a short distance of source, and add to lead contents of dusts, soils and food. A weak link between levels of lead in air and exposed populations has been established. The WHO recommended an air quality standard in 1987 of 0.5-1.0µg/m<sup>3</sup>. The EU lead in air standard is currently 0.5µg/m<sup>3</sup> and the UK has set an air quality target of 0.25µg/m<sup>3</sup>. Air lead levels are falling in Western Europe, as leaded petrol is being phased out. Elevated levels can be found in some industrial areas.
- **Soil and dust** – Ingestion of soil and house dust is a major pathway for the exposure of young children to lead, due to “hand-to-mouth” activity. The

## LEAD: THE FACTS

major source of lead in house dust in older properties is leaded paint (now phased out, but still *in situ* in many dwellings). This is the major source of lead exposure to children living in older dwellings in the USA. Other contributions to dust are from airborne emissions, particularly in countries where leaded petrol is still used. Lead contents in house dusts in urban areas of the UK are declining. Lead contents of soils cannot be expected to decline for many years, as lead has a low mobility in soil.

Lead exposure levels in the general population have markedly declined over the past 30 or so years and by the 1990s average national levels for blood lead in the EU were mostly well below 10µg/dl.

### TRENDS IN LEVELS OF LEAD EXPOSURE IN HUMANS

Levels of lead exposure in the general population have fallen in the USA and Western Europe, with average national values for blood lead in the EU in the 1990s mostly well below 10µg/dl. Decreased exposure from several sources has brought this about, though it is believed that the reduction of leaded petrol is a major contributory factor. Other measures have included: improved water treatments reducing plumbosolvency; phasing out of leaded solders in food cans; and phasing out of the use of leaded paints. Improved industrial practices have resulted in lower emissions. A small proportion of individuals continue to receive doses of lead which are deemed unhealthy, particularly in the developing World and in Eastern Europe. The most highly exposed individuals tend to be the more deprived members of society. Occupational exposure has also decreased dramatically in the western world with improved technology, hygiene and management practices.

### EFFECTS OF LEAD EXPOSURE ON HUMAN HEALTH

A small number of adults occupationally exposed to lead have in the past shown increased risk of kidney damage, nerve damage, infertility and, possibly, a small increase in blood pressure and the risk of contracting certain cancers at high levels of exposure. However, today such effects are rarely observed. The greatest concern for the general population is that lower levels of lead exposure, which some of the general population may receive, appear to cause a small decrease in the intellectual development of young children. Children are more vulnerable because their nervous system is developing; they absorb more lead than adults because of behavioural and physiological differences. There is no accepted threshold level, but the body of evidence to date does not find any effect below 10µg/dl blood lead. Individuals whose diet is lacking in iron or calcium absorb more lead than those who are well nourished.

## ECOTOXICITY

Lead can have adverse effects on living organisms. High doses can interfere with some biochemical processes required for normal functioning. Most lead compounds have low solubilities in water and are not readily absorbed by most living organisms. Soluble compounds of lead can readily be taken in, and have been studied most widely (particularly for aquatic organisms). However, some organisms (such as molluscs) can absorb solid lead compounds from sediments, and there is little data available on the toxicity of this. Tetraethyl lead is much more toxic than inorganic lead compounds, but it breaks down quickly in the environment. Some aquatic species bioaccumulate lead, but there is no evidence for biomagnification at higher levels in food chains. Lead in soil generally does not have great effects on plants or earthworms except at highly elevated concentrations; its potency varies with soil type. In general, the bioavailability and toxicity of lead compounds are greater in acidic conditions, and less in alkaline or saline conditions.

The major impact of lead on wildlife, particularly waterfowl, results from the ingestion of lead shot (from ammunition or fishing weights). This can cause acute lead poisoning, sometimes fatal. For this reason, the use of lead shot for small fishing weights, and in some cases, in ammunition, is restricted in an increasing number of countries.

## POLICY APPROACHES

A strategy based on risk assessment is generally used to predict the potential harm to target populations and to assist the regulatory process. This requires knowledge of the nature of the hazard (i.e. the lead compound), the exposure pathways to the target population, and the dose-response relationship. Sources of uncertainty in these predictions should be clearly stated. The precautionary principle can be used when there is lack of data on risk, and the potential for harm exists.

## **7.1 PATHWAYS TO THE BIOSPHERE AND HUMANS**

### **7.1.1 LEAD IN AIR**

Natural and anthropogenic sources of lead in the atmosphere and their dispersion have been discussed in Chapter 6. Direct inhalation of lead-bearing particles in air is one route of exposure for both humans and other animals. For most people, this is a minor exposure route, the majority of lead being taken in by ingestion (described later). However, leaded air particles fall to earth and contribute to lead levels in dusts, which can contaminate foods, hands, etc and thus be ingested. People exposed to lead fume at work can absorb significant amounts by inhalation if protective equipment is not worn and good working practices not followed.

The World Health Organisation set an air quality guideline for lead of between 0.5 and 1.0 $\mu\text{g}/\text{m}^3$  as an annual average (WHO, 1987), though a WHO working group recently recommended revising this guideline to 0.5 $\mu\text{g}/\text{m}^3$  (WHO, in press, cited in DETR, 1998). The EU lead in air standard is currently 0.5 $\mu\text{g}/\text{m}^3$ . Ambient lead levels in air peaked in the early to mid 1980s in Britain. Annual average concentrations of airborne lead at the kerbside of a busy London road were around 1.4 $\mu\text{g}/\text{m}^3$ , and in 1985 were still higher in Manchester (2.0 $\mu\text{g}/\text{m}^3$ ); general urban levels of lead were in the range of 0.2-1.0 $\mu\text{g}/\text{m}^3$ . Since then, lead levels in urban areas have significantly declined, as the use of leaded petrol has been phased out. In the UK in 1995-6, the urban and kerbside lead levels measured were not above 0.2 $\mu\text{g}/\text{m}^3$ , well within the WHO recommended levels. It is not expected that urban areas will now have lead levels above the lower WHO limit of 0.5 $\mu\text{g}/\text{m}^3$ , though two industrial sites still exceeded this level. The upper WHO limit of 1.0 $\mu\text{g}/\text{m}^3$  was not exceeded at any of the 24 lead monitoring sites (chosen to represent urban, urban kerbside, rural and industrial locations) (UK DETR, 1998).

The relationship between lead levels in the air, and levels of lead absorbed by the body (blood lead levels) is complex, but evidence suggests that a standard for the general population should not be above 1 $\mu\text{g}/\text{m}^3$  (UK DETR, 1998). To allow for some individuals being more vulnerable, the UK Expert Panel on Air Quality Standards recommended a safety factor of 50% and a further safety factor of 50% to allow for uncertainties, resulting in a recommended value of 0.25 $\mu\text{g}/\text{m}^3$ . It is believed at this level any effects on health, even to vulnerable individuals, will be too small to be detectable. This recommendation has, however, been criticised by industry as not being based on sound science.

### **7.1.2 LEAD IN WATER**

Lead in drinking water is of intermediate significance as a source of lead intake, but is highly significant for both children and the foetuses of pregnant

women. Lead levels in drinking water, sampled at source, are usually below  $5\mu\text{g/l}$ . However, many old houses still have drinking water distribution pipes made of lead. This can result in tap water concentrations above the maximum safe level recommended by the WHO of  $10\mu\text{g/l}$ , and even above the EU statutory limit of  $50\mu\text{g/l}$ ; occasionally, levels of over  $100\mu\text{g/l}$  have been found. When the pipes need replacing, alternative materials are used, but it is expensive to replace all existing lead pipes within the home. The greatest problems are in areas where the water has a higher concentration of dissolved organic compounds, which increase plumbosolvency (Alloway and Ayres, 1997).

*Case study of a city with relatively high lead contents in drinking water - Glasgow, Scotland, UK*

In the UK, higher levels of lead in water are found in many areas of Scotland, where the water supply is from upland areas (and consequently, usually acidic, soft, and containing organic acids, which all aid dissolution of lead) and lead piping was commonly installed up until the 1960s. The city of Glasgow receives its water from such a source. It was reported that in 1974, the majority of water samples taken (84%) contained over  $50\mu\text{g/l}$  of lead. However, following the implementation of a programme to treat the water with lime, making it alkaline and less corrosive to lead, the proportion of water samples exceeding this level had dropped to 7% by late 1989. However, a 1981 EC study of mothers living in households in this supply area, found that over 50% of households received water supplies exceeding the WHO recommended level of  $10\mu\text{g/l}$ , and 13% exceeding the UK statutory limit of  $50\mu\text{g/l}$ . (Some samples contained considerably higher lead concentrations.) An improved treatment programme, which took effect from 1989-1992, consisted of treating the water with orthophosphate, which further reduces the tendency of lead to dissolve. A study in 1993 found that over 90% of the households studied had less than  $10\mu\text{g/l}$  of lead in their water, and less than 1% had over  $50\mu\text{g/l}$  lead in the water, though again some received water with well over  $50\mu\text{g/l}$  lead.

This shows that treatment of the water, with lime or preferably orthophosphate, can reduce plumbosolvency and thus lead concentrations in water to low levels, for the majority of households. Also, lead pipes for mains water have been replaced by the water company, up to the property. However, replacement of lead piping in the home is the only way to remove the possibility of lead being dissolved in water, and this is only being done in a relatively small number of buildings, because of the cost and disruption involved.

The study also found a direct relation between lead concentrations in water and in blood of the subjects (mothers of young children) studied. However, blood lead levels had declined over these 16 years for a number of reasons, and the blood lead levels associated with particular concentrations of lead in tap water

had also declined (Glasgow 93 Lead Study, 1996). This shows that lead intake through water is a significant source of exposure in some areas, though it is one of many other sources.

### 7.1.3 LEAD IN SOIL AND DUST

As detailed in Chapter 6, soils can contain lead from many sources and this can remain for centuries. Housedusts contain lead from road dusts brought indoors on shoes, as well as sources within the home, primarily leaded paint, and a small potential contribution from some window blinds which contain lead, e.g. some vinyl types.

Plants can take up that fraction of lead which is present in the soil in a soluble form and this will add to their lead content. However, there is general agreement that only a small proportion of the total soil lead content is available for uptake by plants, that much of this is then accumulated in root cell walls, and that little is translocated to the plant shoot (Davies and Thornton, 1989). Animals which eat the plants will ingest their lead content. This can be increased by particles of soil attached to the plants and lead dusts which fall on the plants from the air. Some animals, particularly grazing animals, ingest large quantities of soil - up to 20% of the dry matter intake in cattle, and up to 30% in sheep which graze closer to the ground, although statutory limits for lead in edible animal tissues are rarely exceeded (MAFF, 1989).

Ingestion of housedust and soil, which contain small amounts of lead, is one source of lead intake in humans. Dust can contaminate hands, food, etc., but this is not considered an important exposure route for adults, except possibly for occupationally exposed workers, if hygiene practices are poor. However, this route is significant for children, who spend considerable time playing on the floor, in gardens, etc. In infants aged 1-3 years, "hand-to-mouth activity" has been shown to account for 50% of their total lead intake (Davies et al 1990). Furthermore, some individuals, particularly very young children, have a pica (a habit of eating non-food substances) for leaded paint or soil, and exposure in these individuals will be higher.

A number of countries have set standards, defining maximum acceptable levels of lead in soil. These are aimed at the protection of human health. In the USA there is also a standard for lead levels in housedust. Different countries have taken varying approaches to the setting of permitted levels.

A number of studies have attempted to find a link between lead levels in soils, and exposure to humans. In some cases, the population living adjacent to industrial areas show elevated levels of lead exposure, believed to be caused by the higher level of lead in the soil (following a study of an old lead mining and smelting town, Leadville, in Colorado, USA (Cook et al, 1993, cited in INSERM, 1999), and Broken Hill, a major lead mining area in Australia (Gulson et al,

1994). However, this is not always the case: a survey in the UK identified a village with very high lead concentrations in soils (ranging from several hundred mg/kg to 3% lead in local gardens) arising from historical mining and smelting activities (Colbourne and Thornton, 1978), but where the local population did not appear to be significantly exposed. The differences are believed to be largely due to different chemical and mineral forms of the lead: analysis of the soil dusts in the UK site found much of the lead appeared to be in a relatively insoluble type of lead phosphate (pyromorphite) which is not readily absorbed by living organisms (Cotter-Howells and Thornton, 1991). Other differences could include climate, lifestyle, and nutritional status. In Northern Europe, children spend less time outdoors, and thus exposed to soil, than in other areas such as Australia.

The Society for Environmental Geochemistry and Health has proposed a method of calculating maximum permissible soil lead content needed to protect populations from exceeding a given blood lead concentration. Typical values given are presented below (from Wixson and Davies, 1994, cited in INSERM, 1999).

Guidelines for acceptable concentrations of lead in soils in the UK, Canada and the Netherlands are given below.

**TABLE 7.1** Acceptable Lead Concentration in Soils (ppm, or  $\mu\text{g/g}$ )

Blood lead concentration not to be exceeded ( $\mu\text{g/dl}$ )	Percentage of the population to protect		
	95%	98%	99%
10	880	500	300
15	2300	1860	1400
20	3750	3000	2600

*Note:* these concentrations are based on a fairly low lead bioavailability, and other sources of lead exposure in the population giving a blood lead concentration of  $4\mu\text{g/dl}$ . Where these assumptions are not valid, the calculation must be modified, and the permitted soil lead levels will be different.

## UK

UK Department of the Environment ICRCCL threshold trigger concentrations (DoE, 1987), below which there is no cause for concern, and above which professional judgement may require more detailed investigation and/or remediation. These are “more pragmatic, and based mainly on effects to human health” (Alloway and Ayres, 1997).

Parks, playing fields, open space	2000 $\mu\text{g/g}$
Gardens, allotments	500 $\mu\text{g/g}$

## Canada

Selected values from the Canadian interim environmental quality criteria for soil (Canadian Council of Ministers of the Environment, 1992).

“Normal” background	25µg/g
Agricultural	375µg/g
Residential	500µg/g
Industrial	1000µg/g

## Netherlands

The standards used in the Netherlands are based largely on the concept of multi-functionality, including ecological function. These standards comprise target values for soils which represent the final environmental quality goals for the Netherlands. Guide values and quality standards used in the Netherlands for assessing soil and water contamination by heavy metals (Netherlands Ministry of Housing, Physical Planning and the Environment, 1991; Moen et al, 1986).

Soil target value	85µg/g
<i>Surface waters</i>	
total content - target value	4µg/l
total content - limit value	25µg/l
dissolved content - target value	0.2µg/l
dissolved content - limit value	1.3µg/l

It should be noted that the Netherlands also uses a series of intervention values at which the authorities are required to investigate the level of contamination and decide on what action, if any, is required. The intervention value for soil in the Netherlands is 530µg/g compared to the target value of 85µg/g.

### *Groundwater*

dissolved content - target value	15µg/l
(from 1991 Environment Quality Standards for soils and waters)	

## USA

### *Lead in soils*

Soil-lead hazard > 2000µg/g in bare residential soil. Remedial action necessary (such as turfing, removing top 15cm and replacing with uncontaminated material, covering with gravel). Where there are young children or pregnant women resident, placing of washable doormats at house entrance, and more frequent washing of hands and toys are recommended.

Soil-lead level of concern > 400µg/g. This is a level for guidance only, suggesting that there is at least a small risk to young children living at the property, and some less costly action should be taken. No action is required by law.



*Lead in dusts*

Dust lead hazard in residential dwelling equals or exceeds  $50\mu\text{g}/\text{ft}^2$  on uncarpeted floor, or  $250\mu\text{g}/\text{ft}^2$  on interior window sills.

*Lead-based paint*

Lead-based paint hazard: requires action when property has lead-based paint in poor condition (over  $10\text{ ft}^2$  of deteriorated paint on exterior components, over  $2\text{ ft}^2$  of deteriorated paint on interior components with large surface areas, or over 10% of the total surface area of interior or exterior components with small surface areas) (U.S. Environmental Protection Agency, 1998).

**7.1.4 LEAD IN FOOD**

Ingestion of traces of lead with food is the main source of lead intake to the general adult population. Lead is ubiquitous in the environment, and all foodstuffs contain small amounts of the metal. Fresh food may be contaminated by small amounts of lead (as well as many other undesirable substances) from airborne fallout, particularly noted for foods such as lettuce, parsley and mint, which have a very large surface area compared to their mass (Sherlock, 1987); vegetables grown in soils with high lead contents can also contain traces of soil. In both these cases, careful washing will reduce the amount of lead consumed in vegetables by as much as 70 per cent (Thornton and Jones, 1984).

Lead-containing solders used in food cans could cause lead contamination, particularly of foods containing acidic fruits, tomatoes or similar, until their use was prohibited in the early 1980s. A study of lead contents of foods in the UK in 1984 found canned foods, including fruit and food in tomato sauce, often contained elevated lead contents. However, this use of leaded solder in food cans was starting to decline at that time, as manufacturers were switching to different can designs, and no longer presents a problem for food canned in the West. Offal, such as animal liver and kidney also sometimes contain elevated levels of lead, because lead taken in by livestock tends to be stored in the liver and kidneys (as well as the bones), rather than the muscle (Sherlock, 1987). Cooking food in lead-contaminated water has also been shown to result in increased levels of lead in the food (Sherlock, 1987).

Beverages consumed from or stored in lead crystal containers, or ceramic vessels glazed with leaded glazes, are another potential source of lead intake. However, products made by manufacturers in most countries, including Europe and North America, must comply with standards which ensure that lead leaching rates are acceptably low. The tests in the UK involve adding a solution of acetic acid (4% strength, which is approaching that of vinegar), which is very potent at dissolving lead, at room temperature ( $22^\circ\text{C}$ ) for 24 hours. The acid solution is then analysed for its lead content. However, the USFDA (1997) recommend that pregnant women should avoid drinking hot tea, coffee, or other hot acidic

beverages from glazed cups and pottery as high temperature can increase dissolution of lead. Storage of acidic fruits or beverages in such vessels over a longer period of time could lead to increased lead content.

### 7.1.5 ESTIMATES OF TOTAL LEAD ABSORBED BY HUMANS (ADULTS AND CHILDREN) FROM AIR, DUST, FOOD AND WATER

The table presented below is adapted from the WHO (1987) report.

**TABLE 7.2** Estimated Daily Intake of Lead

Mean Air Concentration (µg/m <sup>3</sup> )	Dust Intake (mg/day)	Lead Uptake				
		Air	Dust	Food	Water	Total Absorbed (µg/day)
<b>ADULTS</b>						
0.3	non-smoker	2.4	-	10	2	14.4
0.5	non-smoker	4.0	-	10	2	16.0
1.0	non-smoker	8.0	-	10	2	20.0
2.0	non-smoker	16.0	-	10	2	28.0
<b>CHILDREN (1 - 5 years)</b>						
0.3	-	0.6	-	25	5	30.6
0.5	-	1.0	-	25	5	31.0
1.0	-	2.0	-	25	5	32.0
2.0	-	4.0	-	25	5	34.0
1.0	25	2.0	12.5	25	5	44.3
1.0	50	2.0	25.0	25	5	57.0
1.0	100	2.0	50.0	25	5	82.0
1.0	200	2.0	1.0	2	5	132.0
		0.0		5		

*Assumptions on which tabulated data is based:*

**Air:** Respiratory volume in adults is 20m<sup>3</sup>/day, and in children 5m<sup>3</sup>/day, and the respiratory absorption is 40%.

**Dust:** Dust concentration of lead is 1000µg/g, and absorption 50%.

**Food:** Intake of lead by adults is 100µg/day with 10% absorption, and 50µg/day for children.

**Water:** A lead concentration of 20µg/l, with adult consumption of 1 litre per day, 10% absorption; for children 0.5 litre consumption per day, 50% absorption.

## 7.2 ENVIRONMENTAL EFFECTS AND ECOTOXICITY

Lead is not an essential trace element for either plant or animal nutrition. However, lead and its compounds, if present in sufficient amounts, are responsible for toxic effects to populations of both terrestrial and aquatic ecosystems. The form which the metal is in is a crucial factor in determining its mobility, bioavailability and toxicity (Chimie et Ecologie, 1998).

Measured effects of lead on living organisms include those related to survival, growth, learning, reproduction, development, behaviour and metabolism. Lead has no known essential biological functions and all lead compounds are potentially harmful or toxic, especially tetraethyl lead. Lead functions as a cumulative poison (Environmental Contaminants Encyclopaedia, Lead Entry, 1997). However, many effects are reversible once exposure levels fall.

Populations can be exposed to lead in the following media:

- water soluble compounds of lead are readily absorbed into living cells. Compounds which are insoluble, in suspension or in sediments, can be ingested or filtered by benthic organisms (those which live on the floor of the watercourse);
- soil soluble compounds are the most bioavailable and can be taken up by organisms. However, most compounds of lead have very low solubility, except in very acid or very alkaline conditions;
- air plants, insects, birds and other organisms can be exposed to vapours, aerosols or particles of lead-rich material (Chimie et Ecologie, 1998).

Exposure can be a single dose, such as in the rare case of an accident or production incident, or continuing over a long period, as is the result of routine industrial and natural emissions. The potential toxic effects depend largely upon the form of the lead, the “target” population, and the conditions of exposure. The presence of other pollutants or naturally occurring constituents of the environment can modify the effects of the lead (Chimie et Ecologie, 1998).

### Results of field studies

There are not many studies on actual ecosystems, and the results of these are difficult to interpret, because

- lead and its compounds are only one of a number of substances present in the environment, and it is difficult to establish which effects are due to which pollutant;
- though the total lead content can be determined, the concentrations of different chemical forms of lead, and thus its actual available dose, are often not known (Chimie et Ecologie, 1998).

Under normal conditions, it does not appear that lead has a marked effect on ecosystems, because of its generally low bioavailability. In waters, lethal poisoning of fish has not been observed, even when concentrations of lead exceed 3,000mg/kg in aquatic bryophytes (moss-like plants which readily absorb pollutants from their surroundings and are used as a measure of long-term pollution) (Chimie et Ecologie, 1998). In soils, lead generally has a low bioavailability and total concentrations reaching or exceeding 1,000mg/kg do not necessarily cause significant effects on vegetation. The damage to some forests near roads with heavy traffic is generally considered the result of atmospheric pollutants, (such as SO<sub>2</sub>, NO<sub>x</sub> and ozone) rather than lead (Académie des Sciences, 1998).

The impact of lead is more clearly established in the case of bird mortality due to exposure to lead shot from fishing or shooting (Académie des Sciences, 1998). This has been widely reported, particularly in the USA (for example, US Department of Interior, Fish and Wildlife Service, 1986, cited in Chimie et Ecologie, 1998) and Nordic countries. Birds which ingest lead show anorexia and ataxia, weakness and loss of condition. Egg production, fertility and hatchability decrease and mortality may be high; high doses cause coma and death (Booth et al, 1982 and Clarke et al, 1981, cited in Irwin et al, 1997). At least 2% of waterfowl in North America are estimated to die as a result of ingesting lead shot (Canadian Environmental Protection Branch, from web page, 1999). Black ducks in urban areas in Nova Scotia (Canada) have been found to have high concentrations of lead in their blood, though many had not ingested lead shot. The source of exposure was believed to be from run-off from road dusts, contaminated with leaded petrol derivatives, being deposited and accumulated in the sediments of ponds. As lead is relatively immobile in sediments, this will continue to pose a hazard to the ducks unless the contaminated sediments are removed (Canadian Environmental Protection Branch, from webpage, 1999). Similarly, in Europe, the deaths of seagulls which have been noted, could be caused by lead alkyl compounds from petrol (Académie des Sciences, 1998).

### **Laboratory studies**

There are many results from experimental studies, though most concentrate on soluble inorganic compounds of lead. The insoluble forms which can be ingested or filtered are rarely studied. Most studies are on aquatic ecosystems, rather than terrestrial ones. There is much more data on lethal or severe effects following high exposure; long term low exposure is more rarely studied, even though this is more likely to occur in practice (Chimie et Ecologie, 1998; Académie des Sciences, 1998).

### **Bioaccumulation, biomagnification, biomethylation**

Little bioaccumulation of inorganic bioavailable forms of lead has been found in plants and earthworms. In contrast, there is evidence of significant

bioaccumulation in phytoplankton, filter-molluscs and bryophytes (moss-like plants) and, to a smaller degree, in fish and micro-crustaceans. Lead-alkyl compounds appear to be the most easily bioaccumulated, especially in algae, molluscs and fish. There is no evidence of biomagnification (increasing concentrations found in organisms at higher levels in the food chains) of lead. The possibility of conversion of inorganic lead compounds to organic, methylated compounds (which could potentially be much more toxic) by biota, has been demonstrated in sediments, but the reaction is extremely slow and only occurs to a small degree (Académie des Sciences, 1998).

Inorganic lead compounds have greater solubility and thus potential toxicity in more acidic conditions, and are less toxic in more alkaline or more saline environments (Chimie et Ecologie, 1998). Lead-alkyl compounds have important ecotoxicological effects, though these effects diminish rapidly as the compounds break down (Académie des Sciences, 1998).

A selection of results from toxicological tests are presented below.

**TABLE 7.3** Examples of Lead Toxicity Tests

Species	Effect	Inorganic dissolved lead compound	Organic lead compound (tetraethyl lead)	Concentration of lead (mg/l)
bacteria	inhibition of bioluminescence	inorganic		0.4 - 30
marine micro-organisms	inhibition of respiration		tetraethyl	0.08
daphnia (water flea)	inhibition of reproduction	inorganic		0.012
Artemia salina (a salt-water shrimp)	LD50 (96hrs)	lead nitrate		>100
Artemia salina	LD50 (96hrs)	lead nitrate	tetraethyl	0.003
molluscs	LD50 (96hrs)	inorganic compounds		10 - 2000
molluscs	LD50 (96hrs)		tetraethyl	0.1 - 1
fish	LD50 (96hrs)	ionic compounds		0.6 - 242
fish	LD50 (96hrs)		tetraethyl	0.02 - 0.03
fish	effects on juveniles and on reproduction			

*Note:* LD50 (96hrs) is the lethal dose for 50% of the specimens within the time interval of 96 hours.

(Source: Académie des Sciences, 1998)

### **Effects on plants**

Lead in soil - effect on test plant (radish): inhibition of germination or growth is observed at concentrations of 125 $\mu\text{g/g}$  in sandy soils, but no effects are observed in chalk soils up to concentrations of 200 $\mu\text{g/g}$ .

Solution of lead nitrate - disturbances in the development of the root systems are found at concentrations of 13.1mg lead/l.

Excessive concentrations of lead in plants have been found to cause a number of biochemical effects, including upon the processes of respiration, photosynthesis, transpiration and the proper functioning of dark green leaves (Kataba-Pendias and Pendias, 1984). Normal concentrations of lead generally found in plant leaves (in the range 5-10 $\mu\text{g/g}$ ) are not far below concentrations which cause toxic effects (30-300 $\mu\text{g/g}$ ). However, it must be stated that this is also true for many other metals, including copper, chromium, zinc, arsenic and cadmium (Alloway, 1995).

Elevated concentrations of lead in water are particularly toxic to many species of algae. Synergistic effects of lead and cadmium, and additive effects of lead, mercury, copper, zinc and cadmium, have been documented for aquatic biota (Irwin et al, 1997).

### **Effects on animals**

Some lead compounds are classified as ecotoxic. Like arsenic, lead exposure can lead to excess mucous formation which can coat the gills and impair respiration. In vertebrates, sub-lethal lead poisoning is characterised by neurological problems, kidney dysfunction, enzyme inhibition and anaemia. Animal studies indicate that high levels of lead exposure interfere with resistance to infectious disease (Gainer et al, 1974, cited in Irwin et al, 1997). Both water hardness and acidity are important factors affecting lead toxicity.

It is doubtful whether the term "toxic dose" has any real meaning when applied to lead, as it is affected by many factors. These include: environment, nutrition, disease and, most importantly, age, with young animals being considerably more sensitive than adults. Lead is cumulative and ubiquitous, and all living creatures are continually absorbing it - the toxic dose is only the amount necessary to bridge the gap between normal intake and a potentially dangerous level. Three or four lead shot will kill a duck, 10 a goose (Clarke et al, 1981). Lead shot poisoning of waterfowl has been widely publicised, but can also occur in bald eagles and other species of fish and wildlife (Irwin et al, 1997).

The acute lethal dose for lead (LD50), tested by injection into rats, was found to be 70mg/kg bodyweight. Lead administered in this way is less toxic than many other elements, including silver, gold, platinum and tin. When taken in by ingestion, much of the lead is not absorbed but passes out in the faeces (Alloway and Ayres, 1997).

## **7.3 HEALTH EFFECTS ON HUMANS**

### **7.3.1 HISTORICAL ACCOUNTS OF PLUMBISM**

It has been known for many centuries that excessive intake of lead causes a number of adverse health effects, and very high doses are fatal. Even the Romans were familiar with some of the toxic effects of lead. Several writers of the time (including Pliny and Vitruvius) refer to ill effects that craftsmen could suffer as a result of working with lead, though it must be stated that many of the miners and artisans would have been exposed to very high doses of lead. Even among the general population, it is believed that many, particularly in the wealthier classes, were exposed to lead from its use in piping, and much more seriously, in kitchenware in the preparation and storage of acidic dishes. There are accounts of epidemics of colic, occasionally paralysis, and general poor constitution, which are consistent with plumbism, though of course could have many other causes. It has even been suggested that chronic lead poisoning in the nobility, was a contributory factor (though it must be said, one of many) in the downfall of the Roman Empire, as severe lead poisoning would have affected the judgement of the rulers, and the failure to produce heirs capable of government could have contributed to political instability (Nriagu, 1983, citing his own work, and that of Kobert, 1909, and Gilfillan, 1965).

Another example was the “Devonshire colic” in England, diagnosed as lead poisoning by Baker, in 1767 resulting from the addition of lead acetate to locally produced cider.

### **7.3.2 ABSORPTION OF LEAD**

Adults absorb only about 5-15% of the lead they ingest, and generally retain less than 5% of what is absorbed (American Council of Science and Health, 1997). However, absorption of inhaled lead is much higher, about 50%. Children absorb much more of what they ingest (approximately 30-40%, can be up to 50%), because of physiological and metabolic differences.

Absorption by individuals is also influenced by a number of factors. Besides the chemical form which the lead is in (which has already been discussed in Chapter 6), the nutritional status of the individual is important, as people whose diet is low in iron or calcium absorb more lead. Lead absorption is also higher if ingested in water or other beverages than in food. Ingestion after fasting is also increased compared with ingestion after or with food.

### **7.3.3 FATE OF LEAD IN THE HUMAN BODY**

Once lead has been absorbed into the bloodstream, it is distributed between the bones and teeth, the soft tissues (kidneys, brain, liver) and the blood, and in part

excreted in the urine and in bile. Lead can cross the placenta and be transmitted in the breast milk.

The body does not distinguish between lead and calcium, and so the majority of lead which is absorbed is stored in the bones and teeth. In children, about 70% of lead is distributed in this way; in adults up to 95%. However, physiological stress, such as pregnancy, chronic disease or demineralisation of the skeleton after the menopause, can cause small amounts of this stored lead to be mobilised and blood lead levels to increase. However, the clinical significance of this mobilisation is still uncertain.

### **7.3.4 MEASURES OF LEAD EXPOSURE**

Blood lead levels are the usual measure of lead exposure and indicate recent exposure to lead. Blood plasma may reflect the “active” fraction of lead in blood, which can determine the accumulation of lead in the organs. However, blood lead concentrations do not give an indication of previous exposure to lead, or the amount of lead stored in the body. (After a single exposure, blood lead levels fall to about half of their initial value after about 20 days depending on length and intensity of the exposure, age of the exposed subject, etc.)

Children’s teeth give an indication of cumulative lead exposure, and have been used in some studies. However, the type and part of the tooth and presence of any plaque, dental caries and fillings, all influence the measured lead concentrations. Milk teeth are usually assessed, although these are not available until the child is at least 6 years old, which is several years past the age of maximum exposure and maximum effect on the nervous system.

A more recent approach is to measure bone lead by non-invasive X-ray fluorescence (Todd and Chettle, 1994). This also gives measurements of cumulative exposure, but improved standardisation is still needed.

Workers who are occupationally exposed to lead, should be routinely monitored for blood lead concentration and possibly other measures such as haemoglobin level, d-amino laevulinic acid in urine (ALA-U), and zinc-protoporphyrin (ZPP) in the blood, to indicate previous exposure and general health (CEDAC-Plomb, 1996). Lead in urine measurements are mainly useful on a group basis, but are limited by contamination and differences in urinary output. Some such measures are required by law in many countries (ILZSG, 1996).

Hair has not been found to be a good way to measure exposure to lead, mainly because of problems of surface contamination.

### **7.3.5 HEALTH EFFECTS OF LEAD EXPOSURE**

#### **7.3.5.1 Effects of lead exposure on mental development and IQ**

It has been shown that lead can impair the mental development of young children, and even relatively low levels of exposure can cause a measurable reduction in IQ



(Pocock et al, 1994; Smith, 1998). This effect of lead is of particular concern, because evidence from prospective longitudinal studies (which study the same children over a period of several years) has shown that neurobehavioural effects, such as impaired academic performance, may persist even after blood lead levels have returned to normal. Although no threshold level for these effects has been established, the available evidence suggests that lead toxicity may occur at blood lead levels of 10-15µg/dl, or possibly less (ATSDR 1988).

Young children are much more susceptible to damage than adults, because their nervous system is developing. Children can be exposed both before and after birth. The foetus can receive lead from the bloodstream of the mother, as lead can pass through the placenta after the 14th week of pregnancy; the blood lead level of the foetus is often similar to that of the mother (INSERM, 1999). Continued exposure of the infant can occur during lactation, as human milk can also contain lead (which follows the same route as calcium in the body). As previously stated, lead stored in the skeleton of the mother can be mobilised during pregnancy, so the exposure of the foetus reflects the mother's exposure to lead both during and before the pregnancy. Animal experiments have shown effects on the developing brains of foetuses, but it has been difficult to demonstrate similar effects in humans.

Children are likely to have higher blood lead levels than adults, because of increased absorption of lead, and behaviour which increases exposure, as outlined above. Those aged 2-3 may be most at risk from lead-contaminated soil, and Mahaffey et al (1982) reported that children in this age group had the highest blood lead concentrations. This is also the age at which pica tendencies are most prevalent.

The symptoms of chronic low level lead exposure are non-specific and include: poor concentration, lower vocabulary and grammatical-reasoning scores, poorer hand-to-eye co-ordination, insomnia, hyperactivity, increased absenteeism, and lower class standing in high school. They are rarely diagnosed and epidemiological studies, comparing similar populations with differing lead exposure levels, are necessary to determine any effects.

The results from many studies show an association between blood lead levels in early childhood and performance of young children at school. A reduction of 1-3 IQ points appears to result from an increase in blood lead concentrations from 10µg/dl to 20µg/dl. This is only a small reduction in IQ compared with the variation in IQ in the general population, but if the population is widely exposed to lead, this could have important consequences for public health (INSERM, 1999). The International Programme on Chemical Safety (WHO, 1995) reported a possible IQ deficit of 1-3 points for each 10µg/dl increment in blood lead concentration, based on populations with blood lead levels generally below 25µg/dl. At higher concentrations, effects may be greater. In the USA, 10µg/dl blood lead is the level above which further surveillance or action is deemed necessary.

### **Confounding factors**

There are many factors which can influence a child's development, including: its home environment, the amount of stimulation which it receives, the intelligence of its parents, and its nutrition. Many of these factors are influenced by socio-economic status. Exposure to lead is also influenced by socio-economic status, with children from poorer backgrounds being more likely to be exposed to lead. This is certainly the case in the USA and Europe, where the major cause of lead exposure in young children is from old leaded paint - most common in older, dilapidated houses, which are generally occupied by poorer sections of the community. There are methods of allowing for these potential sources of error, which have been included in the more recent studies; however, older studies were not fully adjusted to take account of these factors. A further factor of confusion is that hyperactive children could be more highly exposed to lead because of their behaviour (ACSH, 1997; INSERM, 1999).

### **7.3.5.2 Other Effects of Lead Exposure**

Lead exposure is associated with a range of effects on many different parts of the body. These effects vary from subtle biochemical changes to severe clinical symptoms such as lead poisoning (plumbism).

#### **Biochemical effects**

Lead has been shown to have effects on many biochemical processes. The most widely studied is the effect on the synthesis of haem (a vital constituent of red blood cells) in children and adults. Lead inhibition of haemoglobin synthesis has caused anaemia in children at blood lead levels above 25 - 40µg/dl (Fergusson, 1990, INSERM, 1999), and in adults above 50µg/dl.

Low blood lead levels are known to cause altered levels of some blood enzymes (which are essential to normal functioning of the body). In the haem synthetic pathway, the maximum blood lead levels at which a change cannot be detected are: for zinc protoporphyrin (ZPP) - 20µg/dl; coproporphyrin - 40µg/dl; urinary blood aminolaevulinic acid (ALA) - 30µg/dl; and aminolaevulinic acid dehydratase (ALAD) - 10µg/dl. These changes show that lead is having an effect on normal body functioning and the body is responding. The significance of these subtle changes is arguable, as there is little clear evidence that these are harmful in themselves. The practical significance of some of these effects is their use as measures of lead exposure.

#### **Nervous system**

Adverse effects of lead on the central nervous system have been found in individuals occupationally exposed to lead. At blood lead levels of approximately 30µg/dl, slowing of nerve conduction in peripheral nerves has been observed. Distinct symptoms of peripheral neuropathy, such as wrist drop

(weakness of the wrist and fingers) appear at higher blood lead levels of around 60µg/dl or greater. These effects are largely reversible if exposure ceases, though recovery is slow (INSERM, 1999). Encephalopathy (a severe effect on the functioning of the brain) giving rise to epileptic seizures, and coma may occur when acute lead exposure results in blood lead concentrations exceeding 80-100µg/dl (WHO, 1995).

### **Kidneys**

High blood lead levels (in excess of 60µg/dl) have been shown to cause renal dysfunction, one of the effects of acute lead poisoning in occupationally exposed individuals. However, chronic kidney effects require relatively high and prolonged exposure to lead. It is not known how reversible these effects are (INSERM, 1999). Lower blood lead levels can cause subtle effects to kidney biomarkers, and some studies suggest there could be effects on kidney function at blood lead concentrations as low as 10µg/dl (INSERM, 1999).

### **Bone function and vitamin D metabolism**

Numerous studies have found associations between blood lead levels (ranging from 12-120µg/dl) and decreased metabolism of vitamin D (which is required for bone formation). It has been suggested that low levels of lead exposure could have adverse effects on bone growth in children. There is no conclusive evidence of a threshold (a "safe" level of blood lead) for this effect. However, some other studies have reported that low to moderate lead exposure does not cause any effect on vitamin D metabolism or bone mineral content in children who are adequately nourished (American Council on Science and Health, 1997).

### **Reproductive health**

#### *Men*

High levels of lead exposure can result in decreased sperm count and mobility, and an increased number of morphologically abnormal sperm. However, these effects are unlikely to affect the general population, or occupationally exposed individuals with low or moderate blood lead levels. A range of studies on workers exposed to lead for between 6 and 10 years suggest that blood lead levels above 40µg/dl cause a reduction in the production of sperm. Exposure to levels below 40µg/dl appears to cause little or no effect (INSERM, 1999). Current data suggest that effects on fertility are most likely when blood lead levels are 50-60µg/dl or higher for prolonged periods.

#### *Women*

High levels of lead exposure resulting from occupational exposure have been known to cause serious adverse effects. Severe lead intoxication is associated with sterility, miscarriage, stillbirth and effects upon the foetus.

Evidence for the effects of low-level exposure is less clear. Data are mixed with respect to the risk of spontaneous abortion and reduced birthweight associated with maternal blood lead levels below 30µg/dl (WHO, 1995). Recent epidemiological studies have shown exposure-related perturbations in length of gestation, significantly greater risks being associated with blood lead levels of 15µg/dl or more (Murphy et al, 1990; WHO, 1995). Bellinger et al, 1991, cited in INSERM, 1999, investigated birthweights at blood levels below 15µg/dl but did not find any effect related to blood lead.

### **Cancer**

A number of studies have been performed on workers occupationally exposed to lead, often at high levels. Exposure to lead (and its inorganic compounds) gives a possible increased risk of contracting certain cancers, namely of the lungs, the stomach and perhaps also the kidneys. However, the results of these studies are not conclusive because the individuals were also exposed to other substances, such as chromium, arsenic, or certain hydrocarbons at work, and of course cigarette smoke, which are all known to cause cancers (INSERM, 1999). There are no studies on lead exposure in the general population and the occurrence of these cancers (INSERM, 1999). Animal experiments have found that long term exposure to high doses of lead acetate have caused kidney cancer in rats and mice (Kazantzis, 1990), brain cancer in rats, and lung cancer in mice. It is not known how relevant these results are to humans (ACSH, 1997), but it is considered that certain lead compounds should be regarded as potential carcinogens to humans (INSERM, 1999). The International Agency for Research on Cancer (IARC, 1987) has classified, lead and lead compounds as possibly carcinogenic to humans, based on evidence from animal experiments.

### **Blood pressure**

Animal experiments show that exposure to lead can result in increased blood pressure, but epidemiological evidence of effects on humans is not conclusive. Several studies have found a weak association between lead exposure and elevated blood pressure, though these are generally for fairly high exposures (over 45µg/dl, ACSH, 1997) which are relevant only to individuals occupationally exposed to lead. An analysis of 15 studies suggested that reduction of blood lead concentrations in men from 10µg/dl to 5µg/dl (levels commonly found in the general population) could be associated with a small reduction in blood pressure (Schwartz, 1991 and 1995, cited in INSERM, 1999). However, other studies have found only a weak association, or an association which was not statistically significant. As with studies on cancer and other potential effects of exposure to lead, confounding factors such as environment, lifestyle, and socio-economic status, obscure the results (INSERM, 1999). A dose-response relationship for lead exposure and blood pressure has not been established (ACSH, 1997).

### Thyroid gland

Lead exposure in animal experiments and cases of severe lead poisoning in humans have been reported to reduce the functioning of the thyroid gland (Sandstead et al, 1969, Sandstead, 1967, cited in INSERM, 1999). Two studies on occupationally exposed workers (some very highly exposed to lead) found an association between lead exposure and reduced function of the thyroid gland, and previous exposure appeared to be an important factor. Two other studies on exposed workers and exposed children in the USA failed to find an association. Tuppurainen et al (1988) found no correlation between blood lead levels (mean 56µg/dl) in workers in secondary lead smelters and total thyroxin, total triiodothyronine or thyroid stimulating hormone. They reported a weak negative correlation between durational exposure and total thyroxin and free thyroxin. However, Gennart et al (1992) examining a group of battery workers found no lead-related effects on the same endocrine parameters. No effects of lead on thyroid function have been found in children (ATSDR, 1998). It has been concluded that there is only an effect at high levels of lead exposure (above 60-70µg/dl) and children do not appear to be any more vulnerable than adults (INSERM, 1999). It has also been concluded by an EU scientific committee that there is no scientific evidence that lead is an endocrine disruptor.

The effects of lead on health are summarised in table 7.4 below. **This table is to be taken only as a guide.** Also, while there is general agreement about the effects, the exposure levels at which they generally occur is open to some debate, as different studies obtain different findings. Symptoms do not start abruptly at set levels, but affect different individuals over a range of exposures. Some studies may use different definitions of an ailment.

### 7.3.6 LEAD POISONING

Elevated lead exposure may affect many organs of the body, particularly the nervous system, reproductive system, the blood and the kidneys. However, confirmed cases of actual non-occupational lead poisoning in the EU are now rare. For example, only one death, of a two year old child, was ascribed to lead poisoning in England over the period 1981-1996 (Elliott et al 1999). The initial symptoms of inorganic lead poisoning are non-specific, the most important being fatigue and lassitude, anorexia, headache, joint pains, indigestion, constipation or intermittent diarrhea, and a metallic taste in the mouth. During the later stages there may be abdominal discomfort, colic, vomiting, and weakness of the muscle groups most often used. Encephalopathy may develop, with headache, confusion and epileptic seizures.

Poisoning by lead alkyls (petrol additives) causes a rapidly developing and life-threatening encephalopathy. Initial irritability, restlessness and confusion may be followed by ataxia, tremor, disorientation and coma.

**TABLE 7.4** Health Effects of Lead

	Concentration of lead in blood (in µg/dl) above which an effect may be observed
Likelihood of small impairment to mental development and probable reduction in IQ	10
elevated levels of biomarkers, indicating an effect on the production of haemoglobin	
ALAD	10
ZPP	20
ALA in urine	30
coproporphyrin	40
anaemia in children	25 - 40
anaemia in adults	50
renal dysfunction - biomarker	10
renal dysfunction - kidney damage	60
slowing of nerve conduction velocity	30
peripheral neuropathy (e.g. wrist drop)	60
male - reduced sperm count	approximately 40 - 50
female - small reduction in birth weight	may be around 20
colic	above about 80
encephalopathy	80 - 100

Prolonged high exposure to lead may cause reduced fertility, and any offspring born may suffer some damage to the nervous system.

In the human diet, a high dose of lead is needed to cause death, the lethal dose being around 10g per day, higher than silver, cadmium, chromium or zinc (lethal doses of these elements ranging from 1.3 to 9g per day). Of elements for which data are available (but excluding the extremely toxic uranium, plutonium and beryllium) only mercury has toxic effects at lower doses. Slightly higher amounts of even arsenic and cadmium are needed to give toxic effects (Bowen, 1979, cited in Alloway and Ayres, 1997).

Cases of such very high exposure are now extremely rare (in the Western World), and would result from the person being at exceptional risk, in most cases from occupational exposure.

## 7.4 EXTENT OF LEAD EXPOSURE IN THE GENERAL POPULATION

### 7.4.1 THE GENERAL POPULATION (non-occupational exposure)

#### USA

Measures to reduce exposure to lead began in the 1950s and 1960s, as the number of cases of severe lead poisoning in the cities was high. Prevention efforts included screening of children (even those not displaying symptoms), efforts to reduce exposure to leaded paint in the home, and research into the effects of low level exposure to lead. The National Health and Nutrition Examination Survey (NHANES) has performed surveys of the general population. There was a dramatic decline in the blood lead levels in pre-school children from the late 1970s to the early 1990s (Pirkle et al, 1994). The earlier survey found geometric mean blood lead levels of the order of 15µg/dl, but the more recent survey found a geometric mean level of only 2.7µg/dl. This reduction has benefited all groups in society, though exposure to lead varies substantially with race, income, urban status and age of dwelling in which the child lives. Low income children living in housing built before 1946 are over 30 times more likely to have elevated blood lead levels (taken as over 10µg/dl in the USA) than middle income children living in housing built after 1973.

There are several reasons for this change:

- The use of leaded petrol began to decline in the late 1970s.
- High levels of lead in most paint used in homes was found until the 1950s. Around 1950, the US paint industry began to voluntarily phase out the use of leaded pigments, though smaller amounts of other lead additives continued to be used. The addition of lead to house-paint was banned in 1978. The number of older houses still containing leaded paints is falling as older buildings are demolished. Measures for assessing the risk of lead exposure in the home have been put in place, along with measures aimed at reducing exposure.
- The phasing out of leaded solder on food and beverage cans (resulting from different manufacturing processes for food cans), which was previously a major contributor to lead exposure in the general population.
- Lead levels have fallen in drinking water because leaded solder is now banned in household plumbing (since 1988) and public water systems are required to test for lead contamination at taps, and treat water to reduce its tendency to dissolve lead if high lead concentrations are found (since 1990).
- Ongoing screening programmes and public education are believed to have reduced exposure in the more highly exposed sections of the population.

## France

Blood lead levels have significantly declined over the period from around 1980 to 1995. A study of the adult populations of Paris, Lyon and Marseille, found a decline in blood lead levels of approximately 50% (INSERM 1999). The reduction was greater for men than for women, of the order of about 6µg/dl blood lead, though men had higher lead exposure than women. Other studies of blood lead levels of expectant mothers show a similar drop in blood lead, for example from an average of 6.1µg/dl in 1984 to a current level of 3.3µg/dl, in mothers in Brittany. Similar results have been found in Lorraine (INSERM, 1999).

The major cause of this reduction is believed to be the phasing out of leaded petrol. However, petrol is not the only source of lead exposure. The age of dwellings is another important factor, because of the presence of leaded paint in older buildings, which contributes to levels of lead in house dusts. A significant association has been found between the age of dwellings, (before or after 1945) and blood lead levels of inhabitants. Also, residents of some geographical regions have higher exposure to lead and receive above-average levels of lead in drinking water. Smoking and drinking habits were also observed to have a small effect on blood lead levels, by a number of authors. Levels of blood leads in populations living in some industrial regions are also elevated (INSERM, 1999).

## England

A survey of blood lead levels in the population in 1995 (Primatesta et al, 1998) found the following results:

“the population in general had low blood lead levels, most in the range 1-4µg/dl, for individuals exposed only to environmental lead. There were small differences in blood lead levels related to smoking, alcohol consumption, manual work/lower social class, urban residence as compared with rural. Males had higher lead exposure than females. Exposure increased with age. Whites had higher lead exposure than non-whites (all treated as one category). Age of dwelling (before/after 1945) gave a possible small increase in blood lead but, in contrast to surveys in France and the USA, this difference was not statistically significant”.

Blood lead values in the general population have fallen from around 10-16µg/dl in 1980, to around 1-4µg/dl in 1995 (Delves et al, 1996). Blood lead levels above 10µg/dl are now unusual and indicate some additional exposure source. However, some 4,400 blood lead analyses undertaken by the Medical Toxicology Unit at St Thomas' Hospital London over the period 1991-1997 found that among 547 children aged 0-4 years, 45 (8.2%) had blood lead concentrations in excess of 25µg/dl, the action level in the UK for investigation/removal of environmental sources of lead (Elliott et al 1999). It should be noted however that these tests were undertaken in cases of suspected high lead exposure and/or lead poisoning.



**Scotland**

There are no available data from similar large scale surveys. However, a study in Glasgow in 1993 of young mothers resident in areas supplied with soft water from a particular source which had caused enhanced plumbosolvency, found that the geometric mean blood lead level was 3.7µg/dl. This compared with a mean level of 11.9µg/dl in 1981. A small proportion of the mothers had blood lead levels above 10µg/dl, but none above 25µg/dl. Lead in tap water was believed to be the cause of elevated blood lead levels (over 10µg/dl) in approximately 70% of cases. However, blood lead levels of mothers exposed to tap water containing above 50µg/dl was on average 7.2µg/dl in 1993, compared with 21.6µg/dl in 1981. This clearly shows that exposure from other sources had greatly declined. Similar trends have been noted in other industrialised countries.

**Belgium**

A dramatic decline in the levels of lead in blood has been found in the urban Belgian population over the period from 1970 (14-21µg/dl) to 1988 (7-11µg/dl) (Ducoffre et al, 1990). This study covered both smoking and non-smoking males and females. The fall in blood lead corresponded with a parallel reduction in the lead content of petrol.

The WHO recommend that action be taken for individuals with blood lead levels above 25µg/dl, and the current EU standard is that no more than 2% of the population should have blood lead levels above 35µg/dl. In the US, the aim is to reduce exposure in the population to blood lead levels below 10µg/dl.

#### **7.4.2 EXPOSURE OF INDIVIDUALS OCCUPATIONALLY EXPOSED TO LEAD**

Individuals working in many diverse industries can be exposed to lead. Besides mining and metal smelting, industrial workers can be exposed during activities including lead-acid battery manufacture, scrap metal work, painting, soldering, ship repair and demolition, plumbing, manufacture of pottery etc. (UK DETR, 1998). Other activities which could cause exposure include waste disposal, particularly at incinerators, manufacture of leaded PVC or the lead-containing additives, work in steelworks, and petrol stations. Certain leisure pursuits can also result in increased lead exposure, particularly pottery making and enamelling (using leaded glazes and enamels), stained glass working, and target practice in enclosed firing ranges.

In the Western World, there are regulations in place to protect workers from excessive exposure. Many countries have laws stating maximum permitted levels of lead in air, and good hygiene and regular medical surveillance are either obligatory or recommended. Many countries also have regulations stating the

maximum concentration of lead in blood or other measures of exposure. In the EU, the maximum allowable level is currently 70µg/dl (with 80µg/dl permitted if standard measures of urine or haemoglobin, indicating lead exposure, are acceptably low), (Directive 82/605 on Risk at Work due to Lead (1982), cited in ILZSG, 1996). Some Member States have stricter regulations (50µg/dl in Denmark, Sweden, Finland and Norway). In the UK, the Control of Lead at Work Regulations, 1998, require suspension from further exposure to lead at work at a blood lead level of 60µg/dl (for young persons aged 16-17, of 50µg/dl, and for women of reproductive capacity, of 30µg/dl) (HSE, 1998). Furthermore, an action level, to prevent the employee's blood lead concentration from reaching a suspension level, has been set at 50µg/dl (for young persons at 40µg/dl and for women of reproductive capacity at 25µg/dl). For comparison, the maximum permitted blood lead concentrations in the USA is 50µg/dl; in Canada 50-80µg/dl (in different Provinces) and in Australia 50-75µg/dl (in different States) with a recommended level below 50µg/dl. Some countries specify much lower levels for women of reproductive age (20-40µg/dl) to protect any future children (Source: ILZSG, Environmental and Health Controls on Lead, November 1996). Any individuals showing excessive lead exposure (in blood or urine) are required to be moved away from areas of high lead levels in the workplace until their blood or urine lead concentrations fall to an acceptable level. These permitted levels of exposure are set by governmental Departments of Health to provide adequate worker protection; many companies aim for much lower levels of lead exposure for their workers.

There is a legal requirement for medical surveillance of the workforce in most countries and this is generally satisfactory in large companies; however, employers of smaller businesses may not be so well informed about risks and necessary procedures, and medical surveillance may not be routine (CEDAC-Plomb, 1996).

There are possibly many cases of industrial exposure in other countries, particularly in the poorer developing countries, where reasonable conditions of work are not always provided. This is likely to be a particularly severe problem where lead is collected and melted informally by individuals, with no protection or controls on fume. This can also cause other individuals (such as other family members) to be exposed to lead fumes and dusts.

### **7.4.3 TRENDS AND HEALTH IMPLICATIONS**

In the Western World, blood lead levels have decreased significantly in the last two decades. The phasing out of leaded petrol is believed to be a major contributor to this, particularly in urban areas. However, other sources of lead exposure have also decreased. Phasing out of lead piping for the distribution of drinking water, and improved treatment to reduce lead dissolution in water, have

reduced lead contents of the most highly contaminated waters in the UK, though lead in drinking water still continues to be a source of lead intake in some soft water areas. The phasing out of leaded solders in canned food has also removed a general exposure route for the population. Leaded paint, though no longer used except in a few specialist outdoor applications, is still a significant source of lead intake by children living in older houses, where paint residues remain.

Blood lead levels of the vast majority of the population in Western Europe and the USA are well below  $10\mu\text{g}/\text{dl}$ . However, in some countries significant numbers are still exposed to elevated levels. In the USA this is strongly linked with low income and race, with non-whites being particularly exposed. In the USA and France, the age of the dwelling is significant, showing paint from older houses is an important exposure route.

Problems of lead exposure therefore appear to be very few in some countries, though significant minorities continue to be exposed in others.

Individuals occupationally exposed to lead are required to be monitored to limit their exposure. Exposure levels are generally declining with improved practice and stricter legislation, and most employees have blood lead levels well below the legal limits.

The graph below, Figure 7.1, gives a summary of some surveys of population exposure to lead, performed in many countries during the past 3 decades. The absolute levels cannot be directly compared, because the surveys tested different populations. For example, even within one country, the blood lead concentrations are different for men, women and children, and also vary with the age of the individual. Blood lead levels also depend upon many factors including location, occupation, social status, smoking habits. This figure is included to give an overview of trends in population exposure to lead in Europe and a few other countries based on survey results. It is not necessarily representative of the whole populations of countries. Despite these limitations, it is quite clear that there is a marked universal decline in lead exposure, and that this is still continuing.

Outside the Western World, there are instances of elevated exposure to lead in the population, particularly in large urban areas such as Mexico City, where very high levels of blood lead have been found in residents. Similarly, in South Africa in 1984, athletes who trained in urban areas had much higher median blood lead levels ( $55.5\mu\text{g}/\text{dl}$ ) than athletes training in rural areas ( $17.7\mu\text{g}/\text{dl}$ ). Ten years later, the concentration of lead in petrol had halved (from  $0.8\text{g}/\text{l}$  to  $0.4\text{g}/\text{l}$ ) and blood lead levels of urban and rural athletes had declined to  $13.0\mu\text{g}/\text{dl}$  and  $8.5\mu\text{g}/\text{dl}$  respectively (Grobler et al, 1996, cited in IEH, 1998). Lead in petrol is still permitted and continues to expose the population. Occupational exposure is also likely to be higher in some poorer countries, where standards of health and safety at work are less strict than in the West, and control measures may not always be used.

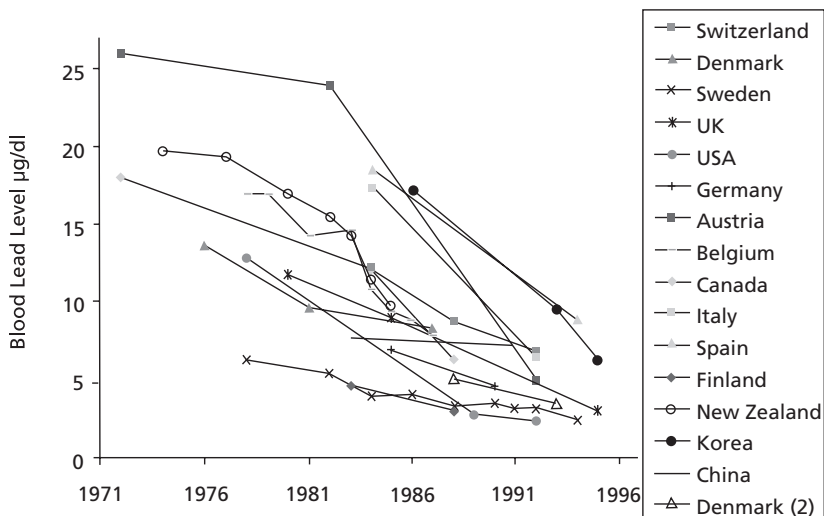


Figure 7.1 Blood lead trends reported in literature

## 7.5 POLICY APPROACHES TO LEAD

### Risk assessment or the precautionary principle?

Two different approaches can be taken to develop policy options for the regulation of a potentially hazardous substance such as lead, where knowledge of the full effects is incomplete. Lead (and other metals) present a special case in that they are sparingly soluble in most products and in most chemical and mineral forms in the environment, but at the same time are persistent in many environmental media.

### Risk assessment

Environmental risk assessment involves a search for a “best route” between social benefit and environmental risk, and providing a “tool” in decision making and in the process of risk management. It is a balancing or trade-off process in which various combinations of risks are compared and evaluated against particular social or economic gains. It does not necessarily imply a no-risk policy, or a minimum one. However, risks should be as fully understood as possible if they are to be effectively managed (SCOPE 15, 1980).

Making a risk assessment involves identifying:

- a hazard (in this case lead),
- a target population which can potentially be affected,
- an exposure pathway by which it reaches the target population, and

- the effect which it has on the population at a given dose, and whether there is a “safe” dose which gives no detrimental effects.

Just because a substance is hazardous, it does not necessarily pose a risk to human health, an ecosystem, or any other “target” population. There must be a route, or pathway, by which a population is exposed to the hazard. For example, a contaminated industrial area which is occasionally visited by adults will pose a much smaller risk than a garden with similar contamination (i.e. a similar hazard), but which is used as a play area for children. Similarly, the risk of using a material which is hazardous, such as lead, depends on there being some way that humans, or other living organisms, are exposed to that material, either during the preparation and manufacturing processes, the use of the article, or its final disposal.

The technique of risk assessment can model both the severity of the hazard to the population, and the probability of the population being exposed to the hazard. The final outcome, i.e. the predicted risk, depends upon the combination of all of these factors. Answers are complex and are given in terms of probabilities, because within a population there are always individual differences in susceptibility and exposure from different sources. However:

- There is no single universal approach used in all situations, and calculations using alternative risk assessment methodologies can yield different end results. A diversity in methodologies should be encouraged, so that all possible risk outcomes can be considered and the potential for error is minimised (Hallenbeck, 1993, *Quantitative Risk Assessment for Environmental and Occupational Health*).
- The calculations assume that all possible exposure routes have been considered, (which may not always be the case, particularly in the long term).
- Even though much study has been done on the behavior of lead in the environment, and its effects, particularly on human health, knowledge is not complete. (This is also true for other substances; in fact, lead has been more widely researched than some alternatives.) Thus, some parameters used in the computations are not known, and must be estimated - and these estimates (often termed default assumptions) can be inaccurate.
- Calculations should take into account the natural background levels in soils, which vary considerably between locations, and where possible the forms of the lead present which will influence its solubility and bioavailability.

Though the technique is being developed to improve predictions, as yet risk assessment is not an exact science.

### **Precautionary Principle**

The Precautionary Principle is defined as an approach to risk management that is applied in circumstances of scientific uncertainty, reflecting the need to take

action in the face of a potentially serious risk, without awaiting the full results of scientific research. This is a political approach, exercised in order to protect citizens or the environment from a threat. When scientific data are incomplete and there is a significant danger to human, animal or plant life, decision-makers are justified in taking action. Such action could involve refusing to license or allow a potentially hazardous activity (for example, an industrial process) or substance (such as lead), unless it can be demonstrated that any risks involved would be acceptably small. The Precautionary Principle is enshrined in international law, including European Community legislation and the Rio Declaration of 1992.

Recent guidance on the implementation of the Precautionary Principle, states clearly that:

- implementation of an approach based on the Precautionary Principle should begin with an objective risk assessment, identifying the degree of uncertainty at all stages,
- all the stakeholders involved should be involved in the decision to study the various management options that may be envisaged once the results of risk assessment are available, and the procedure should be as transparent as possible,
- measures based on the Precautionary Principle must be proportionate to the risk which is to be limited or eliminated,
- measures based on the Precautionary Principle must include an overall cost benefit assessment (advantages /disadvantages) with a view to reducing the risk to a level which is acceptable to all stakeholders,
- measures based on the Precautionary Principle must be able to establish responsibility as to who must furnish the scientific proof needed for a full risk assessment, and
- measures based on the Precautionary Principle must always be of a provisional nature, pending the results of scientific research performed to furnish the missing data and perform a more objective risk assessment.

(*Source*: European Commission DG XXIV Consumer Policy and Consumer Health, “Guidelines on the Application of the Precautionary Principle” (draft), 17th October 1998).

### **Summary**

The two above approaches are not contradictory, but should be used together when making policy decisions. The Precautionary Principle is justified when knowledge is incomplete and there is significant potential for harm. Policies based on this Principle should take account of all available information and be reviewed as more detailed knowledge emerges. All risk assessments must include an account of their uncertainties and limitations in order to be useful.

# INDUSTRIAL EMISSIONS AND CONTROLS

Emissions of lead, together with other harmful or potentially hazardous substances, can occur at all stages of production, from mining of ore, during smelting and refining, and also, potentially, during the manufacture of the finished products. Lead emissions also occur from non-related industries, such as other metal works, incinerators and in, small amounts, from power stations. The quantities of emissions are declining in the Western World as environmental legislation reduces permitted releases, increasingly effective pollution abatement technologies are used, and industry moves gradually towards inherently cleaner, more efficient technologies. However, some emissions are inevitable, especially from older plants which process many thousands of tonnes of material per year. However, the requirement to use Best Available Techniques under forthcoming IPPC legislation will further reduce emissions from older plants.

The bulk of emissions are in the form of solid wastes; a much smaller amount is emitted to air, and less still to water. The form of the emissions determines their likely mobility, bioavailability and potential to reach and affect a target ecosystem or human population. Other important factors are whether the emissions are part of controlled, measured releases, uncontrolled fugitive emissions, or resulting from a plant incident.

Despite the recognition of historical environmental damage and health effects in the work force connected with the lead industry over many centuries, it is only in the past hundred or so years that effective control measures began to be implemented, both to protect the health of workers and to reduce pollution. Good plant design, with reduction of the potential for the emission of contaminating substances, is of paramount importance, and the newer smelting processes are inherently much cleaner than traditional blast furnaces. Pollution abatement technologies, including the treatment of exhaust gases and liquid effluents to remove a proportion of the metal content, have also significantly reduced emissions. Other general measures to improve the cleanliness of sites are implemented to varying degrees. These measures, taken together, have considerably reduced emissions.

Throughout the Western World, factories are legally required to operate within the limits on discharges set by their regulatory authority, although not all

emissions are continuously monitored. In this respect, many plants in the EU have some form of perimeter monitoring. There are inherent problems in measuring fugitive emissions, such as windblown dusts, can be addressed by monitoring air quality within and at the perimeter of the site and modelling the results. In general it is difficult to estimate the percentage of the emission arising from fugitive sources. In certain countries allowable discharges are set individually for each plant.

There are legal limits and recommended guidelines for concentrations of lead in air outside plants, and monitoring is usually practised. Sites with the highest concentrations of lead in air are in the vicinity of industrial locations. Compliance with the former EU standard of  $2\mu\text{g}/\text{m}^3$  is now virtually universal, though there are still a few sites which exceed the new standard and the WHO guideline value of  $0.5\mu\text{g}/\text{m}^3$ .

Those mostly exposed to releases within the plant are the workforce. Before industrial controls were introduced around the turn of the century, lead poisoning was common in foundry workers, and was also found in other trades which used lead. The implementation of controls such as maintaining minimum standards of air quality within the works, medical surveillance of employees, use of protective equipment, and provision of conditions of good hygiene in general, have made excessive occupational lead exposure a rare occurrence.

Outside the Western World, control measures are not always enforced to the same degree and there are still undoubtedly many cases of high occupational exposure to lead and environmental damage resulting from industrial emissions in the developing world.

In short, while it is important to recognise the huge improvements made by industry in recent decades, there are considerable variations between standards in the developed and the developing world. Emissions from some plants outside the EU continue to contribute towards elevated exposure of local residents, and high lead levels in soils leave a legacy for centuries. It is therefore important to continue to work toward implementation of best practice, and to aim for a level of emission that is globally sustainable.



## 8.1 INDUSTRIAL EMISSIONS

### 8.1.1 SOURCES OF EMISSIONS

#### **Mining**

*Solid wastes* - ores and mine tailings (the residual material after metal extraction, which may still contain significant amounts of the metal) stored on the ground can contaminate underlying soil. Dusts can be transported by wind onto surrounding land.

*Airborne emissions* - windblown dusts from mining operations and stock piles of ore can result in dispersion of lead downwind, though most is deposited on land nearby.

*Water-borne emissions* - from washing of ore and from water flowing past old mine wastes and mine shafts. This can continue to be a source of pollution long after the mine has ceased to operate.

#### **Smelting and refining**

*Solid wastes* - slags may contain up to a few percent of lead (typically less than 5%) and may also contain other contaminants such as arsenic and antimony. Silica slags mainly comprise glassy and crystalline phases which are subject to varying degrees of weathering, and which may release lead in more soluble forms. Lead has been found to occur in several different forms in weathered slags, including lead oxide (PbO), pyromorphite ( $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ ), cerussite ( $\text{PbCO}_3$ ), hydrocerussite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ), galena (PbS), anglesite ( $\text{PbSO}_4$ ) and leadhillite ( $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$ ) (Gee et al. 1996). Soda slags contain a lot of soluble metals. However, these will need to be phased out with ongoing environmental regulations. Dusts from pollution control equipment and drosses may contain lead and other metals in relatively active forms; these are usually recycled, though a small proportion containing for example arsenic and cadmium may be disposed of in landfill.

*Airborne emissions* - lead begins to fume significantly at temperatures above around 500°C. Vapours and dusts of lead and lead oxide, together with other materials present in the raw materials (such as acidic sulphur-containing gases, arsenic and other metals) can be present in air, both within the plant and the external environment. Protective measures are taken to reduce exposure to workers within the plant, where pollution abatement equipment is now mandatory.

*Water-borne emissions* - water used at several process stages and from surface rain water must be cleaned before discharging. Beside neutral salts it contains some lead, arsenic, tin, cadmium and other metal ions depending on the water cleaning technology used.

### **Manufacture of products containing lead**

Though the main industrial emissions are generally from the extraction and production of metallic lead (INSERM, 1999), lead is used in a wide variety of products (as described in Chapter 3) and their manufacture also has the potential to release lead. These include batteries, some alloys, glass, ceramics, paints, ammunition and petrol, as well as pesticides and explosives (INSERM, 1999).

### **Other industries**

Lead emissions occur from the following:

- metal works in general (including copper smelting and steelworks)
- incinerators of domestic and industrial waste
- power stations (as small amounts of lead and other metals are found in coal and oil)
- cement works

It should be noted however that these emissions are in the majority of cases well within the legal limits established in the relevant environmental regulations.

## **8.1.2 QUANTITIES OF EMISSIONS**

The large scale of the modern lead industry inevitably leads to some accumulation of lead from fugitive emissions to soils around the works, despite strict environmental controls. In addition, some of the modern mines and smelters are located on the sites of older works, which have left a legacy of environmental contamination over hundreds of years. Very high levels of lead in soils (up to a few percent) have been found at locations of old mine workings, dressing floors and railway ore loading places. Levels decline rapidly away from the works but deposition of lead has been detected several kilometres away. In surveys around other smelters, maximum lead accumulations occur close to the stack. There is a rapid decline away and the distance - decline curve is usually exponential. It is difficult to be categorical about the soil lead levels likely to be encountered around lead smelters. However, on the basis of available data, it may be concluded that background levels of lead in soils are likely to be exceeded up to 3 km downwind of primary smelting activities.

Accumulations of lead may also be expected in the soils around secondary smelters and other lead using industries, though much of the contamination may be historical (Davies, 1995). For example, lead concentrations are elevated in surface soils (0 – 15 cm) up to 3.5 kilometres downwind of the only secondary lead smelter in Scandinavia, though the main area of contamination, with soils ranging up to 2,000 mg/kg lead, is limited to within 1 kilometre of the smelter

(Farago et al, 1999). Most of this contamination is thought to arise from the early operation of this facility which dates back to the 1940s. Measures taken by the operators since 1983 have resulted in reductions of lead emissions from about 2.25 tonnes per annum at that time to less than 0.5 tonnes by 1990.

Emissions from old mines and works, even from many centuries ago, continue to be a source of pollution in the environment. Sources of lead in the environment in general are discussed in Chapter 6.

Quantitative information on lead emissions to the atmosphere arising from lead production, manufacture, etc have been published but are difficult to validate. Estimates are subject to a high degree of uncertainty and tabulated information from different sources may show considerable variation. Thus while actual and projected emissions listed by country in Table 8.1 by Pacyna (1996) provide a useful database, more recent estimates published by TNO (1998) in Table 8.1b would indicate that these earlier data may well be over estimated.

**TABLE 8.1** Emissions to Atmosphere from Lead Smelters (primary and secondary) in EU countries (estimated actual and projected data)

Emissions (tonnes) from 1955-1985, projected emissions to 2010						
Country	1955	1965	1975	1985	2000*	2010*
Austria	113.6	165.0	157.1	73.0	8.1	6.5
Belgium	1812.0	1100.0	651.5	195.4	250.6	218.5
Denmark	#	#	#	3.0	1.5	1.5
France	1034.0	1648.4	709.7	911.0	337.3	287.0
Germany (FDR)	3800.0	3900.0	1570.9	170.0		
Germany (DDR)	194.0	264.3	169.0	222.0		
Germany (total)	3994.0	4164.3	1739.9	392.0	76.4	59.7
Greece	6.4	21.3	37.5	27.0	31.6	30.2
Ireland	30.7	36.7	36.2	33.0	28.7	23.1
Italy	454.8	502.1	302.9	432.0	233.3	198.7
Luxembourg	1.1	1.8	0.8	#	#	#
Netherlands	212.6	392.4	6.0	1.7	0.2	0.1
Portugal	1.8	5.8	10.3	8.0	8.6	5.6
Spain	733.0	837.3	631.6	927.0	862.1	648.9
Sweden	289.3	644.3	250.0	110.0	24.6	22.4
United Kingdom	947.3	665.8	486.4	528.0	323.2	137.7
<b>EU Total</b>	<b>13786.1</b>	<b>14709.3</b>	<b>7278.4</b>	<b>4058.1</b>	<b>2186.2</b>	<b>1640.0</b>

\* projected emissions # no data

(Pacyna, 1996)

**TABLE 8.1b** Estimated and Projected Emissions (tonnes) of Lead from the Lead Industry in Europe

Estimated and Projected Emissions (tonnes/year x 10 <sup>2</sup> of Lead)		
Region	1990 (estimated)	2010 (projected)
Western Europe	190	170
Southern Europe	150	140
Central and Eastern Europe	100	83

*(TNO Report, January 1998)*

### 8.1.3 NATURE OF EMISSIONS

Emissions generally can be categorised as point sources (from a single known source) or diffuse sources (such as from petrol or from sewage sludge applied to land). The nature of emissions can be controlled (e.g. from a stack after gas cleaning operations) or uncontrolled (i.e. fugitive emissions). Attempts are made to limit the latter with the use of water sprays and sweeping equipment within the perimeter of works' premises and by covering storage areas.

**Controlled emissions** include

- solid waste sent to landfill, spoil heaps (of mine tailings, slags etc.)
- stack emissions
- discharge outlets for liquid effluent.

These are from point sources and a consequence of routine operations. Both the quantity and nature of emissions are relatively easy to measure. Thus they can be regulated and controlled.

**Fugitive emissions** can include

- downward migration of metals into soil, from the storage of raw materials, scrap metals etc, though in modern plants these are usually present on a concrete base
- windblown dusts or solid matter carried on the wheels of vehicles
- waterborne runoff from site (e.g. from rain, washing, etc)
- leaks from equipment for storage or transportation of materials.

Such emissions may occur from sites of industrial processes, transport, storage or collection of lead-containing material. By definition, fugitive emissions are very difficult to quantify. Losses must be estimated by indirect means, such as mass balances, or by comparing predictions with actual measurements of

concentrations of metals in surrounding air, water or land (procedures to reduce emissions are discussed later).

**Uncontrolled emissions** could also occur in the event of an incident at a site.

### **Type of emissions**

Simply quoting the total quantity of lead emitted does not give much information about whether it is inert or potentially mobile.

Large amounts of solid waste are generated. In the EU, slags are mostly stored under cover. However, if they are stored dry in the open, dispersion by wind can carry dusts to surrounding areas. However some waste, particularly slags from primary smelting, are in a relatively inert form, so mobility and bioavailability will be low. Some lead-containing wastes such as flue dusts are usually recycled, though small amounts may be disposed of in controlled landfills as they are covered by special waste regulations. Though the potential for dispersal of these wastes in the short term is low, in the long term some migration is possible (as discussed in Chapter 6).

Emissions to water are frequently widely dispersed and have greater potential to interact with ecosystems. However, most data available show that fairly high concentrations of lead are needed to cause measured toxicity effects. It must be noted that most toxicity tests involve high doses on test animals for short times; this does not give clear information about effects of lower doses for longer times.

Emissions to air from chimneys, windblown dusts etc have the greatest potential to disperse, and thus may increase lead exposure in people living in the locality of lead processing plants. However, recent measurements have shown that ambient levels are generally below the  $0.5\mu\text{g}/\text{m}^3$  limit.

(Refer to Chapter 6 for further discussion about dispersion of lead in the environment, and to Chapter 7 for the sources of human exposure.)

## **8.1.4 LEAD DEPOSITION**

Quantitative measurements of lead deposition are difficult to obtain and much of the published information is based on calculations from computer-based models such as TRACE - developed at IIASA to compute air concentrations and depositions of metals including lead on a European scale (Olendrzynski et al 1996). This approach, which accepts a high level of uncertainty, calculates the highest cumulative lead deposition over the period 1955-1987, exceeding  $20\text{ mg}/\text{m}^2$  in France, Germany and the UK.

A specific study in the UK which monitored deposition of 23 elements onto agricultural land at 34 locations over a period of 3 years to 1999, reported lead deposition ranging from 19.5 to 139.0, median  $43.4\text{g}/\text{ha}/\text{year}$  (Alloway et.al, 1999).

### 8.1.5 IMPACTS OF INDUSTRIAL EMISSIONS

Risk assessment techniques can be used to calculate and predict the impacts of contamination on people and ecosystems. As discussed in Chapter 7, the presence of lead does not in itself present a risk. For example, lead in an inert form, underground, is unlikely to have a direct impact upon human health unless it migrates significantly, is exposed at the surface, or has some other pathway to reach a “target” population. Risk assessments can predict the likelihood of different types of emissions causing harm to workers, to other people in the area and to ecosystems.

However, it must be stressed that risk assessments always contain uncertainty. The behaviour of materials, particularly in the future, is not known, and predictions are invariably based upon assumptions and incomplete data, and different calculation can yield differing results. For risk assessments to be useful, assumptions and uncertainties must be clearly stated.

The following targets may be considered:

**Table 8.2** Potential for Lead Exposure among Target Groups

Target	Potential effect
workers	occupational exposure
families of workers	elevated exposure
local residents	elevated exposure
the local environment	increased burdens of lead and other metals in soils, potential impact on ecosystems
the wider environment	increased burdens of lead and other metals, potential impact on ecosystems (much smaller)

#### Occupational exposure

##### Historical situation

Illness resulting from exposure to lead in the workplace used to be common. Prior to 1895, when control measures were implemented, over 70% of workers at a lead smelting works in Hungary (Schemnitz) were reported to suffer lead poisoning (Hamilton, 1914, cited in Nriagu, 1983). In the UK, at around the same time, there were many thousands of cases every year. Exposure was not confined to workers employed in the manufacture of lead and its compounds. Recorded cases of lead colic in a Paris hospital from 1830-1838 included patients who were painters, potters, plumbers, workers in production of lead shot and a small number of glazers and workers in glass factories (Tanquerel des Planches, 1848 cited in Nriagu, 1983).

**Present situation**

As a result of implementation of procedures to improve health and safety at work, the number of cases of occupational lead poisoning is now extremely small. However, there are many different industrial activities during which workers can be exposed, which include: production and refining of metal, construction and demolition of structures painted with leaded paint, preparation of stabilisers for PVC or additives to glass, sanding down leaded paint and the manufacture of lead batteries.

In France, the number of cases of occupational lead poisoning since 1969 peaked at over 200 in the early 1970s and declined to around 15-50 per year from the early 1980s to 1992 (INSERM, 1999). In the UK, in the period 1988-1998, there were 32 reported cases of lead poisoning in the workplace, with between 0 and 7 per year (UK Health and Safety Statistics Book 1997-1998). There may be differences in the definition of "lead poisoning" and reporting procedures between these two countries, so these figures should not be compared directly.

Though cases of lead poisoning are now extremely rare, less obvious effects on health can occur in some individuals at even moderate exposure levels, as discussed in Chapter 7.

Workers in small businesses, for example ornamental casting or jewellery makers and casual workers, can be at greater risk as they or their employers may not be aware of necessary procedures to reduce exposure. They are also much less likely to undergo routine medical surveillance (CECAD-Plomb, 1996).

**Elevated environmental exposure**

Emissions from industry can contribute to elevated concentrations of lead in air (refer to section 8.3 for fuller discussion) and soils, both at the plant itself and nearby. Soil lead concentrations can be very high in locations where solid process wastes are stored, particularly around some processing plants. However, modern covered storage practices have reduced this problem. These wastes may be in a fairly immobile, unavailable form (such as some slags from lead smelting); less stable forms of lead can be prone to leaching or removal by wind, which transports the lead containing dusts. Airborne particles fall to earth and contribute to elevated levels of lead in soils and dusts (refer to Chapter 6 for discussion about fates of lead in the environment and the importance of the form which it is in). This can be a pathway to human exposure.

High levels of lead in soils in the vicinity of industrial sites frequently occur, though these are not necessarily harmful. The significance of this for humans again depends upon such factors as the chemical form of the lead and its solubility, and whether or not people have access to the site. Risk assessments make predictions on exposures, which may or may not prove accurate. Effects on

ecosystems are less well known. Available data suggest that, though living organisms can be affected by exposure to lead, high concentrations are required to give noticeable effects.

## **8.2 CONTROL MEASURES**

### **8.2.1 HISTORICAL BACKGROUND**

Impacts of metallurgical industries on workers' health and the environment have been noted since ancient times, though few controls were implemented. Reference was made (by Pliny and several others, cited in Nriagu, 1983) to foundry workers and miners tying cloths around their faces to protect them from the metal fume and dust. A review of reasons for closure of lead-silver mines (and banning of gold and silver as currency) during part of the Ancient Greek era, was considered partly to avoid the environmental damage caused by mining (Del Mar, 1880, cited in Nriagu, 1983).

At the end of the 19th century, reported cases of workers suffering ill effects from lead poisoning were estimated at thousands, with many deaths. Measures to improve standards of health and safety in the workplace began in Europe around 1900.

### **8.2.2 MEASURES TO CONTROL LOSSES OF LEAD TO THE ENVIRONMENT**

Enterprises which produce or use lead are required to conform with regulations to:

- protect the health of their workers, and
- control releases to the environment.

A full account of such measures would require a detailed description of the individual processes, which is beyond the scope of this book. However, certain principles and measures are in common use.

Minimisation of discharges is always preferable to attempts to clean up emissions. The avoidance of pollution is now a factor in selecting the site design and layout (for example, storage of materials on a suitable surface and under cover, to avoid removal by wind, rain and seepage to earth), and choice of suitable equipment (such as enclosed systems for conveying powdered materials and molten lead).

Emissions inevitably occur in the course of operations. Recommended procedures which reduce the amount of dust (including condensed lead vapour) in the air within the plant include:



- regular cleaning to prevent accumulations of dust,
- the use of water sprays around the site,
- fume extraction, for specific operations, and for whole buildings,
- closed systems for handling dirty materials.

Treatments to reduce the quantity of discharges include:

- treatment of exhaust gases to remove most of the dust (termed flue dust) and acidic gases,
- collection and treatment of liquid effluent to remove most of the dissolved or suspended metal,
- washing vehicles before they leave site.

The efficiency of these procedures is usually assessed by the monitoring of lead in air, both at the plant boundary and up to several kilometres away (particularly in nearby populated areas).

The lead-containing solids collected in the cleaning equipment are often returned to the smelter to make use of their lead content. Similarly, flue dusts etc. from other industries (e.g. copper smelting and steelworks) are also treated at smelters. Procedures to reduce emissions of these very light dusts are important, and they are commonly transported in a damp form. Alternatively, small amounts of flue dusts are disposed of to landfill. The choice of disposal route is generally on economic grounds, and depends on the composition of the dust and the relative charges of landfill disposal.

There are various alternative technologies for the collection of such emissions, which have differing degrees of effectiveness (no measure is 100% effective, though very high removal rates are possible), suitability for different processes and costs.

In many countries factories are licensed to allow emissions up to levels set by the regulatory authority. Regulations regarding monitoring and reporting of discharges are set. Some emissions are continuously monitored, including concentrations of metals in liquid effluent and in stack emissions. In some smaller plants monitoring is not done continuously when limits are not likely to be exceeded; however, samples are taken periodically and these are used to estimate total emissions.

### **8.2.3 CHOICE OF PROCESS**

It is unrealistic to expect plants built to older specifications to operate to the same standards (in terms of emissions and energy efficiency) as modern plants which use newer technologies. For example, the traditional blast furnace allows much greater opportunity for the escape and discharge of materials than the newer,

inherently cleaner, single-stage processes for smelting ore. The Kivcet furnace, which is one example of a single-stage smelting furnace, is considered a “Best Available Technique” (BAT) by the UK pollution inspectorate (UK HMIP, 1993) for processing lead concentrates (while the Imperial Smelting Process, similar to the blast furnace, but allowing for simultaneous lead and zinc removal, is considered BAT for mixed lead/zinc concentrates). Modifications to existing older furnaces can achieve the lower specifications needed to comply with “Best Available Technique Not Entailing Excessive Cost” (BATNEEC) status.

#### **8.2.4 ADDITIONAL MEASURES TO PROTECT THE HEALTH OF EMPLOYEES**

- Regular cleaning of the workplace to avoid accumulations of dusts.
- Monitoring air lead concentrations and observing limits. The maximum permissible workplace level of lead in air in the EU is  $0.15\text{mg/m}^3$  (as specified in Directive 82/605 on Risks at Work due to Lead (1982)). Some Member States have stricter regulations (ILZSG, 1996). However, opinion is divided about the choice of standards adopted and their usefulness in assessing the risk to workers. It is deemed risky to assume that compliance with a set air concentration will by itself guarantee protection to workers, especially considering the variability in exposures and absorption of lead between individual workers (CECAD-Plomb, 1996).
- Use of appropriate personal protection equipment (particularly respiratory protection).
- Periodic screening of employees for general health and lead exposure. There are statutory levels of exposure above which the employer must take action to reduce the exposure of the individual, and above which the individual must be removed from the area where he will be exposed to lead.
- Good hygiene practices can do much to reduce the exposure of personnel, for example: provision of clean areas for eating and drinking; provision of clothes to be worn on site and changed when leaving (this also eliminates a pathway for the exposure of the families of workers); discouraging/not allowing smoking on site; encouraging hand washing before eating.

#### **8.3 EXAMPLES OF THE CURRENT STATE OF EMISSIONS BY INDUSTRY**

##### **France**

The Ministry of the Environment in France lists 40 installations which emit lead and its compounds to air (Ministrie de l’Amenagement du Territoire et de l’Environnement, 1997). In 1996, these were between 0.2 and 67.4kg per day (to

atmosphere). Five of these sites emitted over 10kg of lead per day. These included foundries, factories which manufacture batteries and lead additives, and incinerators of municipal waste.

The highest concentrations of lead in air are found at sites which are affected by municipal waste incinerators and industrial sources, in particular primary lead and lead additives production. Even though industrial emissions have decreased since the 1960s following regulations to control pollution, reductions are still being observed (mean annual lead concentrations in air in 31 industrial monitoring sites, mainly in the Nord-Pas-de-Calais region, declined by 27% between 1992 and 1995) (ADEME, 1997; INSERM, 1999). 70% of these sites showed an annual average below  $0.41\mu\text{g}/\text{m}^3$  and 90% were below  $0.56\mu\text{g}/\text{m}^3$ . Although the majority of 62 monitoring sites in industrial and urban areas had acceptably low ambient air concentrations of lead, a small proportion (in 1995, 18% of monitoring sites near industrial sources of lead pollution, and one town centre site out of about 30), exceeded the World Health Organisation recommended level (and new EU limit from 2005) of  $0.5\mu\text{g}/\text{m}^3$  lead in air (annual arithmetic mean) (World Health Organisation, 1987). All the industrial monitoring stations meet the old European value of  $2\mu\text{g}/\text{m}^3$ . Short term concentrations can be very much higher (3 sites recorded mean values of the maximum concentrations over 24 hours of over  $20\mu\text{g}/\text{m}^3$ , though it is the long-term average concentrations which are important). Short term concentrations are an important factor in monitoring discharges from plants, though impacts to human health depend upon total exposure over a period of months or even years.

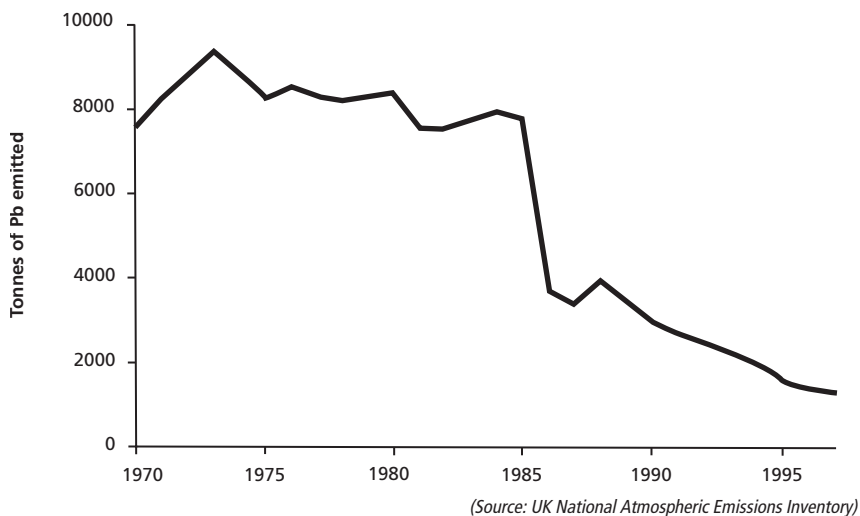
The INSERM Report (1999) concluded that, despite the progress made in France, it is still necessary to maintain the efforts undertaken [to improve air quality], particularly concerning emissions and monitoring of lead from industrial sources. This is of importance as the new EU Daughter Directive on Ambient Air Quality published in 1999 establishes a new limit value for lead of  $0.5\mu\text{g}/\text{m}^3$  measured as an annual average. This will eventually become effective on 1 January 2005 being successively reduced by  $0.1\mu\text{g}/\text{m}^3$  each year for the previous five years. Derogations will be available for some industrial sites up to 2010.

## UK

In the UK, air quality measurements taken some 10 years ago at 24 sites, including eight sites close to large lead works, found that only one industrial site exceeded the EU statutory limit of  $2\mu\text{g}/\text{m}^3$  lead in air between 1985 and the end of 1989. Since 1990 this site has complied with the limit. However, up to and including 1996, two industrial sites continued to exceed the WHO recommended guideline of  $0.5\mu\text{g}/\text{m}^3$  (UK DETR, 1998). It should be noted that an Air Quality Standard for lead in the United Kingdom of  $0.25\mu\text{g}/\text{m}^3$  measured as an annual average has been agreed and will come into force in 2009. However, plants will

not be required to go beyond Best Available Techniques to achieve this limit (UK – DETR, 1998).

Overall emissions of lead to the atmosphere in the UK have fallen considerably from the 1970s and early 1980s to the present time (see Figure 8.1); the greatest fall can be associated with the reduction in sales of leaded gasoline (and the lower permissible maximum lead content of gasoline of 0.15g/l introduced in 1985).



**Figure 8.1** UK Emissions of Lead to Air

### **Emissions from industry outside the EU**

Despite the enormous improvements in emissions control achieved in the developed world there are still some plants in newly industrialising countries which do not operate to strict environmental standards. Some such installations are sources of severe environmental contamination, and some workers (and possibly local residents) can suffer health damage as a result.

As lead is very easy to melt, it lends itself to being processed by small scrap collectors (particularly in less developed countries) and in such enterprises there are unlikely to be controls, thus workers and their families can be highly exposed.

The lead industry has set up and funds the International Lead Management Center as a vehicle for the transfer of information on good practice to plants in developing areas. This organisation is currently involved in projects in many countries, with the aims of reducing occupational exposure and limiting releases to the environment.

## **Conclusion**

The production of lead and other metals, together with some other manufacturing processes, gives the potential for contamination within the work place and in the surrounding environment. However, good practice by industry and regulatory measures to limit pollution and safeguard the health of employees have resulted in dramatic reductions in emissions to the environment, and cases of occupational lead poisoning are now very rare. However, though many sites observe strict procedures to limit discharges, some older plants continue to be less efficient than modern facilities. These emissions, particularly in central and Eastern Europe and in some developing countries continue to result in elevated levels of lead in air, soil and water. This in turn can lead to elevated levels of exposure in local populations. Historical contamination of soils at some industrial locations will continue to be a source of contamination for many centuries. Emission and thus deposition of lead in the future must of necessity be minimised.



# IS LEAD A SUSTAINABLE COMMODITY?

- The use of lead in many products, particularly those of major importance, gives little cause for concern, and offers considerable economic and practical advantages.
- Levels of lead exposure in the general population have fallen over the past two decades in many countries, particularly the EU and USA. The vast majority of the population now receives doses well below levels of concern.
- Some of the minor applications of lead have impacts, or the potential for impacts, either in use or disposal, and the use of suitable risk management measures should be pursued. The most damaging applications of lead have been phased out in the West, although some old products such as paint and pipes continue to cause elevated exposure to a minority of the population. Some of these products are still used outside Western countries.
- As the use of lead in dispersive applications declines, emissions from manufacturing industry and from refuse disposal by incineration and landfill, are becoming proportionally more significant sources of lead in the environment.
- Good practice in the production of lead can reduce, though never eliminate, emissions, and corresponding risks to workers, local residents, and the environment. Standards vary even between different plants in the EU, and much more so world-wide. Though great improvements have been made, industrial emissions remain a matter for close attention.
- Changing patterns of lead use are likely to help reduce impacts during manufacture, use and disposal of products, as dispersive applications are phased out, and higher proportions are recycled.
- Historical practices have resulted in contamination which remains in soils for centuries. Present practice has significantly reduced emissions, and impacts on the environment have decreased markedly. The long term fate of lead, particularly in refuse, is likely to be an important focus of attention in the future.
- It may be concluded that lead is a sustainable commodity when produced, used and recycled in a responsible manner. Efforts to restrict or even ban its

use are not backed up by sound scientific evidence, but rather based on emotive comment and misguided public perception.

- compare the impacts of lead with those of alternative products.

The pattern of lead usage and production has changed dramatically during recent decades, and thus so have the impacts. It is helpful to consider the current situation.

### **CURRENT STATUS OF LEAD CONSUMPTION**

- total world-wide consumption is slowly rising (currently 6 million tonnes per year 1995-1998 (ILZSG, 1999));
- batteries (for vehicles and for emergency power supply) account for the majority of lead use, and are of growing importance;
- other significant uses of metallic lead are in building, alloying, cable sheathing, and shot and weights;
- the major use of lead compounds is in glass for television and computer monitor screens. Other important uses include PVC, lead crystal and some ceramics glazes. Small quantities are used in some paints for special applications;
- uses which have been or are in the process of being phased out in the EU include white lead paints, petrol and pipes.

### **CURRENT STATUS OF LEAD MANUFACTURE**

- total production is slowly rising to keep pace with demand, particularly in some parts of the developing world;
- world-wide, around 50% of lead is produced from scrap batteries and other products. The proportion is higher in many industrialised countries. Recycling rates of lead compare very favourably with other materials;
- the proportion of secondary production is increasing as dispersive applications of lead (petrol and paint) are phased out in many countries. As a result more of the lead used is suitable for recycling;
- in many recycling processes (steel, copper, brass, etc.), lead is concentrated via flue dust and recovered in the recycling chain for zinc, tin and other metals;
- some losses to the environment are inevitable from the production of lead (as with all manufacturing processes);
- secondary production of lead from scrap results in less solid wastes, uses less energy and reduces the consumption of mineral resources, compared to the production of lead from ore;
- control measures implemented in the EU have greatly reduced the emissions from factories in recent decades. However, the situation is less certain in parts of the developing world.

### **CURRENT STATUS OF HUMAN EXPOSURE**

- the level of lead exposure in the general population in the EU and other Western countries has fallen dramatically in the last 2 decades;



- this is partly attributable to the phasing out of lead in petrol. Other contributions have been from reduced use of leaded pipes, paints, solder in food cans, plumbing solders and reductions in industrial emissions;
- the majority of the general population in the West has very low levels of lead exposure which give no cause for concern;
- a small minority of the population in some Western countries continues to receive elevated exposure. This is mainly from old lead products which remain in service (pipes in the water distribution system and paint). Proximity to industry contributes to some cases;
- exposure to lead in the workplace has fallen dramatically as a result of various control measures. However, there continue to be very small numbers of cases causing concern.

The questions to be addressed here include:

- does the continued use of lead and lead containing products present significant risks to human health or the environment?
- do the advantages of using lead for certain applications justify its use, when considering potential risks to health or the environment?

It must be recognised that:

1. In the past, widespread use of lead in dispersive applications (particularly petrol and paint) has caused considerable environmental contamination, with consequences for human health and the environment which can sometimes still be observed today. The elevated environmental levels will remain for centuries in soils, although mostly in a non-bioavailable form. Similarly, lead water pipes continue to contribute to elevated levels of lead intake to a proportion of the population in areas of soft water. The risks arising from these uses have been reduced as a result of controls and legislation.

2. In the Western World, exposure of humans to lead has fallen considerably in the last two decades. The phasing out of leaded petrol is considered the most significant single factor in this. Other contributing factors are: phasing out of leaded paints; phasing out of leaded solders in food cans; phasing out of leaded water pipes and improved treatments of waters to reduce plumbosolvency; improved industrial controls. As a result, the majority of the population has lead intakes which are well within accepted limits, and not believed to be detrimental to health. However, certain minority groups have levels of exposure which could be detrimental, particularly to children. These are generally related to industrial sources, high lead content in water, some hobbies which involve lead or lead compounds; or, most importantly for young children, exposure to old leaded paint and lead-rich soil and indoor dust.

3. Major modern uses of lead (particularly in batteries, television glass, radiation shielding) offer considerable advantages over alternatives and present no recognisable hazard to humans or ecosystems.
4. Some minor applications can have impacts and alternatives are available, or could be in the future, though they may be more expensive. Lead shot and fishing weights can poison waterfowl and add to lead levels in soils and sediments; their use is restricted or banned in wetland areas in some EU Member States. Lead incorporated into glass or glazed tableware has the potential to leach into food or beverages (particularly acidic fruit or beverages) which are stored in them; such items are required to pass standard tests to ensure that leaching rates are low. These potential impacts are recognised, and some measures are taken in the EU and elsewhere to avoid problems.
5. Many of the minor and dispersive applications of lead end up in the ground or in waste streams. There is thus the possibility of migration into soils and waters, and uptake by living organisms in the future. The fate of lead in waste streams is likely to be the subject of increasing attention in the future.
6. The long term fate of lead in the environment depends upon the chemical form in which it occurs, since this affects its ability to migrate and enter food chains. Many forms of lead have low mobility and little effect on living species; the chemical forms of lead can change over time, particularly if the water table moves, or if the acidity of the environment changes.
7. Production of lead invariably results in some releases and can, in certain cases, cause adverse effects on health. Significant improvements in industrial practice have been made, which have lowered the impacts of the manufacture of lead and its products in many countries. However, this still remains an important issue.
8. Most of the lead used at present is for products suitable for recycling, and recycling rates of lead are far better than those of most other materials. However, efforts should be made to improve recycling rates still further in order to avoid lead losses in the waste stream and to reduce the potential impacts of lead production on ecosystems and on human exposure.

## **CONCLUSIONS**

- The use of lead in many products, particularly those of major importance, gives little cause for concern, and offers considerable economic and practical advantages.

- Levels of lead exposure in the general population have fallen over the past 2 decades in many countries, particularly the EU and USA. The vast majority of the population now receives doses well below levels of concern.
- Some of the minor applications of lead have impacts, or the potential for impacts, either in use or disposal, and the use of suitable risk management measures should be pursued. The most damaging applications of lead have been phased out in the West, although some old products such as paint and pipes continue to cause elevated exposure to a minority of the population. Some of these products are still used outside Western countries.
- As the use of lead in dispersive applications declines, emissions from manufacturing industry and from refuse disposal by incineration and landfill, are becoming proportionally more significant sources of lead in the environment.
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- Changing patterns of lead use are likely to help reduce impacts during manufacture, use and disposal of products, as dispersive applications are phased out, and higher proportions are recycled.
- Historical practices have resulted in contamination which remains in soils for centuries. Present practice has significantly reduced emissions, and impacts on the environment have decreased markedly. The long term fate of lead, particularly in refuse, is likely to be an important focus of attention in the future.
- It may be concluded that lead is a sustainable commodity when produced, used and recycled in a responsible manner. Efforts to restrict or even ban its use are not backed up by sound scientific evidence, but rather based on emotive comment and misguided public perception.



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**DATA SOURCES FOR FIGURE 7.1 – TRENDS IN BLOOD LEAD LEVELS**

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- **Denmark**, *Moller et al., American Journal of Epidemiology, 1992, Vol. 136, p1091*. Data for men aged 40-51 living in Copenhagen County. Sample size was 439-504 depending on year.  
*Nielsen et al., Scandinavian Journal of Environmental Health, 1998, Vol. 21, p153*. Data for men and women aged 20-89 living in both city and rural communities. The sample population was chosen to closely reflect the general Danish adult population and therefore can be used as a national adult average. Two comparable data points are presented.
- **Switzerland**, *Weitlisbach et al., Environmental Research, 1995, Vol. 68, p82*. Data for men aged 25-74 living in Vaud and Fribourg. Sample size was 804-931 depending on year.
- **United Kingdom**, *Delves et al., British Medical Journal, 1996, Vol. 313, p883*. Data taken from three national health surveys. Over 6000 participants including men, women and children living a variety of areas both urban and rural. This effectively provides a national average.
- **United States**, *Morbidity and Mortality Weekly Report, 1997, Vol. 46, p141*. Results taken from the US National Health and Nutrition Examination Surveys (NHANES II, NHANES III Phase 1, NHANES III Phase 2). These studies examined 10,000 participants of both sexes covering all age groups taken from both urban and rural areas. This effectively provides a national average.
- **Austria**, *Federal Ministry for Environment, Youth and Family, Austria, 1992*. Data submitted to Environment Canada in preparation for the OECD Risk Reduction Monograph on Lead. Data represents general population blood lead levels. No further information available.
- **Belgium**, *Ducoffre et al., Environmental Research, 1990, Vol. 51, p25*. Data collected from a large number of people of all ages and inhabiting a wide variety of areas. This effectively gives a national average.

LEAD: THE FACTS

- **Canada**, *Environmental and Health Directorate, Health and Welfare Canada, 1992*. Data submitted to Environment Canada in preparation for the OECD Risk Reduction Monograph on Lead and represents the average national blood lead level for children.
- **Italy**, *Bono et al., Environmental Research, 1995, Vol. 70, p30*. Data collected from approximately 200 adults (male and female) living in urban Turin.
- **Spain**, *Rodamilans et al., Bulletin of Environmental Contamination and Toxicology, 1996, Vol. 56, p717*. Data collected from a wide range of people living in urban Barcelona.
- **Korea**, *Yang et al., International Archives on Occupational and Environmental Health, 1996, Vol. 68, p199*. Three separate studies involving a wide range of people living in both urban and rural areas. The results have been adjusted so as to provide an average for the general population.
- **China**, *Qu et al., International Archives on Occupational and Environmental Health, 1993, Vol. 65, pS202*. Data collected from adults living in Jinan City. Data shown refers to the female population although data for the male population is also available.
- **Germany**, *German Federal Environment Report, 1992/3*. Average blood lead levels for the general public.
- **New Zealand**, *Hinton et al., Journal of Epidemiology and Community Health, 1986, Vol. 40, p249*. Data refers to nearly 3,000 men, women and children living in Christchurch.
- **Finland**, *Ponka et al., Science of the Total Environment, 1993, Vol. 138, p 301*. Data refers to children living in Helsinki.



# HISTORICAL PRODUCTION AND USES OF LEAD

## HISTORICAL ACCOUNTS OF LEAD SMELTING

Primitive lead smelting hearths and furnaces, dating from ancient times, have been found in many parts of the world. The smelting of pure galena is a simple operation, and appears to have been discovered independently wherever the ore was found. (Pulsifer, 1888.)

The ancient Egyptians, Phoenicians and others in the Middle East were well acquainted with simple metallurgy, and are believed to have imparted their knowledge to the Hebrews, Greeks and Romans. There are several references to extraction metallurgy made in the Old Testament of the Bible, showing that this was known at the time (e.g. Ezekiel, 22:19-20 - dated 593 BC - “As they gather silver, and brass, and iron, and lead, and tin, into the midst of the furnace, to blow the fire upon it, to melt it . . .” - cited by Nriagu, 1983).

Many simple hearths consisted of little more than a low circular wall of stones built on a hillside, with perhaps a channel to direct the molten metal. This technology had hardly changed from ancient times until the Industrial Revolution in Europe. A German scientist, George Agricola, gives exhaustive descriptions of mining and metallurgy technology in his work (1556, *De Re Metallica*). A description of one type of “furnace”, cited by Tylecote (1992) follows:

“They heap up two wagon loads of charcoal on some hillside which adjoins a level place, a layer of straw is placed on top and on this is laid as much pure lead ore as the heap can bear; then the charcoal is kindled and when the wind blows, it fans the fire so that the ore is smelted. In this way the lead, trickling down from the heap, falls on to the level and forms broad thin slabs.”

This furnace type was also typical of British furnaces of the time. Agricola also describes some more sophisticated versions, some involving chimneys and upper chambers to collect some of the metal vapour and dust lost (Pulsifer, 1888).

The interested reader can refer to Pulsifer, 1888, Notes for a history of lead; Nriagu, 1983, *Lead and Lead Poisoning in Antiquity*; and Tylecote, 1992, *A History of Metallurgy*, for descriptions of simple furnaces and smelting

techniques used by native American women, ancient Britons, native Peruvians, and other accounts of smelters in India, Iran and Japan. A more recent example of the crudest of methods is how early European settlers in Missouri learned how to smelt lead for bullets. They made a fire in the hollow of a fallen tree or old tree stump, threw in pieces of galena found on the ground, and recovered the lead from the ashes. (Pulsifer, 1888, and Nriagu, 1983 citing Schoolcraft, 1819.)

Such simple technology is possible for lead, as lead oxide can be reduced in charcoal or wood fires below 800°C, and more importantly, lead can undergo a double decomposition reaction, in which lead ore reacts with ore which has been oxidised at the top of the furnace, to yield lead metal and release sulphur dioxide gas.

This process was very simple, but had a number of problems. No more than two thirds of the lead was recovered by such primitive methods (Pulsifer, 1888), often a lot less. The remainder was lost to the slag (the material which collects over the top of the molten metal, also called “lead ashes” by early writers) and as fume. Thus it was only worthwhile exploiting ores very rich in lead, and even ores containing 20% lead would probably be discarded. (Pulsifer, 1888.)

It was observed that vegetation was damaged for a considerable distance around such furnaces, and the soil was poisoned (Tylecote, 1992), probably from the lead fume and sulphur dioxide liberated.

Old lead workings are a current source of lead in the environment. Some of these early slags have proved to be a profitable source for lead exploitation by more modern methods. Smelting is now carried out under more controlled conditions.

## **HISTORICAL OVERVIEW OF THE USES OF LEAD**

There is evidence of lead workings and artefacts from very early periods, in excavations dating well before the time of the Roman Empire. The earliest known example of metallic lead is a metal figure recovered from the Temple of Abydus in Upper Egypt, considered to date from 4000BC; lead-rich glazes have also been found on pottery in ancient Egypt. A host of other applications are described below. However, such finds are generally small in number. Lead was less prized than the other metals - gold, silver, copper, tin and later iron - known in antiquity, as its dull lustre and softness did not make it particularly suitable for jewellery or weapons.

Prior to the time of the Roman Empire, lead extraction appears to have been principally in order to obtain silver, as the two metals frequently occur together. (Nriagu, 1983.) However, following the beginning of this era, lead was used on a large scale, as a useful material in its own right, for plumbing, tank linings, kitchenware and a host of miscellaneous uses. The use of lead declined after the collapse of the Roman Empire, but in the Middle Ages in Europe, lead began to

be used again for many applications. Some of these applications, such as for water piping and in paints, have recently been phased out, or at least greatly reduced, in view of the potential for risks to health; however, some continue to this day.

### **Lead piping**

Lead has been used in water piping in many cultures since ancient times. Examples include pieces recovered from 4th millenium remains in Mesopotamia (Aitchison, 1960, cited in Nriagu, 1983), from Persia, dated from 1000-500BC (Partington, 1935, cited Nriagu, 1983), Egypt (Pulsifer, 1888) and ancient Greece. However, it was during the Roman Empire, with the large demand for water supplies, that the demand for lead took off. It is believed that the Romans could have learnt lead plumbing technology from the Greeks (Nriagu, 1983); their advances were in terms of implementing large scale application. The English word *plumbing*, referring to water piping, derives from the Latin word for lead, *plumbum*.

It was known since early times that lead could cause ill health (Pulsifer, 1888), and an ancient writer Vitruvius recommended that earthenware pipes be used to ensure wholesome water supply. (Pulsifer, 1888) Another writer, Pausanias referred to a particular area where the water from the hot springs destroyed the pipes within a few years - it is assumed by Pulsifer, (1888) that the water contained hydrogen sulphide, and thus was unusually corrosive. However, this did not deter the Greeks and Romans from using lead for most of their piping.

### **Constructional / architectural purposes**

Lead used as flashings (the weathering of intersections, for example, between roof and chimney, or where a drain joins the gutter), covering of cesspools, roofing, and damp-proofing of foundations, was known in ancient times (Nriagu, 1983). Perhaps the most striking example is the huge hanging gardens of Babylon, presumed to have been built by King Nebuchadnezzar (605-562BC) for his wife: these contained lead linings separating the soil from underlying stone structure, to retain the soil's moisture. (Mothes, 1889, cited in Nriagu, 1983; Diodorus, cited in Pulsifer, 1888)

Lead was also widely used for joining masonry, by pouring molten led into the joints themselves, or around iron or bronze clamps for extra strength. (Nriagu, 1983, Pulsifer, 1888) For more ordinary applications, wire or bands of lead metal were used to provide reinforcement, for example, for large amphorae used to store water and wine. (Nriagu, 1983, Pulsifer, 1888)

As already mentioned, extensive usage of lead began with the Roman Empire, and the great desire for water, and bathing. In addition to piping, water supply required the construction of tanks, baths and the like, which were commonly lined with lead. Lead was sometimes used for other purposes, such as the roofing

of the old senate building in Constantinople, erected by Emperor Constantine, (306-336 AD).

Later, from Medieval times in Europe, lead was used in came for stained glass windows, for roofing, piping, and other uses. Its use was not universal: lead being abundant in Britain, has traditionally been used there for roofing and even cladding of furnishings (Pulsifer, 1888); however, some other countries have traditionally favoured alternative materials, such as copper and zinc, for such purposes.

### **Leaded bronzes**

Leaded bronze artefacts, dating from bronze age era, have been found in many areas, including Babylonia, Egypt, Greece and China and Europe. It is believed that lead was added deliberately, to lower the melting temperature and thus facilitate casting, and possibly also to harden the copper. It could also have been added as a cheap diluent in the more expensive copper (Tylecote, 1992), though in later times highly leaded bronzes were more prized (Pulsifer, 1888) It is interesting to note that leaded bronze was widely used for statues and statuettes, but weapons found at such sites contained much smaller amounts of lead. (Adding tin instead would give much better properties)

### **Statues, statuettes, figures**

Such articles made of lead or lead alloys have been found from many ancient cultures. Artefacts from ancient Egypt date from earlier than 3000BC; small figures of soldiers from Sparta and Athens are believed to be even older (Rhousoopoulos, 1909, cited in Nriagu, 1983). Effigies of sacred figures, particularly animals, were used in Assyria from 1400BC; more recently, Greek and Roman finds include a great number of figures of nude women, believed to represent Diana and other goddesses. Small figures were probably also used as children's toys. (Nriagu, 1983, Pulsifer, 1888)

Several thousand lead-based axes, found in Brittany (north west France), are dated to around 700BC (Nriagu, 1983). These would have been useless as tools or weapons; it is believed they were made for ritualistic purposes (Tylecote, 1992) or possibly as a form of currency (Nriagu, 1983).

### **Currency and tokens**

Lead, and alloys rich in lead, have been used for millenia in the form of weights, figures, and coins. Its use was widespread in ancient Assyria, from around 2000BC, with lead animal heads being used as currency. (Nriagu, 1983)

Many finds of coins with high lead contents at sites from ancient Greece, India - the Andraha dynasty, dating from late second century BC to early third century AD, and ancient China. (Nriagu, 1983) Lead and leaded bronze coins were widely used in the Roman Empire. A large number of lead medals and tokens

were also in use, which may also have had a monetary value. (Pulsifer, 1888) The use of lead for counterfeit purposes, either by addition to bronze, or plating coins with silver or gold, has also been known since ancient times. It is referred to in texts from ancient Rome, Greece and China. (Nriagu, 1983, Pulsifer, 1888) Lead money has also been used in Europe from about the Middle Ages. It was not the preferred metal for coinage, and some lead coins would have been counterfeit, plated with silver; others were probably tokens, with presumably little monetary value. Official money was made from lead, for example, at times of war, when other metals were in short supply. (Pulsifer, 1888)

Many finds of lead tokens in Medieval France have been made. From 15th to 17th centuries, they were commonly used to denote membership of a professional guild. (Pulsifer, 1888) Others would have been used for religious purposes, or as lucky charms.

### **Vessels, kitchenware**

Lead and pewter have been used for such purposes since very early times, in ancient Persia, Egypt, and later by the Greeks and Romans. A whole assortment of vases, kettles, tableware and cooking pots were in wide use during the Roman Empire. Pewter tableware - consisting of about 50% tin, 50% lead, was generally used by those who could not afford silver, but lead pots were actually preferred for preparation of certain dishes. The most notable were residues of boiled down fruit, which were used as cheap sweetening ingredients. Cooking in lead vessels, rather than copper, was reported by classical authors (Pliny, Cato, Palludius, cited in Nriagu, 1983) to improve the flavour (sweeten the food) and aid preservation of the dishes. Lead readily dissolves in organic acids such as those present in fruit and wine, and some such dishes would have undoubtedly been contaminated with dangerously high levels of lead.

Similarly, pewter and lead tableware was demanded by the nobility in Europe in the centuries after the Middle Ages, as silver was scarce. It was certainly in use in England by the 15th century, and in France before then. Pewter was also used to make objects of art. (Pulsifer, 1888)

The possibility of plumbism from drinking from cups made of lead, or highly leaded bronzes, or using these metals for wine storage vessels, is also discussed by Nriagu (1983). Such vessels were apparently widely used by nobility in several Chinese dynasties, for drinking fermented “wines”. Bronze vessels made by European Celts generally had very high lead contents, and drinking wines from such vessels was probably not advisable. Early Christian missionaries would have usually used lead or leaded bronze cups for sacramental wine, again, potentially dissolving significant amounts of lead. Lead itself was also widely used for repairing broken pottery jars and pots, including those used for the storage of wine.

A more bizarre application of lead, and also tin and copper, was in the quality control of wine. Strips of the metals were glued to the inside of the vat lid, the vat

sealed for 40 days. If the strips were found to be clean, rather than covered with scale or bubbles, the wine was pronounced good. This practice developed into leaving metal strips permanently in wine vats, presumably highly contaminating the beverages. This was performed in Europe until well into the Middle Ages. (Nriagu, 1983)

### **Stationery and seals**

Lead tablets used for inscriptions were used in Roman and Medieval times. They were used to provide durable written records, or to record prayers, invocations and curses. (Pulsifer, 1888) The Phoenicians used inscribed lead sheets, dropped into the tomb, as a means of sending messages to the dead. (Partington, 1935, cited in Nriagu, 1983) Lead seals have been attached to messages and merchandise since ancient times, In fact, their use on bales of cloth was required by law in England during the reign of Henry VIII. (Nriagu, 1983) Lead and lead compounds were also used as “pencils” or incorporated into inks.

### **Weights**

Lead has been used since ancient times as standard weights, because of its high density, and inertness in air. The metal was used in almost every ancient weight class known (Nriagu, 1983), and became widely used in the Greek period, and more so during the Roman Empire. There are numerous references to the use of lead as anchors for ships. (Pulsifer, 1888) Unscrupulous use of lead to weight dice in ancient Greece was noted by Aristotle. (Pulsifer, 1888)

### **Burial of the dead**

Lead has been used for coffins and coffin linings because it does not perish. Many examples have been found in England dating from Roman times, though few elsewhere from that period; it is thought to have been used here because lead was abundant and relatively cheap. (Pulsifer, 1888, Nriagu, 1983). The Anglo-Saxons did not bury their dead in lead, but it was sometimes used after the Middle Ages for the burial of nobility, for example for King Richard II. Some tombs included inscriptions and ornamental patterns. (Nriagu, 1983, Pulsifer, 1888)

### **Warfare, weapons, punishment**

One of the earliest weapons of war was the sling, initially used to project stones at the enemy. Slugs or pellets of lead came in to use by Greek armies in the 5th century BC; it is reported that slingers from Rhodes could throw their missiles twice as far as the opposing Persians, who were using rocks. (Xenophon, cited by Nriagu, 1983) They were cast to shape, and often bore inscriptions such as an invocation to the gods, an insult or joke about the enemy, or message to companions. (Nriagu, 1983, Pulsifer, 1888) Other uses of lead in ancient warfare

were the pouring of molten lead from battlements on to invaders, or dropping large masses of solid lead on to them or their equipment. (Nriagu, 1983, Pulsifer, 1888) Later applications of lead in battles included cannon balls. Punishment for crimes in Greek and Roman times included lifetime of labour in the mines, with large pieces of lead strapped to the convict's body.

### **Glazes, enamels and glasses**

A glaze is a glassy coating applied to ceramics, for reasons of decoration, or to give a gloss. Examples of pottery glazed with glazes which are rich in lead (in the chemical form lead oxide) are found in ancient Egypt, China, the Near East, and Rome. Besides being cheap, readily available, and easily fusible, such glazes have advantages of good adherence to, and compatibility with the substrate, high gloss and bright colours are possible, and the glaze lasts without devitrifying (crystals forming within the glaze, which can spoil it). However, such glazes were not universally used, and unleaded alkali glazes appear to have been more widespread. Vessels glazed with lead compounds have the potential to release lead into contents, particularly acidic wines and fruit juices, and to contribute to lead poisoning (though modern manufacturing and testing procedures limit this).

Leaded glasses, though sometimes of similar composition to glazes, apparently developed separately. Many examples of opaque, brightly coloured glass, have been found in many areas of the Middle East, dating from around the 15th century BC. Lead was added to silicate glasses in order to make melting easier, and also to add colour, opacity, or increase the brilliance of the glass.

### **Pigments and paints**

Many compounds of lead are strongly coloured, and also durable, and this has been exploited since very early times. Red and yellow oxides of lead were used for purposes of decoration, and it is thought that early peoples attributed magical properties to them. (Nriagu, 1983) Ancient Egyptians, Assyrians and Hindus decorated their temples with bright colours, which would have included some compounds of lead. (Nriagu, 1983, Pulsifer, 1888) Galena (lead sulphide) was widely used as black eye paint in many ancient Middle Eastern cultures (Nriagu, 1983); its use continues to this day in India. (This eye paint was believed to be able to treat eye diseases.)

There are several forms of lead oxide, and the colour of oxidised lead can range through white to shades of yellow and red. These were used as cosmetics in Europe, the Middle East, India and China, and also found use with artists for painting and decoration. Red lead was less favoured, because it darkened with time.

“White lead”, an intimate mixture of lead carbonate, hydroxide, and possibly oxide, makes a very durable white paint, which has been much exploited from ancient times until a few decades ago. This compound was manufactured by the

ancient Greeks, Romans and Chinese. (Nriagu, 1983.) Later, it was manufactured in many countries in Europe from the late Middle Ages, and appeared to be the preferred choice of white pigment. (Pulsifer, 1888.)

### **Medicinal uses of lead**

Present day understanding of the effects of lead and its compounds on health, of both humans and other organisms, is that it does not have any beneficial effects whatsoever, and that excessive amounts can be very harmful. However, although the poisonous effects of lead were known even in ancient times, it was actually prescribed for medicinal purposes. Lead was used in ancient India to treat indigestion. (Pulsifer, 1888.) The Egyptians, Hippocrates and others, also considered it therapeutic, and Pliny describes several remedies which use lead: “for the removal of scars . . . and as an ingredient in plasters, for ulcers, and for the eyes etc.” (Pliny, Natural History, book XXXIV chapter 1, cited Pulsifer, 1888.) Lead was generally considered to have cooling properties; even last century lead acetate was regarded as cooling, and used as a soothing lotion. Medicinal ointments were believed to work much better if kept in lead containers. (Pulsifer, 1888.) Lead also found application in dentistry, and was used in fillings in Europe up to the 17th century. (Nriagu, 1983.)

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